

Efficiency of Rice Bran for the Removal of Selected Organics from Water: Kinetic and Thermodynamic Investigations

MUBEENA AKHTAR,[†] M. I. BHANGER,[†] SHAHID IQBAL,[†] AND
 S. MOOSA HASANY*[‡]

National Center of Excellence in Analytical Chemistry, University of Sindh,
 Jamshoro 76080, Pakistan, and Pakistan Institute of Nuclear Science and Technology,
 P.O. Nilore, Islamabad, Pakistan

The sorption efficiency of indigenous rice (*Oryza sativa*) bran for the removal of organics, that is, benzene, toluene, ethylbenzene, and cumene (BTEC), from aqueous solutions has been studied. The sorption of BTEC by rice bran is observed over a wide pH range of 1–10, indicating its high applicability to remove these organics from various industrial effluents. Rice bran effectively adsorbs BTEC of 10 $\mu\text{g mL}^{-1}$ sorbate concentration from water at temperatures of 283–323 \pm 2 K. The effect of pH, agitation time between solid and liquid phases, sorbent dose, its particle size, and temperature on the sorption of BTEC onto rice bran has been studied. The pore area and average pore diameter of rice bran by BET method are found to be 19 \pm 0.7 $\text{m}^2 \text{g}^{-1}$ and 52.8 \pm 1.3 nm. The rice bran exhibits appreciable sorption of the order of 85 \pm 3.5, 91 \pm 1.8, 94 \pm 1.4, and 96 \pm 1.2% for 10 $\mu\text{g mL}^{-1}$ concentration of benzene, toluene, ethylbenzene, and cumene, respectively, in 60 min of agitation time using 0.1 g of rice bran at pH 6 and 303 K. The sorption data follow Freundlich, Langmuir, and Dubinin–Radushkevich (D–R) models. Sorption capacities have been computed for BTEC by Freundlich (32 \pm 3, 61 \pm 14, 123 \pm 28, and 142 \pm 37 m mol g^{-1}), Langmuir (6.6 \pm 0.1, 7.5 \pm 0.13, 9.5 \pm 0.22, and 9.4 \pm 0.18 m mol g^{-1}), and D–R isotherms (11 \pm 0.5, 16 \pm 1.3, 30 \pm 2.2, and 33 \pm 2.5 m mol g^{-1}), respectively. The Lagergren equation is employed for the kinetics of the sorption of BTEC onto rice bran and first-order rate constants (0.03 \pm 0.002, 0.04 \pm 0.003, 0.04 \pm 0.003, and 0.05 \pm 0.004 min^{-1}) have been computed for BTEC at their concentration of 100 $\mu\text{g mL}^{-1}$ at 303 K. Studies on the variation of sorption with temperatures (283–323 K) at 100 $\mu\text{g mL}^{-1}$ sorbate concentration gave thermodynamic constants ΔH (kJ mol^{-1}), ΔG (kJ mol^{-1}), and ΔS ($\text{J mol}^{-1} \text{K}^{-1}$). The results indicate that the sorption of organics onto rice bran is exothermic and spontaneous in nature under the optimized experimental conditions selected. This sorbent has been used successfully to accumulate and then to determine benzene, toluene, and ethylbenzene in wastewater sample.

KEYWORDS: Rice (*Oryza sativa*) bran; benzene, toluene, ethylbenzene, cumene (BTEC); water; sorption; kinetics; thermodynamics

INTRODUCTION

Volatile organic compounds (VOCs), that is, benzene, toluene, ethylbenzene, and cumene (BTEC), are important environmental contaminants because of their high toxicity and widespread occurrence (1, 2). BTEC frequently co-occur at hazardous waste sites. Media contaminated with these chemicals include air, water, and soil. Contamination of groundwater with VOCs may lead to their volatilization into indoor air when groundwater is used for domestic purposes. BTEC are present in aviation fuel (gasoline) and are widely used as industrial solvents and raw

materials for the production of different commodities (3, 4). The action and risk level of benzene, toluene, ethylbenzene, and cumene are described in the European Quality Standards for the assessment of soil and water contamination (5, 6). The determination of BTEC in environmental matrices is difficult because of their trace level presence and losses that occur during sample handling, extraction, etc. Exposure to these chemicals leads to several health-related problems (7, 8). To remove these compounds from chemical and industrial wastewater, adsorption on activated carbon (9, 10), photochemical decomposition by ultraviolet radiations (11, 12), or aeration (13) is normally used. However, all of these methods have certain drawbacks, especially their cost (14, 15). Presently, there is an increasing trend to evaluate some indigenous materials having good sorption

* Corresponding author (e-mail hasany@pinstech.org.pk; fax +92-51-9290275; telephone +92-51-9290279).

[†] University of Sindh.

[‡] Pakistan Institute of Nuclear Science and Technology.

potential for the purification of water (16–20). Adachi et al. (21) reported some preliminary results of the use of rice bran for the removal of certain organochlorine compounds from water.

Neither detailed paper describing sorption capacities and energies of sorption of BTEC onto rice bran by Freundlich, Langmuir, and Dubinin–Radushkevich (D–R) isotherms nor any work discussing the kinetic and thermodynamic studies of such sorption process in detail, as has been carried out in the present study, has appeared in the literature. This paper deals with the sorption potential of rice bran, an inexpensive indigenous agricultural waste, over a wide range of pH along with other parameters affecting the sorption of BTEC onto rice bran using HPLC methodology.

EXPERIMENTAL PROCEDURES

Reagents and Materials. All of the reagents used in the present investigation were of analytical grade and procured from Fluka Chemical Co. or E. Merck. BTEC of 99.9% purity were obtained from Sigma Chemicals Ltd. Methanol (HPLC grade) was procured from Merck and used for making synthetic aqueous solutions and for HPLC technique. All glassware was of Pyrex and cleaned with a 20% nitric acid solution and repeatedly washed with deionized water followed by drying at 383 K in an oven for 5 h. Stock solutions of BTEC have been prepared by dissolving 1 g (appropriate volume from mass density ratio) of each analyte in 5 cm³ of methanol and then diluting up to 1000 cm³ with doubly distilled deionized water as reported (22, 23). The solubility of these compounds in alcohols is indicated in the literature (24). The samples of required concentrations have been prepared by further diluting the stock solutions. Buffers of pH 1–3, 4–6, and 7–10 were prepared by mixing an appropriate volume of 0.1 M solutions of HCl and KCl, CH₃COOH and CH₃COONa, and H₃BO₃ and NaOH, respectively (25).

Rice bran (*Oryza sativa*), from an indigenous variety, that is, super kernel basmati, was purchased from the local market, washed thoroughly with doubly distilled deionized water to remove impurities, and dried in sunlight for 2 days. The washed and dried material was sieved to different mesh sizes from 100 to 1000 μm by a Ro-Tap type electrical sieve shaker. The sieved material was washed thoroughly again with distilled deionized water to remove the fine particles and dried at 383 K for 10 h, then placed in a desiccator at room temperature to be used as a sorbent. The pore area and average pore diameter of rice bran were measured by BET method using nitrogen as a standard as 19 ± 0.7 m² g⁻¹ and 52.8 ± 1.3 nm, respectively, greater than those of rice bran variety reported earlier (21).

Instrumentation. A Hitachi model 6200 HPLC equipped with a Licrosorb octadecylsilane (ODS) column, 5 μm (150 × 4 Ø mm), and UV–visible detector loaded with a CSW32 software was employed for data acquisition, integration, and processing. Water/methanol mixture (80:20) v/v was used as a mobile phase at a flow rate of 1 mL/min. Arbitrary unit full-scale deflection (AUFS) was 0.005, and the wavelength used was 254 nm. Redistilled methanol and doubly distilled deionized water (0.8 μS cm⁻¹ conductance and pH 5.8) were used as a mobile phase. The limits of detection (signal-to-noise ratio of 2:1) were found to be 0.1, 0.05, 0.05, and 0.05 ng μL⁻¹ for benzene, toluene, ethylbenzene, and cumene, respectively. The pH measurements were made on a digital (inlab level 1) pH meter.

Sorption Method. Appropriately weighed adsorbent (0.1–0.8 g) was placed in a 100 cm³ glass-stoppered Erlenmeyer flask, to which 25 cm³ of sorbate solution containing various amounts of analyte (100–1000 μg mL⁻¹) was added. The flask was then agitated using a Gallenkamp 350-010 Stuart scientific wrist-action shaker at a speed of 100 rpm at 303 ± 2 K from 5 to 120 min. Finally, the sample was filtered using a Whatmann filter paper 44 to remove rice bran. To assess the evaporation losses of BTEC compounds, a control experiment was conducted following the same methodology except the addition of rice bran. No difference between control and treated samples has been observed, which indicates no losses due to evaporation of organics. A 10 μL solution was then injected to the HPLC under optimized

conditions. The sorbed concentration of the chemicals was calculated by the difference in the detector response to peak height (mV) before (C_i) and after shaking (C_e). The removal efficiency or percent sorption is calculated as

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

where C_i and C_e are expressed in mol/dm³. The distribution coefficient (R_d) may be evaluated using following equation:

$$R_d = \frac{\text{amount of analyte onto rice bran}}{\text{amount of analyte in solution}} \times \frac{\text{volume of solution (V)}}{\text{amount of rice bran (W)}} (\text{cm}^3 \text{ g}^{-1}) \quad (2)$$

The percent sorption and distribution coefficient (R_d) may be correlated by the following relationship:

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

The effect of temperature on percent sorption of BTEC onto rice bran has been studied by employing the concentration of each BTEC component, 10 μg/mL, 0.1 g sorbent dosage at pH 6, and 100 rpm shaking speed using an agitation time of 60 min. Experiments were conducted over the temperature range of 283–323 K, and the sorption potential of rice bran at each temperature was measured.

The influence of agitation time on the percent sorption of BTEC onto rice bran was monitored over the range of 5–120 min using 100 μg/mL of BTEC solution concentration, at pH 6 and 303 K; all remaining parameters were the same as for the evaluation of the effect of temperature.

Under the same set of conditions, namely, 0.1 g of sorbent dose, 100 rpm shaking speed, 60 min of agitation time, and 100 μg/mL of BTEC solution concentration, the effect of pH was investigated over the range of 1–10 using different buffers.

Effect of sorbent dosage on percent sorption of BTEC was monitored by employing 0.05–0.8 g of rice bran at pH 6 using 60 min of agitation time, 100 rpm shaking speed, and 100 μg/mL sorbate concentration.

The variation of sorption of benzene onto rice bran was examined with particle size in the range of 100–1000 μm particle size of sorbent onto 0.1 g of rice bran at a solution concentration of 100 μg/mL at pH 6.

The concentration effect of benzene, toluene, ethylbenzene, and cumene on their sorption onto rice bran surface was assessed from 100 to 1000 μg/mL, with all cited conditions kept constant.

All experiments were performed at least in triplicate at pH 6 and 303 K or at pH values and temperatures specified otherwise. The results are the average of three independent measurements along with standard deviation (SD), showing 95% confidence level with the precision in most cases being ±3%. Linear regression analysis was used both to determine slopes and intercepts of the linear plots obtained and also for statistical analysis of the data.

RESULTS AND DISCUSSION

The sorption of BTEC onto rice bran is affected by the pH, amount of sorbent, temperature, and agitation time between solid and liquid phases. Thus, these have to be optimized one by one using 25 cm³ of 10 or 100 μg/mL sorbate concentration, 0.1 g of sorbent, and 100 rpm shaking speed at pH 6 and 303 K, with all other parameters kept constant.

Figure 1 exhibits the effect of temperature on the percent sorption of BTEC onto rice bran over the range of 283–323 (± 2) K at a solution concentration of 10 μg/mL, 0.1 g sorbent dose, 60 min agitation time at pH 6, and 100 rpm shaking speed. A blank sample (without rice bran) is simultaneously run to estimate the losses due to evaporation. An inverse relationship

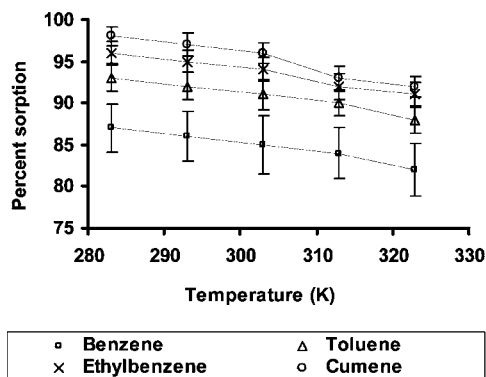


Figure 1. Influence of temperature on percent sorption of BTEC onto rice bran using 0.1 g of sorbent and 25 cm³ of 10 μg/mL sorbate concentration at pH 6.

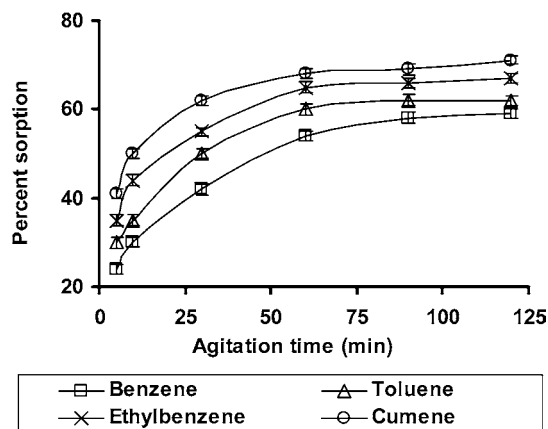


Figure 2. Effect of agitation time on percent sorption of BTEC onto rice bran using 0.1 g of sorbent and 25 cm³ of 100 μg/mL sorbate concentration of BTEC at pH 6 and 303 K.

of temperature with percent sorption is observed. A gradual decrease in percent sorption, although not significant, is observed with an increase in temperature. For further studies, the optimum temperature of 303 K was chosen. Percent sorption was found to be 85 ± 3.5 for benzene, 91 ± 1.8 for toluene, 94 ± 1.4 for ethylbenzene, and 96 ± 1.2 for cumene at the above cited conditions.

Figure 2 shows the results of the removal efficiency of rice bran for BTEC as a function of shaking time. Percent sorption was studied over a period of 5–120 min, using 0.1 g sorbent and 303 K. The sorption increased with an increase in agitation time and acquired equilibrium within 60 min. For further experiments 60 min of agitation time was employed. The order of removal efficiency remained cumene > ethylbenzene > toluene > benzene throughout the entire range of shaking time investigated. This order may be correlated with molecular weight, boiling point, dipole moment, and solubility of BTEC in methanol as given in **Table 1**. The greater are the molecular weight, boiling point, dipole moment, and solubility of organics in methanol, the greater is the sorption onto rice bran. More soluble substances in water prefer to remain in aqueous solution than to be sorbed on the sorbent surface.

Figure 3 indicates the influence of pH on the removing efficiency of BTEC by rice bran using 60 min of agitation time at 0.1 g sorbent dose. BTEC solutions have been prepared in specified pH buffers; sorption was observed over the pH range of 1–10. An inverse relationship of the removal efficiency with pH is observed in the case of all organic compounds monitored. This may be due to the presence of hydrogen ions at lower pH

Table 1. Few Characteristics of Organic Compounds (24)

organic compound and formula	mol mass (g)	bp (°C)	dipole moment (D)	solubility in water ^a (μg/mL)
benzene, C ₆ H ₆	78.11	80.0	0	1800
toluene, C ₆ H ₅ -CH ₃	92.14	110.6	0.37	470
ethylbenzene, C ₆ H ₅ -C ₂ H ₅	106.17	136	0.59	150
cumene, C ₆ H ₅ -CH(CH ₃) ₂	120.19	152	0.79	50

^a Private communication from a referee.

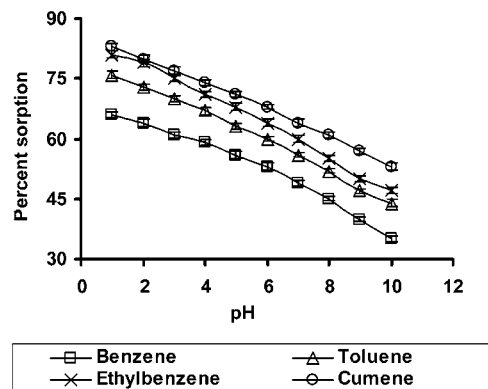


Figure 3. Effect of pH on percent sorption of BTEC onto rice bran using 25 cm³ of 100 μg/mL sorbate concentration and 0.1 g of sorbent dose in the pH range of 1–10 at 303 K.

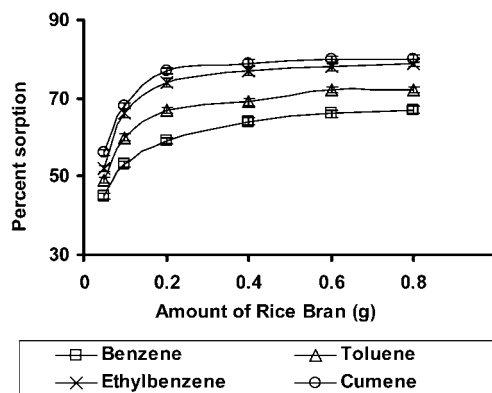


Figure 4. Percent sorption of BTEC as a function of dosage of rice bran using a concentration of 0.05–0.8 g of sorbent and 25 cm³ of 100 μg/mL sorbate solution of BTEC at pH 6 and 303 K.

resulting in an increase in the uptake of BTEC by sorbent surface. The presence of hydroxyl ions at higher pH values is likely to cause suppression of sorption of BTEC onto rice bran (26).

Furthermore, the effect of the sorbent concentration has been investigated for BTEC in the range of 0.05–0.8 g/25 cm³ by employing 60 min of agitation time at pH 6 and 100 μg/mL sorbate concentration. The results are depicted in **Figure 4**. The percent sorption increases with increasing amount of the sorbent and continues to increase up to 0.8 g/25 cm³, whereas the distribution coefficient, R_d , decreases with a further increase in the amount of sorbent. The percent sorption follows the trend cumene > ethylbenzene > toluene > benzene throughout the entire range of sorbent dosage investigated. This order can be attributed to few characteristics of BTEC mentioned in the preceding paragraph. The molecules with higher molecular weights will have more probability to come into contact with the sorbent surface (27).

Figure 5 reveals the effect of particle size of sorbent on the sorption of benzene onto rice bran in the range of 100–1000

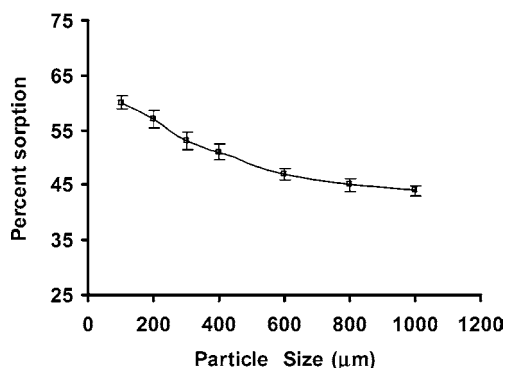


Figure 5. Influence of particle size on the percent sorption of benzene onto rice bran using 0.1 g of sorbent and 25 cm³ of 100 μg/mL benzene solution at pH 6 and 303 K.

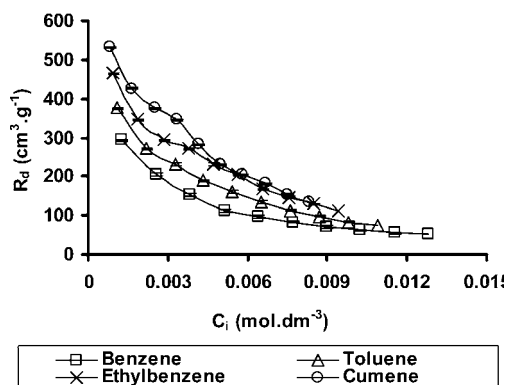


Figure 6. Effect of concentration of BTEC on sorption onto rice bran using 0.1 g of sorbent and 25 cm³ of $(1.3\text{--}13) \times 10^{-3}$, $(1.1\text{--}11) \times 10^{-3}$, $(0.9\text{--}9) \times 10^{-3}$, and $(0.8\text{--}8) \times 10^{-3}$ mol·dm⁻³ BTEC at pH 6 and 303 K.

μm monitored. It is evident that percent sorption increases with a decrease in particle size. This increase may be attributed to an increase in the surface area of smaller particle size of sorbent. However, an average particle size of 300 μm has been selected for further studies.

Figure 6 portrays the influence of BTEC concentration on their distribution coefficient over a 10-fold variation in the ranges of $(1.3\text{--}13) \times 10^{-3}$ mol·dm⁻³ for benzene, $(1.1\text{--}11) \times 10^{-3}$ mol·dm⁻³ for toluene, $(0.9\text{--}9) \times 10^{-3}$ mol·dm⁻³ for ethylbenzene, and $(0.8\text{--}8) \times 10^{-3}$ mol·dm⁻³ for cumene onto sorbent surface using 60 min of agitation time and 0.1 g of sorbent dose at pH 6. The distribution coefficient (R_d) decreases with an increase in the concentration of all BTEC compounds monitored. This may be interpreted in terms of limiting sorption sites, which may not be sufficient to accommodate increasing numbers of BTEC molecules available to be sorbed onto sorbent surface.

The sorption capacities of rice bran for benzene, toluene, ethylbenzene, and cumene have been evaluated using different isotherms, namely, Freundlich, Langmuir, and Dubinin–Radushkevich (D–R), employing data shown in Figure 6. The Freundlich sorption isotherm gives an empirical expression encompassing the surface heterogeneity and the exponential distribution of energies (28). The Freundlich sorption isotherm was tested in the following linearized form

$$\log C_{\text{ads}} = \log C_m + 1/n \log C_e \quad (4)$$

where C_{ads} and C_e are equilibrium concentrations of sorbate on sorbent surface and in solution, respectively, and C_m is the sorption capacity (mol g⁻¹). Log C_{ads} is plotted against log C_e

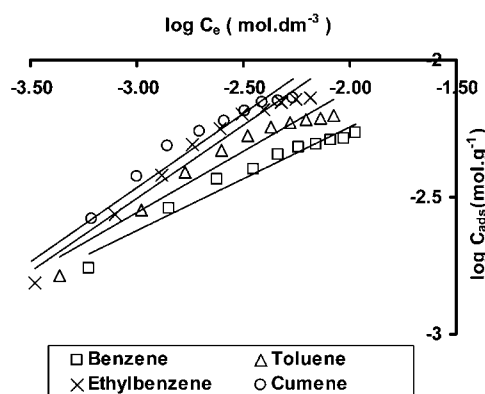


Figure 7. Freundlich sorption isotherms of benzene, toluene, ethylbenzene, and cumene onto rice bran using 0.1 g of sorbent and 25 cm³ of sorbate concentration shown in **Figure 6** at pH 6 and 303 K.

Table 2. Freundlich Characteristic Constants for BTEC onto Rice Bran

analyte	1/n	C_m (mmol g ⁻¹)	R^2
benzene	0.38 ± 0.03	32 ± 3	0.9612 ± 0.0322
toluene	0.45 ± 0.04	61 ± 14	0.9424 ± 0.0483
ethylbenzene	0.53 ± 0.04	123 ± 28	0.9619 ± 0.0463
cumene	0.54 ± 0.04	142 ± 37	0.9557 ± 0.0515

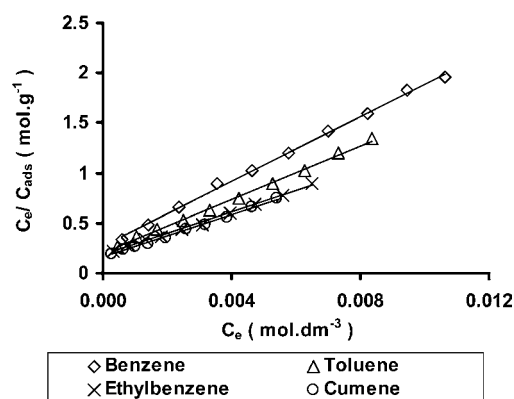


Figure 8. Langmuir sorption isotherms of benzene, toluene, ethylbenzene, and cumene onto rice bran using 0.1 g of sorbent and 25 cm³ of sorbate concentration shown in **Figure 6** at pH 6 and 303 K.

for each of BTEC components, resulting in straight lines as shown in **Figure 7**. The slopes of the straight lines give the values of $1/n$, which are <1, indicating the intensity of sorption. The values of $1/n$ show that the removal of BTEC by rice bran is effective at low concentrations, and the intercepts yield the value of C_m as given in **Table 2**. A value of $1/n = 0.43$ is reported for benzene (21) onto rice bran, which is close to 0.38 ± 0.03 for the same evaluated in the present study.

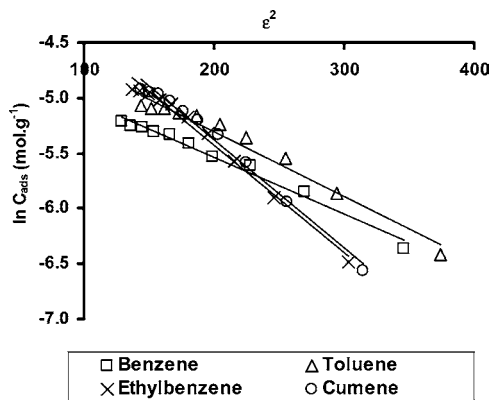
The Langmuir model (29) represents monolayer sorption on a set of distinct localized sorption sites having the same sorption energies and no interaction between sorbed molecules. It is also applied to the sorption data and tested in the linearized form

$$C_e/C_{\text{ads}} = 1/Qb + C_e/Q \quad (5)$$

where Q is the maximum sorption capacity indicating a monolayer coverage of the sorbent with sorbate and b represents the enthalpy of the sorption, independent of temperature. In **Figure 8** C_e/C_{ads} is plotted against C_e , yielding straight lines for all organics investigated, indicating that the Langmuir sorption model is followed by the sorption data very well. The values of Q are calculated from the slopes of the linear plots,

Table 3. Langmuir Parameters for BTEC onto Rice Bran

analyte	Q (mmol g ⁻¹)	b (dm ³ mol ⁻¹)	R^2
benzene	6.6 ± 0.1	592 ± 36	0.9981 ± 0.0257
toluene	7.5 ± 0.13	659 ± 35	0.9976 ± 0.0187
ethylbenzene	9.5 ± 0.22	569 ± 30	0.9956 ± 0.0156
cumene	9.4 ± 0.18	683 ± 29	0.9770 ± 0.0110

**Figure 9.** D–R sorption isotherms of benzene, toluene, ethylbenzene, and cumene onto rice bran using 0.1 g of sorbent and 25 cm³ of sorbate concentration shown in **Figure 6** at pH 6 and 303 K.**Table 4.** D–R Constants for BTEC onto Rice Bran

analyte	β (kJ ² mol ⁻²)	X_m (mmol g ⁻¹)	E (kJ mol ⁻¹)	R^2
benzene	-0.00514 ± 0.00023	11 ± 0.5	9.86 ± 0.09	0.9835 ± 0.0483
toluene	-0.00588 ± 0.00036	16 ± 1.3	9.26 ± 0.1	0.9704 ± 0.0797
ethylbenzene	-0.00966 ± 0.00038	30 ± 2.2	7.19 ± 0.08	0.9880 ± 0.0595
cumene	-0.00982 ± 0.00037	33 ± 2.5	7.14 ± 0.3	0.9889 ± 0.0594

whereas the values of b are estimated from the intercepts of the plots. The results are listed in **Table 3**.

Another dimensionless equilibrium parameter, $R_L(30)$, may be estimated from the relationship

$$R_L = \frac{1}{1 + bC_i} \quad (6)$$

where b is the Langmuir constant and C_i is the initial concentration of BTEC in the solution. The application of this equation led to values of R_L in the ranges of 0.11–0.57, 0.12–0.58, 0.16–0.65, and 0.15–0.64 for benzene, toluene, ethylbenzene, and cumene, respectively, in aqueous solution. The higher range of R_L for each BTEC indicates an appreciable sorption of these compounds onto rice bran.

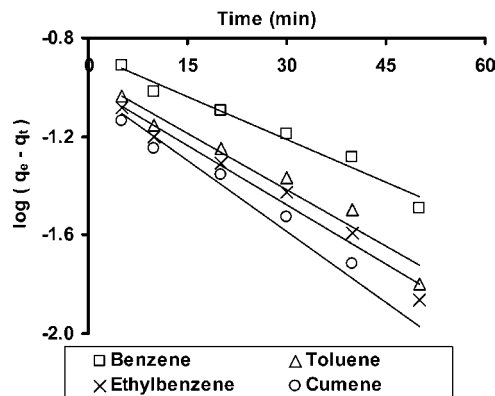
Figure 9 shows the application of the D–R isotherm (31) to the sorption data in the linearized form

$$\ln C_{\text{ads}} = \ln X_m - \beta \epsilon^2 \quad (7)$$

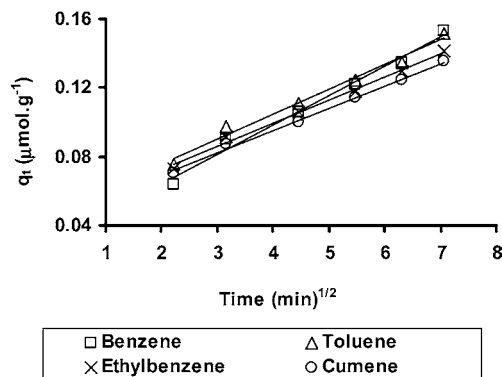
where C_{ads} is the amount of sorbate onto sorbent surface and X_m represents the maximum sorption. β is a constant related to the energy, and ϵ is a Polanyi potential, which is equal to

$$\epsilon = RT \ln(1 + 1/C_e) \quad (8)$$

where R is the gas constant in kJ mol⁻¹ K⁻¹, T is the absolute temperature in Kelvin, and C_e is the equilibrium concentration of sorbate in solution. This model postulates a fixed volume or “sorption space” close to the sorbent surface where sorption takes place. The Polanyi sorption potential, ϵ , is the work

**Figure 10.** Lagergren plots of benzene, toluene, ethylbenzene, and cumene onto rice bran, using 0.1 g of sorbent and 25 cm³ of 100 μg/mL sorbate concentration at pH 6 and 303 K.**Table 5.** Lagergren and Morris–Weber Constants of BTEC onto Rice Bran

analyte	k (min ⁻¹)	R^2	R_{id} (μmol g ⁻¹ min ^{-1/2})	R^2
benzene	0.03 ± 0.002	0.9739 ± 0.0371	0.017 ± 0.001	0.9804 ± 0.0157
toluene	0.04 ± 0.003	0.9557 ± 0.0640	0.014 ± 0.0009	0.9793 ± 0.0168
ethylbenzene	0.04 ± 0.003	0.9739 ± 0.0510	0.013 ± 0.0006	0.9796 ± 0.0143
cumene	0.05 ± 0.004	0.9674 ± 0.0684	0.013 ± 0.0005	0.9775 ± 0.0196

**Figure 11.** Validation of Morris–Weber equation for benzene, toluene, ethylbenzene, and cumene onto rice bran using 0.1 g of sorbent and 25 cm³ of 100 μg/mL sorbate concentration at pH 6 and 303 K.

required to remove a molecule to infinity from its location in the sorption space, being independent of the temperature. This model assumes the heterogeneity of sorption energies within sorption spaces. The plot of $\ln C_{\text{ads}}$ versus ϵ^2 for the data obtained in the present study should yield a straight line. The linear plots shown in **Figure 9** indicate that the D–R isotherm is obeyed over the entire BTEC concentration range monitored. The values of β and X_m computed from the slopes and intercepts, respectively, are given in **Table 4**. The value of sorption energy, E , can be correlated to β using the following relationship (32):

$$E = \frac{1}{\sqrt{-2\beta}} \quad (9)$$

Values of E for each organic compound calculated from eq 9 are also given in **Table 4**. The higher values of C_m , Q , and X_m (mmol g⁻¹) for ethylbenzene and cumene (**Tables 2–4**) may be due to increased surface activity and higher molecular weights, because surface activity increased strongly and regularly with ascension of a homologous series and as molecular

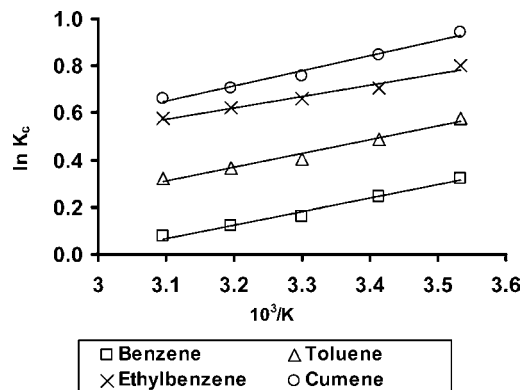


Figure 12. Variation of sorption equilibrium of benzene, toluene, ethylbenzene, and cumene onto rice bran with temperature using 0.1 g of sorbent and 25 cm³ of 100 μg/mL sorbate concentration at pH 6.

Table 6. Thermodynamic Parameters of BTEC onto Rice Bran

analyte	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	ΔG_{303K} (kJ mol ⁻¹)	R^2
benzene	-10.7 ± 0.4	-31.8 ± 1.3	-0.4 ± 0.01	0.9804 ± 0.0054
toluene	-11.1 ± 0.4	-28.5 ± 1.3	-1.0 ± 0.04	0.9793 ± 0.0081
ethylbenzene	-9.5 ± 0.3	-18.5 ± 1.1	-1.7 ± 0.05	0.9796 ± 0.0089
cumene	-12.4 ± 0.5	-25.9 ± 1.6	-1.9 ± 0.05	0.9775 ± 0.0099

weight increases more water molecules will be displaced; thus, points of contact of sorbate onto sorbent surface increase, as larger molecules of sorbate have more points of contact with the sorbent (27).

The kinetic data of BTEC sorption onto rice bran were applied to the Lagergren equation (33)

$$\log(q_e - q_t) = \log q_e - \frac{kt}{2.303} \quad (10)$$

and tested by plotting $\log(q_e - q_t)$ versus t , which would give a straight line for each organic compound as shown in **Figure 10**, where q_e and q_t are the equilibrium and sorbed concentration at a time t . The values of k , the first-order rate constant, were computed from the slopes of the linear plots shown in **Figure 10**. The results are listed in **Table 5**.

Another kinetic relationship, that is, the Morris–Weber equation (34), was examined in the form

$$q_t = R_{id}\sqrt{t} \quad (11)$$

where q_t is the concentration of organics sorbed at time t and R_{id} is the rate constant for intraparticle transport. Plots of q_t versus $t^{1/2}$ are shown in **Figure 11**. The sorption data follow linearity up to 60 min of agitation time. The slopes of the linear plots gave values of R_{id} for different organic compounds and are also given in **Table 5**.

The effect of temperature (283–323 K) on the sorption of BTEC (100 μg/mL) onto rice bran at pH 6 is monitored using 0.1 g of rice bran, an equilibration time of 60 min, and a shaking speed 100 rpm. The corresponding plots of $\ln K_c$ versus $1/T$ (K⁻¹), shown in **Figure 12**, are linear over the entire range of temperature investigated. The value of the equilibrium constant, K_c , may be achieved at each temperature from the relationship

$$K_c = F_e/1 - F_e \quad (12)$$

where F_e is the fraction sorbed at equilibrium. The thermodynamic parameters enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG) were estimated using the following equations:

$$\ln K_c = -\Delta H/RT + \Delta S/R \quad (13)$$

$$\Delta G = -RT \ln K_c \quad (14)$$

From the slopes and intercepts of the plots shown in **Figure 12**, the values of ΔH and ΔS have been assessed, whereas ΔG has been calculated using eq 14, and the results are listed in **Table 6**. It may be deduced from the negative values of ΔH , ΔS , and ΔG that the sorption process is exothermic and spontaneous in nature, suggesting no structural changes at the solid–liquid interface, with weak bond formation between sorbent and sorbate (35). Moreover, the negative values of ΔG for all of the organics indicate the feasibility of their sorption onto rice bran surfaces from aqueous solution containing traces of methanol.

These observations indicate that rice bran is very effective for the removal of fat soluble substances and has potential applications for the removal of BTEC from surface waters and groundwater. Rice bran is the outermost coat of the rice grain. Generally, plants store lipids in oil bodies or spherosomes. Spherosomes are organelles rich in lipids, and they differ in morphology and origin from large oil bodies (36). Compounds with high lipophilicity are more easily removed by rice bran (37). The uptake of BTEC by rice bran has been reported mainly to be due to spherosome particles. Spherosomes are intracellular oil-containing particles of ~1 μm in diameter, with an osmophilic matrix, and are bound by unusual single-line membranes (38); these membranes are inferred to be related to the uptake of BTEC compounds into spherosomes. It is suggested that molecular size, molecular structure, steric form, or configuration of sorbate also influences the sorption. The more soluble a substance is in water, the lower its sorption on the sorbent surface is likely to be. In general, a polar sorbate will be strongly sorbed from a nonpolar solvent by a polar sorbent (39).

APPLICATION TO WASTEWATER SAMPLE

A contaminated water sample was collected from Phulaili canal, Hyderabad, from a location containing petroleum-based automobile service station wastewater and pharmaceutical and

Table 7. Percent Sorption and Percent Recovery of Benzene, Toluene, and Ethylbenzene from Contaminated Wastewater

analyte	concn of analyte determined (μg/mL) ± SD	concn of analyte determined with spiked sample ^a (BTE) (μg/mL) ± SD		% sorption	% recovery with 2 mL of methanol
		before sorption	after sorption		
benzene	0.451 ± 0.002	10.45 ± 0.002	0.22 ± 0.001	98 ± 0.13	96.2 ± 0.4
toluene	0.334 ± 0.002	10.33 ± 0.003	0.1 ± 0.001	99 ± 0.22	97.3 ± 0.4
ethylbenzene	0.214 ± 0.002	10.21 ± 0.002	0.1 ± 0.001	99 ± 0.06	97.3 ± 0.4
cumene	ND ^b				

^a Spiked sample (BTE) = 10 μg/mL. ^b Not detected.

other industrial and agricultural effluents from the top of the water surface close to the left bank of the canal. The sample was taken in a rinsed dark glass bottle of 5 L capacity and was transferred immediately to an air-conditioned vehicle for transportation to the laboratory, where it was placed in a freezer at -4°C . Benzene, toluene, and ethylbenzene in the wastewater sample were estimated by comparing the retention times and peak heights (mV) of individual organic compounds with synthetic sample solution, as per the procedure in the literature (40); cumene was not detected in the sample. A 100 mL aliquot of the wastewater was taken into a 250 mL glass-stoppered Erlenmeyer flask spiked with $10\ \mu\text{g/mL}$ of each analyte sample (BTE), containing 0.5 g of rice bran, and agitated for 60 min under the experimental conditions discussed earlier. Ten microliters was injected onto HPLC for the analysis by adopting the sorption procedure as mentioned under Experimental Procedures. Rice bran effectively removed $98 \pm 0.13\%$ of the benzene, $99 \pm 0.22\%$ of the toluene, and $99 \pm 0.06\%$ of the ethylbenzene from the wastewater sample. The sorbed amounts of BTE were recovered with 2 mL of methanol by sonication on an ultrasonic bath for 10 min. The percent recoveries were found to be $96.2 \pm 0.4\%$ for benzene, $97.3 \pm 0.4\%$ for toluene, and $97.3 \pm 0.4\%$ for ethylbenzene, respectively. The results of the analysis along with percent sorption onto rice bran and percent recovery with 2 mL of methanol are listed in **Table 7**.

LITERATURE CITED

- Mottaleb, M. A.; Abedin, M. Z.; Islam, M. S. Determination of benzene, toluene, ethylbenzene and xylene in river water by solid-phase extraction and gas chromatography. *Anal. Sci.* **2003**, *19*, 1365–1369.
- Kango, R. Y.; Quinn, J. G. Adsorption studies of xylene and ethylbenzene on soil and humic acid by a purge and trap gas chromatographic method. *Chemosphere* **1989**, *19*, 1269–1276.
- Quigley, C. J.; Corsi, R. L. Emissions of VOCs from a municipal sewer. *J. Air. Waste Manage. Assoc.* **1995**, *45*, 395–403.
- Henry, V. M. Association of hydrophobic organic contaminants with soluble organic matter: evaluation of the database of K_{doc} values. *J. Adv. Environ. Res.* **2002**, *6*, 577–593.
- Environmental Quality Standards for Soil and Water*; Netherlands Ministry of Housing, Physical Planning and Environment: Leidschendam, The Netherlands, 1991.
- IARC. Benzene. In *Overall Evaluations of Carcinogenicity: an Updating of Selected IARC Monographs from Volumes 1 to 42*; IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Supplement 7; International Agency for Research on Cancer: Lyon, France, 1987; pp 120–122.
- Hattermer-Frey, H. A.; Travis, C. C.; Land, M. L. Benzene: environmental partitioning and human exposure. *Environ. Res.* **1990**, *53*, 221–232.
- Toxicological Profile for Toluene*; Agency for Toxic Substances and Disease Registry, U.S. Department of Health and Human Services: Atlanta, GA, 2000.
- Andrey, B.; Rehman, H.; Teresa, J. B. Study of regeneration of activated carbons used as H_2S adsorbents in water treatment plants. *J. Adv. Environ. Res.* **2002**, *6*, 303–311.
- Kadirvelu, K.; Namasivayam, C. Erratum to activated carbon from coconut. Coirpith as metal adsorbent: adsorption of Cd(II) from aqueous solution. *J. Adv. Environ. Res.* **2004**, *8*, 729–737.
- Robin, H. B.; Jochen, L.; Michael, G. In vitro analogues of photosystem, combined flash photolytic and conductometric study of light-induced oxygen evolution from water mediated by colloidal $\text{RuO}_2/\text{TiO}_2$. *J. Am. Chem. Soc.* **1982**, *104*, 422–425.
- Beltran, F. J.; Garcia Araya, J. F.; Acedo, B. Advance oxidation of atrazine in water—II, ozonation combined with ultraviolet. *Water Res.* **1994**, *28*, 2165–2174.
- McCarty, P. L.; Sutherland, K. H.; Graydon, J.; Reinhard, M. Volatile organic contaminants removal by air stripping. Presented at the 99th Annual National American Water Works Association Conference, San Francisco, CA, June 1979.
- Rominder, P. S. S.; John, C. C. Removal and destruction of organic compounds in water using adsorption, steam regeneration, and photocatalytic oxidation processes. *J. Environ. Eng.* **1999**, *125*, 897–905.
- Sosnowski, P.; Wieczorek, A.; Ledakowicz, S. Anaerobic codigestion of sewage sludge and organic fraction of municipal solid wastes. *J. Adv. Environ. Res.* **2003**, *7*, 609–616.
- Hasany, S. M.; Ahmad, R.; Chaudhary, M. H. Investigation of sorption of Hg(II) ions onto coconut husk from aqueous solution using radiotracer technique. *Radiochim. Acta* **2003**, *91*, 533–538.
- Xia, G.; Ball, W. P. Adsorption-partitioning uptake of nine low-polarity organic chemicals on a natural sorbent. *Environ. Sci. Technol.* **1999**, *33*, 262–269.
- Yan, Fu.; Urmila, M. D. Cost-effective environmental control technology for utilities. *J. Adv. Environ. Res.* **2004**, *8*, 173–196.
- Otoniel, D. S. A.; Luciene, S. J.; Ricardo, J. C.; Marcelo, S. C.; Ricardo, E. S. Solid-phase extraction of Cu(II) as diethyldithiocarbamate (ddtc) complex by polyurethane foam. *J. Braz. Chem. Soc.* **2003**, *14*, 728–733.
- Damaris, N. M.; Paul, M. S.; Rachel, M. N.; Geoffrey, N. K. Adsorption and detection of some phenolic compounds by rice husk ash of Kenyan origin. *J. Environ. Monit.* **2002**, *4*, 978–984.
- Adachi, A.; Ikeda, C.; Takagi, S.; Fukao, N.; Yoshie, E.; Okano, T. Efficiency of rice bran for removal of organochlorine compounds and benzene from industrial wastewater. *J. Agric. Food Chem.* **2001**, *49*, 1309–1314.
- Pyle, S. M.; Gurka, D. F. Volatile organic analysis by direct aqueous injection. *Talanta* **1994**, *41*, 1845–1852.
- Kasthurikishuan, N.; Cooks, R. G. On-line flow injection analysis of volatile organic compounds in seawater by membrane introduction mass spectrometry. *Talanta* **1995**, *42*, 1325–1334.
- Lide, D. R., Ed. *CRC Handbook of Chemistry and Physics*, 83rd ed.; CRC Press: Boca Raton, FL, 2002.
- Perrin, D.; Dempsey, B. *Buffers for pH and Metal Ion Control*; Wiley: New York, 1974.
- Sivaraj, R.; Namasivayam, C.; Kadirvelu, K. Orange peel as an adsorbent in the removal of acid violet 17 (acid dye) from aqueous solutions. *Waste Manag.* **2001**, *21*, 105–110.
- Morrill, L. G.; Mahilum, B. C.; Mohiuddin, S. H. *Organic Compounds in Soils: Sorption, Degradation and Persistence*; Ann Arbor Science: Collingwood, Ann Arbor, MI, 1982; pp 56–57.
- Freundlich, H. *Colloid and Capillary Chemistry*; Methuen: London, U.K., 1926; pp 397–414.
- Langmuir, I. The adsorption of gases on plane surface of glass, mica and platinum. *J. Chem. Soc.* **1918**, *40*, 1361–1403.
- McKay, G.; Blair, H.; Gardiner, J. R. The adsorption of dyes onto chitin in fixed bed column and batch adsorbers. *J. Appl. Polym. Sci.* **1989**, *28*, 1499–1544.
- Dubin, M. M.; Radushkevich, L. V. The equation of the characteristic curve of the activated charcoal. *Proc. Acad. Sci. U.S.S.R. Phys. Chem. Sec.* **1947**, *55*, 331.
- Hobson, J. P. Physical adsorption isotherms extending from ultrahigh vacuum to vapor pressure. *J. Phys. Chem.* **1969**, *73*, 2720–2727.
- Lagergren, S. Zur theorie der sorption geloster stoffe. *Handlingar* **1898**, *24*, 1.
- Morris, W. J.; Weber, J. C. Kinetics of adsorption on carbon from solutions. *J. Sanit. Eng. Div. ASCE* **1963**, *89*, 31.
- Hasany, S. M.; Saeed, M. M.; Ahmed, M. Sorption of traces of silver ions onto polyurethane foam from acidic solution. *Talanta* **2001**, *54*, 89–98.

- (36) Jelsema, C. L.; Morre, D. J.; Ruddat, M.; Turner, C. Isolation and characterization of the lipid reserve bodies, spherosomes, from aleurone layers of wheat. *Bot. Gaz.* **1977**, *138*, 138–149.
- (37) Adachi, A.; Takagi, S.; Okano, T. Studies on removal efficiency of rice bran for pesticides. *J. Health Sci.* **2001**, *47*, 94–98.
- (38) Yatsu, L. Y.; Jacks, T. J. Spherosome membranes. *Plant Physiol.* **1972**, *49*, 937–943.
- (39) Ruthven, D. M. *Principles of Adsorption and Adsorption processes*; Wiley: New York, 1984.
- (40) American Public Health Association. *Standard Methods for the Examination of Water and Wastewater*, 17th ed.; American Water Works Association: New York, 1989.

Received for review March 1, 2005. Revised manuscript received July 25, 2005. Accepted July 26, 2005.

JF058060H