

Sorption potential of *Moringa oleifera* pods for the removal of organic pollutants from aqueous solutions

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Abstract

Moringa oleifera pods Lamarck (Drumstick or Horseradish) is a multipurpose medium or small size tree from sub-Himalayan regions of north-west India and indigenous to many parts of Asia, Africa, South America, and in the Pacific and Caribbean Islands. Its pods (MOP) have been employed as an inexpensive and effective sorbent for the removal of organics, i.e., benzene, toluene, ethylbenzene and cumene (BTEC) from aqueous solutions using HPLC method. Effect of different parameters, i.e., sorbent dose 0.05–0.8 g, 25 cm⁻³ agitation time 5–120 min, pH 1–10, temperature 283–308 K and concentration of sorbate $(1.3–13) \times 10^{-3}$, $(1.1–11) \times 10^{-3}$, $(0.9–9) \times 10^{-3}$, $(0.8–8) \times 10^{-3}$ mol dm⁻³, on the sorption potential of MOP for BTEC have been investigated. The pore area and average pore diameter of the MOP by BET method using nitrogen as a standard are calculated to be 28.06 ± 0.8 m² g⁻¹ and 86.2 ± 1.3 nm respectively. Freundlich, Langumir and Dubinin–Radushkevich (D–R) sorption isotherms were employed to evaluate the sorption capacity of MOP. Sorption capacities of BTEC onto MOP have been found to be 46 ± 10 , 84 ± 9 , 101 ± 4 , 106 ± 32 mmol g⁻¹ by Freundlich, 8 ± 0.1 , 9 ± 0.1 , 10 ± 0.3 , 9 ± 0.1 mmol g⁻¹ by Langumir and 15 ± 1 , 21 ± 1 , 23 ± 2 , 22 ± 3 mmol g⁻¹ by D–R isotherms respectively, from BTEC solutions at 303 K. While the mean energy of sorption process 9.6 ± 0.3 , 9.2 ± 0.2 , 9.3 ± 0.3 , 9.5 ± 0.4 kJ mol⁻¹ for BTEC is calculated by D–R isotherm only. Rate constant of BTEC onto MOP 0.033 ± 0.003 , 0.030 ± 0.002 , 0.029 ± 0.002 , 0.027 ± 0.002 min⁻¹ at solution concentration of 1.3×10^{-3} , 1.1×10^{-3} , 0.9×10^{-3} and 0.8×10^{-3} mol dm⁻³ and at 303 K have been calculated by employing Lagergren equation. Thermodynamic parameters ΔH -8 ± 0.4 , -10 ± 0.6 , -11 ± 0.7 , -11 ± 0.7 kJ mol⁻¹, ΔS -22 ± 2 , -26 ± 2 , -27 ± 2 , -29 ± 3 J mol⁻¹ K⁻¹ and $\Delta G_{303\text{K}}$ -0.9 ± 0.2 , -1.9 ± 0.2 , -2.3 ± 0.1 and -2.6 ± 0.2 kJ mol⁻¹ were also estimated for BTEC respectively at temperatures 283–308 K. The negative values of ΔH , ΔS and ΔG suggest exothermic, stable (with no structural changes at solid–liquid interface) and spontaneous nature of sorption process under optimized conditions. MOP has been used extensively to accrue and then to preconcentrate benzene, toluene and ethylbenzene in wastewater sample.

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Keywords: *Moringa oleifera* (drumstick) pods; Sorption; Benzene; Toluene; Ethylbenzene; Cumene

1. Introduction

Since last two decades, contamination of groundwater with organic pollutants has become great environmental concern. Various kinds of pollutants have been detected in the environment. Among these, volatile organic compounds (VOCs), e.g., benzene, toluene, ethylbenzene, xylene and cumene are important

environmental contaminants because of their high toxicity and widespread occurrence [1,2]. BTEC components are present in aviation fuel (gasoline) and are widely used as industrial solvents and raw materials for the production of different commodities [3]. These may lead to serious safety concerns, when someone comes across these organics [4]. As they are important items of many industries, therefore, it is not practically feasible to eliminate these from the environment; however, it is required to keep their concentrations in water as low as possible. Therefore, it is essential to monitor the environment to ensure that their levels may not increase beyond the tolerance levels [4], otherwise they may adversely affect the well being of animal and human life and cause certain physiological disorders and diseases [5]. Among

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the techniques used for the removal of these contaminants from surface and ground water are adsorption on activated carbon [6], and their photochemical decomposition by ultraviolet radiations [7]. All these processes are too costly to be adopted for practical purposes. Use of synthetic coagulants, e.g., alum lime, aluminum sulphate, polyaluminum chloride, iron chloride, iron hydroxide and soda ash also have not been appreciated owing to their carcinogenic effects on human health [8].

Presently, there is an increasing trend to evaluate some indigenous cheaper materials for the removal of these pollutants and pesticides from aqueous solutions. A large number of cheaper materials including industrial and agricultural wastes have been used to remove different pollutants from the industrial effluents for their safe disposal into the biosphere [9,10].

Adachi et al. [2,11] used rice bran and defatted seeds of soybean, rapeseed, linseed and sesame for the removal of organochlorine compounds and benzene from industrial wastewaters and obtained appreciable results. Damaris [12] employed rice husk for the adsorption and detection of phenolic compounds. Similarly, clay minerals for the sorption of pesticides etc. have been reported to be effective sorbents [13].

Moringa oleifera Lamarck, a member of Moringaceae family is well known and most utilized species. It is indigenous to sub-continent and thrives in tropical temperate and insular climate. It is drought tolerant and has nutritional, medicinal and water cleaning attributes [14]. The leaves, flowers, fruits and roots of *M. oleifera* are used locally as food articles. The medicinal and therapeutic properties of this plant has led to its application as a cure for different ailments and diseases, physiological disorders and in eastern allopathic medicine [15].

No previous work has appeared concerning the removal of BTEC components using *M. oleifera* pods. The present communication deals with the sorption of BTEC components onto cost effective MOP over a wide pH range alongwith other parameters affecting the sorption process using HPLC methodology.

The main objectives of the present investigation are to investigate the sorption potential of MOP for the removal of organics from aqueous media. The data have been analyzed by different statistical models. Besides this, kinetic and thermodynamic studies of the sorption process has been made. No previous report describes the detailed explanation of the sorption process using MOP and exploits the cost-effective abundantly available indigenous agricultural material for the removal of organics from aqueous solutions and to optimize systematically their accumulation onto biosorbent surface. The study of its kinetics and thermodynamics will lead to the better understanding of the sorption process and finally to demonstrate its utility in the pre-concentration of organics from wastewater samples.

2. Experimental

2.1. Reagents and materials

All the reagents used in the present investigation were of analytical grade and procured from Fluka Chemical Co. or E. Merck, Germany. BTEC components of 99.9% purity were obtained from Sigma Chemicals Ltd., USA. Methanol (HPLC grade 99.99%), was obtained from Merck, Germany and used for making synthetic aqueous solutions and for HPLC method. All glassware employed were of Pyrex, Germany. Throughout the experiments, all glassware were cleaned with 20% nitric acid and repeatedly washed with doubly distilled deionized water followed by drying at 383 K 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 made upto 1000 cm³ with doubly distilled deionized water [16]. The solubility of these compounds in alcohol is indicated in the literature [17].

The samples of required concentration were prepared by diluting the stock solutions. The buffers of pH 1–3, 4–6 and 7–10 were prepared by mixing appropriate volumes of 0.1 M solutions of HCl and KCl; CH₃COOH and CH₃COONa; and H₃BO₃ and NaOH, respectively [18].

2.2. Sampling and treatment of sorbent

M. oleifera pods were obtained from Agriculture University, Tandojam, washed thoroughly with doubly distilled deionized water to remove water soluble impurities and dried in sunlight for 8 h. The washed and dried material was pulverized (by mortar and pestle) and sieved to different mesh sizes from 200 to 400 μm in Ro-Tap type electrical sieve shaker. Average particle size of 300 μm was chosen for the present work. The sieved material was rewashed thoroughly with doubly distilled deionized water to remove the fine particles and dried at 383 K for 4 h and treated with 0.1 M nitric acid and methanol for 4 h (MOPCT) to remove inorganic and organic matter from the sorbent surface followed by thermal treatment in an electric furnace (Phoenix furnace alpha-1, Sheffield, England 1983) at 573 K for 1 h (MOP) to increase the surface area [19]. The treated (MOP) and untreated materials (MOPUT) were then placed in a desiccator to be used as sorbents. The results of surface area analysis using Quanta Sorb (QS-7) surface area analyzer are exhibited in Table 1. *M. oleifera* pods after chemical and thermal treatment have greater surface area and pore diameter, may be due to the fact that chemical treatment can dissolve the minerals and functional groups from the sorbent surface and thus enhances the pore volume and

Table 1
Results of surface area analysis for MOP

Sorbents (MOP)	Total intrusion volume (cm ³ g ⁻¹)	Average particle size (μm)	Pore area (m ² g ⁻¹)	Average pore diameter (nm)
MOPUT	0.23	300	16 ± 0.9	49 ± 3
MOPCT	0.29	300	21 ± 0.8	52 ± 2
MOP	0.72	300	28 ± 0.8	86 ± 1

ND: not detected; MOPUT: *M. oleifera* pods untreated; MOPCT: *M. oleifera* pods after chemical treatment; MOP: *M. oleifera* pods after chemical treatment and thermal treatment.

surface area while, thermal activation increases the porosity of the *M. oleifera* pods.

2.3. Instrumentation

Hitachi model 6200 HPLC equipped with a Licrosorb ODS column 5 μm ($\text{Ø}150 \times 4\text{ mm}$) UV/visible detector equipped with a CSW32 software was used for data acquisition, integration and processing. Redistilled methanol and doubly distilled deionized water (80:20) with $0.8\ \mu\text{S cm}^{-1}$ conductance and pH 5.8 were used as a mobile phase at a flow rate of 1 ml/min, arbitrary unit full scale deflection (AUFs) 0.005 and the wavelength 254 nm. The limit of detection (signal to noise ratio 1: 2) was found to be 0.1, 0.05, 0.05 and $0.05\ \text{ng}\ \mu\text{l}^{-1}$ for benzene, toluene, ethylbenzene and cumene respectively. The pH measurements were made on digital (inolab level 1) pH meter, Germany.

2.4. Sorption method

Appropriately weighed adsorbent (0.05–0.8 g) was placed in dry glass stoppered conical flasks; to which $25\ \text{cm}^3$ of sorbate containing varying amount of analyte, i.e., $1.3\text{--}13 \times 10^{-3}$, $1.1\text{--}11 \times 10^{-3}$, $0.9\text{--}9 \times 10^{-3}$ and $0.8\text{--}8 \times 10^{-3}\ \text{mol dm}^{-3}$ was added. The flasks were then fitted to a Gallenkemp No: 350-010 Stuart scientific wrist-action shaker at a speed of 100 rpm and temperature 283–308 K for 5–120 min. In order to assess the evaporation losses of BTEC components onto MOP, controlled sample was also placed in the same shaker without sorbent. Finally, the sample was filtered using Whatmann filter paper 44 to remove the sorbent. Similar results of control and treated samples suggested no losses due to evaporation. A $10\ \mu\text{l}$ of filtered sample was then injected to HPLC under given set of conditions. The sorbed concentration of the sorbate was calculated by the difference in the detector response and peak height (mV) before and after shaking. The removal efficiency or % sorption is calculated as

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

where C_i and C_e are initial and equilibrium concentration of sorbates expressed in mol dm^{-3} . The distribution coefficient (R_d) is assayed using following equation

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

The % sorption and the distribution coefficient (R_d) can be correlated by the following equation

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

All experiments were performed at least in triplicate at pH 6 and 303 K, unless stated otherwise. The results are the average of three independent measurements alongwith standard deviation (S.D.) at 95% confidence level with the precision in most cases

being $\pm 3\%$. Linear regression analysis was used to determine both slope and intercept of the linear plots obtained and also for statistical analyses of the data.

3. Results and discussion

The sorption of BTEC components onto MOP (between liquid and solid phases) is affected by the amount of sorbent, agitation time, pH, concentration of sorbate and reaction temperature, so these parameters have to be optimized one by one. Nevertheless, 1.3×10^{-3} , 1.1×10^{-3} , 0.9×10^{-3} and $0.8 \times 10^{-3}\ \text{mol dm}^{-3}/25\ \text{cm}^3$ of sorbate concentration, 0.05–0.8 g of sorbent, 283–308 K temperature, 100 rpm shaker speed, and pH 6 were used throughout the study for further exploration.

3.1. Effect of sorbent dosage

In order to investigate the effect of sorbent concentration (0.05–0.8 g) on the sorption of BTEC components onto MOP $25\ \text{cm}^3$ of 1.3×10^{-3} , 1.1×10^{-3} , 0.9×10^{-3} and $0.8 \times 10^{-3}\ \text{mol dm}^{-3}$ BTEC concentration respectively, 30 min agitation time were employed at pH 6 and 303 K. A steep increase in % sorption was observed from 0.05 to 0.1 g of sorbent amount for all BTEC components investigated, which remained almost constant from 0.2 to 0.8 g, suggesting 0.1 g to be the sufficient sorbent dose to accommodate all the sorbate molecules. On increasing further sorbent amount, a decrease in distribution coefficient, R_d was observed. For whole range of sorbent amount investigated, sorption follows the order cumene > ethylbenzene > toluene > benzene (Fig. 1). This order may be interpreted in terms of their molecular weight, boiling point, dipole moment and solubility of these compounds in methanol as envisaged earlier [20]. More soluble the substances in water tend to be remain in the aqueous phase rather than to sorbed onto biomass surface.

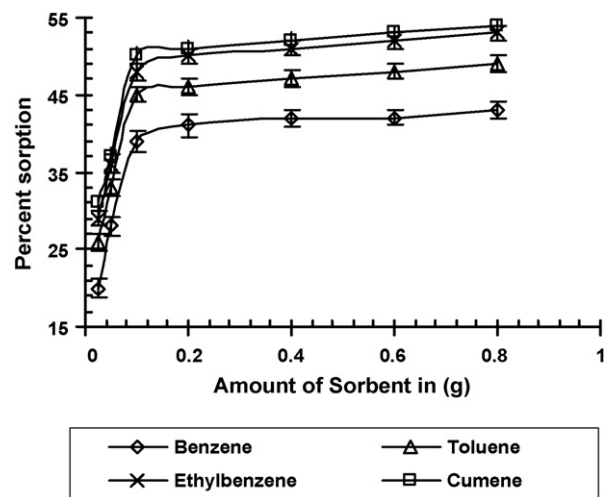


Fig. 1. % Sorption of BTEC as a function of dosage of MOP 0.05–0.8 g using $25\ \text{cm}^3$ of 1.3×10^{-3} , 1.1×10^{-3} , 0.9×10^{-3} , $0.8 \times 10^{-3}\ \text{mol dm}^{-3}$ solution concentration of sorbate respectively at 30 min agitation time, pH 6 and 303 K.

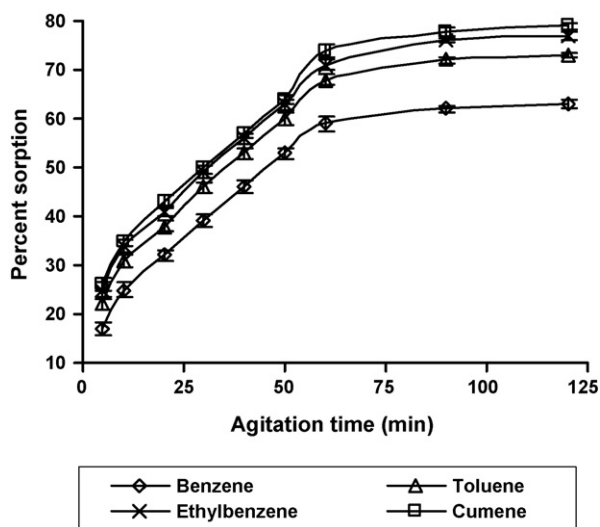


Fig. 2. Effect of agitation time 5–120 min on % sorption of BTEC onto 0.1 g MOP, 25 cm³ of 1.3×10^{-3} , 1.1×10^{-3} , 0.9×10^{-3} , 0.8×10^{-3} mol dm⁻³ solution concentration of sorbate at pH 6 and 303 K.

3.2. Effect of agitation time

Sorption data enlightening the effect of agitation time for the partitioning of BTEC component between liquid and solid phase of MOP is presented in Fig. 2. Agitation time was varied from 5 to 120 min for 0.1 g sorbent dose and 25 cm³ of 1.3×10^{-3} , 1.1×10^{-3} , 0.9×10^{-3} and 0.8×10^{-3} mol dm⁻³ concentration of BTEC components respectively at pH 6 and 303 K. The % sorption and distribution ratio (R_d) increased with an increase in agitation time. The equilibrium was accomplished within 60 min, for the rest of study 60 min contact time was employed. Order of sorption in the shaking time range investigated was similar cumene > ethylbenzene > toluene > benzene as observed in the study of sorbent dose. This order may be correlated with molecular weight, boiling point, dipole moment, solubility of BTEC in water and methanol. Greater are the molecular weight, boiling point, dipole moment, solubility of organics in water and methanol, greater are their sorption onto MOP. More soluble substances in water prefer to remain in aqueous solution than to be sorbed on the sorbent surface.

3.3. Effect of pH

Because *M. oleifera* pods contains 15.6% cellulose, 11.1% hemicellulose, 10.7% lignin and 13.8% crude fiber [21] in its matrix network and contain carboxylic, fiber carbonaceous and amino functional groups [22]. These functional groups may be dissociated at different pH values and consequently take part in the sorption process. Therefore, pH may influence the sorption of organics onto MOP. Moreover, pH of wastewater may be from acidic via neutral to alkaline region. Therefore, the effect of pH on the accumulation of organics onto MOP is necessary to be known.

Effect of pH on % sorption was investigated over the range 1–10 using different buffer systems, keeping all parameters constant as mentioned in the section 3.2. Sorption efficiency of MOP

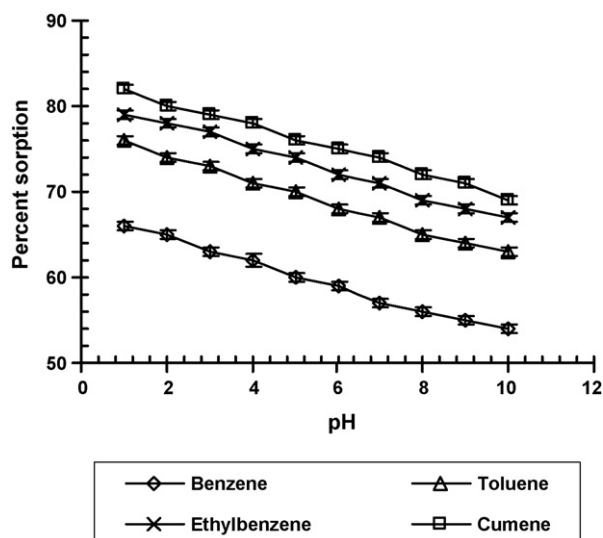


Fig. 3. Influence of pH in the range (1–10) on % sorption of BTEC onto 0.1 g MOP, 25 cm³ of 1.3×10^{-3} , 1.1×10^{-3} , 0.9×10^{-3} , 0.8×10^{-3} mol dm⁻³ solution concentration of sorbate, 60 min agitation time at 303 K.

slightly increased with a decrease in pH (Fig. 3). This may be attributed to the presence of more hydrogen ions at lower pH, resulting in an increased uptake of BTEC components by sorbent surface at lower pH. While on the contrary, presence of hydroxyl ions at higher pH may result in the suppression of sorption for all the BTEC components onto MOP [23]. The order of sorption was same as observed in Fig. 2 over the whole pH range investigated. For the application of proposed method to natural water samples; pH 6 was employed.

3.4. Effect of temperature

Effect of temperature on the sorption of BTEC components onto MOP was monitored in the range of 283–308 K at pH 6 and 60 min agitation time, using 25 cm³ of 1.3×10^{-3} , 1.1×10^{-3} , 0.9×10^{-3} and 0.8×10^{-3} mol dm⁻³ sorbate concentration respectively. Enhanced sorption is noticed at low temperature for all the BTEC components (Fig. 4) revealing exothermic nature of the sorption process. The order of sorption was again the same as of previous studies [20] i.e., cumene > ethylbenzene > toluene > benzene.

3.5. Effect of BTEC concentration

The effect of BTEC components concentration over a 10-fold range 1.3 – 13×10^{-3} , 1.1 – 11×10^{-3} , 0.9 – 9×10^{-3} and 0.8 – 8×10^{-3} mol dm⁻³ on their own uptake by MOP was examined under optimized conditions of 0.1 g sorbent dose/25 cm³ solution using 60 min agitation time and pH 6. The variation in the sorption of BTEC components as a function of concentration is depicted in Fig. 5. With an increase in concentration of BTEC solutions, a corresponding decrease in distribution coefficient (R_d) was observed. These findings may be implicated in terms of limiting sorption sites of sorbent, which may have insufficient capability to accommodate increasing number of

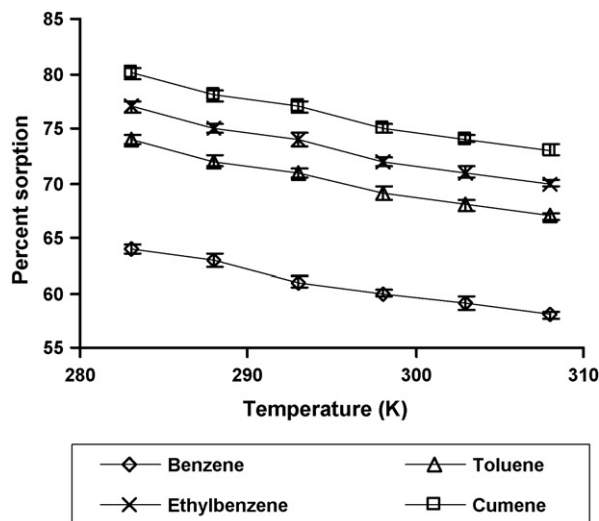


Fig. 4. Effect of temperature 283–308 K on % sorption of BTEC onto 0.1 g MOP, 25 cm³ of 1.3×10^{-3} , 1.1×10^{-3} , 0.9×10^{-3} and 0.8×10^{-3} mol dm⁻³ sorbate concentration, 60 min agitation time at pH 6.

BTEC molecules available to be sorbed onto sorbent surface [20].

3.6. Sorption isotherms

Three sorption isotherms i.e., Freundlich, Langmuir and Dubinin–Radushkevich (D–R) were tested to apply the sorption data of BTEC onto MOP given in (Fig. 5). Freundlich sorption isotherm is the most commonly used empirical expression describing the sorption from solutions and deals with surface heterogeneity, exponential distribution of active sites of sorbent and their energies towards sorbate [24] and is given in the form of linearized equation:

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

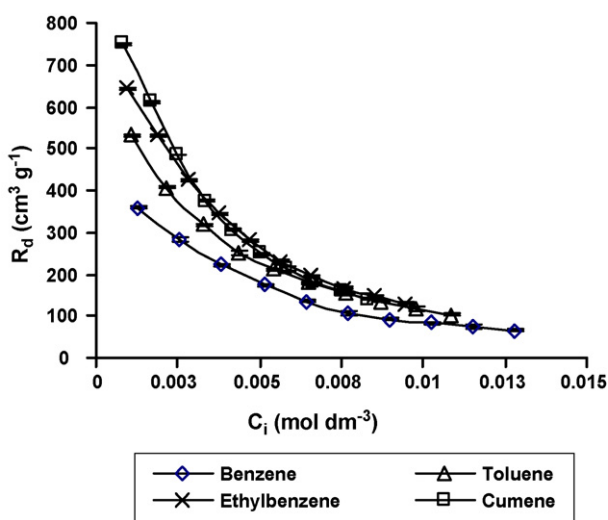


Fig. 5. Effect of BTEC concentration in the range of $1.3\text{--}13 \times 10^{-3}$, $1.1\text{--}11 \times 10^{-3}$, $0.9\text{--}9 \times 10^{-3}$ and $0.8\text{--}8 \times 10^{-3}$ mol dm⁻³/25 cm³ of sorbate on their sorption onto 0.1 g MOP, 60 min agitation time at pH 6 and 303 K.

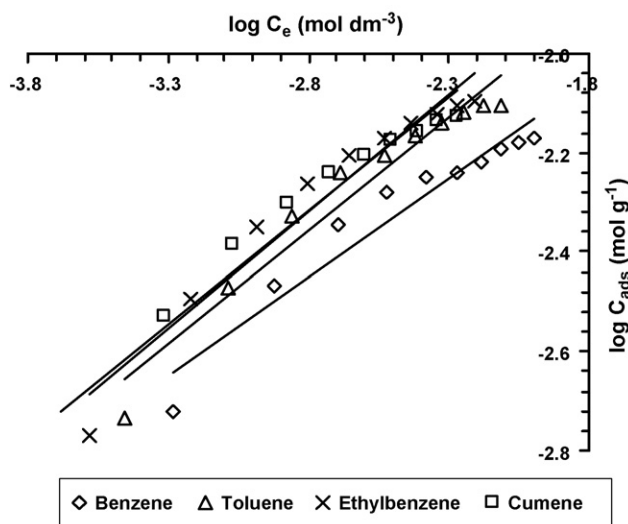


Fig. 6. Freundlich sorption isotherms of BTEC onto 0.1 g MOP/25 cm³ of sorbate, 60 min agitation time at pH 6 and 303 K.

where $1/n$ is a characteristic constant related to sorption intensity; C_{ads} , C_e and C_m represent sorbed amount (mol g⁻¹), residual concentration of sorbate in solution at equilibrium (mol dm⁻³) and sorption capacity of sorbent (mmol g⁻¹), respectively. A straight line is obtained for each BTEC component by plotting $\log C_{\text{ads}}$ versus $\log C_e$ (Fig. 6). The values of $1/n$ derived from slope of the straight lines are $0.40 < 1/n < 0.47$. This indicates effectiveness of MOP for the removal of BTEC components from aqueous solutions at low concentrations. The values of C_m are determined from the intercept of the linear plots and are given in Table 2 along with the values of $1/n$ for the BTEC compounds studied onto MOP. The value of C_m , maximum sorption capacity, increases with an increase in the molecular weight of the sorbate molecule.

Results of C_m estimated previously for BTEC components onto rice bran which were 32 ± 3 , 61 ± 14 , 123 ± 28 and 142 ± 37 mmol g⁻¹ which are less for benzene and toluene but higher in case of ethylbenzene and cumene [20].

The Langmuir model [25] represents monolayer sorption on a set of distinct localized sorption sites having the same sorption energies independent of surface coverage with no interaction and no steric hindrance between sorbed molecules and incoming molecules. The sorption data are also subjected to the following linearized form of Langmuir equation:

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

Table 2
Freundlich characteristic constants for BTEC onto MOP

Analyte	$1/n$	C_m (mmol g ⁻¹)	R^2
Benzene	0.40 ± 0.04	46 ± 10	0.929 ± 0.049
Toluene	0.45 ± 0.04	84 ± 9	0.947 ± 0.050
Ethyl benzene	0.47 ± 0.04	101 ± 24	0.949 ± 0.052
Cumene	0.47 ± 0.05	106 ± 32	0.928 ± 0.063

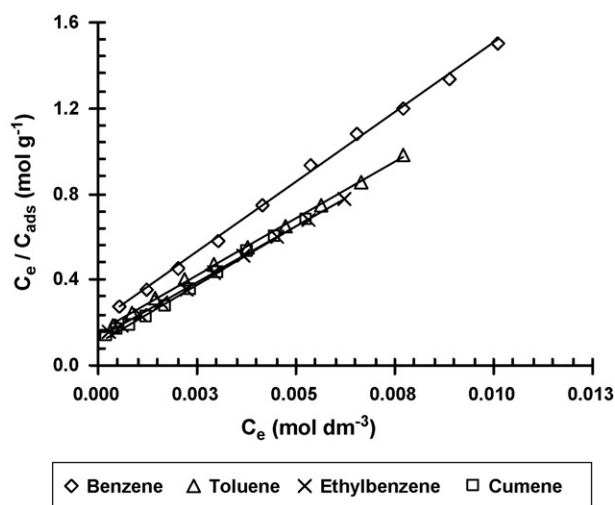


Fig. 7. Langmuir sorption isotherms of BTEC onto 0.1 g MOP/25 cm³ of sorbate, 60 min agitation time at pH 6 and 303 K.

where Q represents sorption saturation capacity (mmol g⁻¹), indicating a monolayer coverage of sorbent with the sorbate, b elucidates the enthalpy of the sorption (dm³ mol⁻¹), independent of temperature and C_{ads} and C_e are as defined earlier. Straight lines are obtained by plotting C_e/C_{ads} versus C_e for all BTEC components, exhibiting applicability of Langmuir model to sorption data (Fig. 7). The values of Q and b estimated from the slope and intercept of the plots respectively are listed in Table 3. The order of Q , the saturation capacity, is of the same order of magnitude independent of the molecular weight of the sorbates. However, the values of b appear to increase with an increase in the molecular weight of the organics studied.

The results of sorption capacities obtained onto rice bran for BTEC were 6.6 ± 0.1 , 7.5 ± 0.13 , 9.5 ± 0.22 , 9.4 ± 0.18 mmol g⁻¹ which are slightly low for benzene, toluene and ethylbenzene; and higher for cumene [20].

Another dimensionless equilibrium parameter, R_L , [26] is computed using the relationship:

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

where b is a Langmuir constant and C_i is the initial concentration of BTEC components in the solution.

The values of R_L are found to be in the range 0.11–0.55, 0.12–0.58, 0.11–0.56 and 0.11–0.54 for BTEC in the aqueous solution almost independent of their molecular weights. The results of R_L for each BTEC component indicate a significant sorption at low concentration.

Table 3
Langmuir parameters for BTEC onto MOP

Analyte	b (dm ³ mol ⁻¹)	Q (mmol g ⁻¹)	R^2
Benzene	641 ± 37	8 ± 0.1	0.998 ± 0.02
Toluene	657 ± 20	9 ± 0.1	0.999 ± 0.008
Ethyl benzene	831 ± 11	10 ± 0.3	0.999 ± 0.002
Cumene	1024 ± 50	9 ± 0.1	0.999 ± 0.008

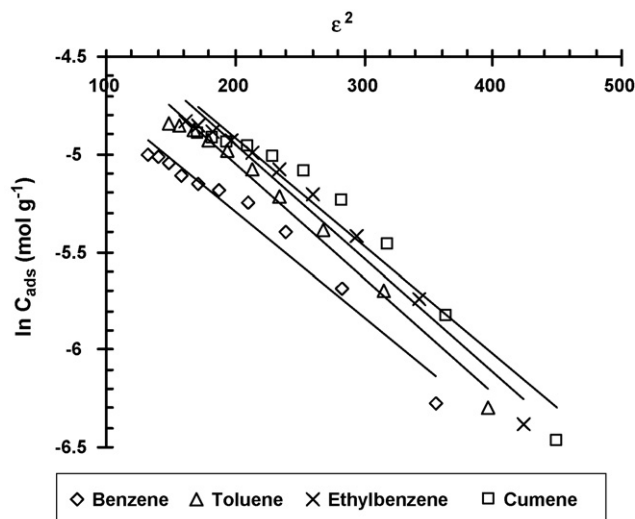


Fig. 8. D–R sorption isotherms of BTEC onto 0.1 g MOP/25 cm³ of sorbate, 60 min agitation time at pH 6 and 303 K.

The R_L values of BTEC onto rice bran 0.11–0.57, 0.12–0.58, 0.16–0.65 and 0.15–0.64 [20] are almost in the same order of magnitude as observed in the present study.

Fig. 8 shows the Dubinin–Radushkevich (D–R) isotherm [27], applied to the sorption data and is tested in the following linearized form:

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

where C_{ads} is the amount of sorbate sorbed onto sorbent surface (mol g⁻¹) and X_m represents the maximum sorption capacity of the sorbent (mmol g⁻¹), β is a constant related to sorption energy and ε is Polanyi sorption potential, the amount of energy required to pull a sorbed molecule from its sorption space to infinity which can be evaluated using the following equation:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (8)$$

where R is the gas constant in kJ mol⁻¹ K⁻¹, T is the temperature in Kelvin while C_e is the equilibrium concentration of sorbate in solution (mol dm⁻³). Polanyi sorption theory assumed [28] fixed volume of sorption space close to the sorbent surface and existence of sorption potential over these spaces. The sorption potential is related to an excess of sorption energy over the condensation energy and is independent of temperature. The plots of $\ln C_{\text{ads}}$ versus ε^2 follow linearity. The values of β and X_m calculated from the slopes and intercepts respectively are listed in Table 4. The values of β and ε estimated from D–R isotherms are almost the same for all BTEC. The maximum sorption capacity, X_m , is also same for all the organics investigated with the exception of benzene, which showed a lower value. Previous results of BTEC obtained onto rice bran for X_m were 11 ± 0.5 , 16 ± 1.3 , 30 ± 2.2 and 33 ± 2.5 mmol g⁻¹ and found to be less for benzene and toluene while higher for ethylbenzene and cumene [20].

Table 4
D–R constants for BTEC onto MOP

Analyte	β (kJ ² mol ⁻²)	X_m (mmol g ⁻¹)	E (kJ mol ⁻¹)	R^2
Benzene	-0.0054 ± 0.0004	15 ± 1	9.6 ± 0.3	0.961 ± 0.083
Toluene	-0.0059 ± 0.0003	21 ± 1	9.2 ± 0.2	0.985 ± 0.062
Ethyl benzene	-0.0058 ± 0.0003	23 ± 2	9.3 ± 0.3	0.976 ± 0.082
Cumene	-0.0056 ± 0.0004	22 ± 3	9.5 ± 0.4	0.953 ± 0.117

The values of sorption energy, E , can be computed [29] using the following relationship:

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

The estimated values of E are almost constant within expected error for all BTEC compounds and are in the range of 8–16 kJ mol⁻¹ indicating ion exchange mechanism [30] for the sorption process (Table 4).

Results obtained for sorption energy, E , for BTEC sorption onto rice bran are almost same for benzene and toluene while slightly different for ethylbenzene and cumene which are 9.9 ± 0.1 , 9.3 ± 0.1 , 7.2 ± 0.1 and 7.1 ± 0.3 kJ mol⁻¹ [20].

The values of C_m , Q , and X_m (mmol g⁻¹) for ethylbenzene and cumene (listed in Tables 2–4) are higher, which may be associated with surface activity and higher molecular weights. Because with the increase in molecular weight in homologous series, a regular increase in surface activity is observed, which results in the displacement of more water molecules leading to an increase in the points of contact of sorbate onto sorbent surface, as larger molecules of sorbate have more points of contact with the sorbent [23].

3.7. Kinetic studies

The kinetics of sorption of BTEC onto MOP is evaluated by employing Lagergren and Morris–Weber equations [31,32], using conditions selected for monitoring the effect of agitation time. The order of the sorption of sorbate onto sorbent is determined by subjecting the data to the linearized form of Lagergren equation:

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

where k , is the first-order rate constant of sorption, while q_e and q_t are the maximum amount sorbed at equilibrium and at time t , respectively. The linear plots of $\log(q_e - q_t)$ versus t yield straight lines (Fig. 9). This observation elucidates that sorption process follows first-order kinetics and the values of k , computed from the slope of the linear plots are depicted in

Table 5
Lagergren and Morris–Weber rate constants for BTEC onto MOP

Analyte	k (min ⁻¹)	R^2	R_{id} (nmol g ⁻¹ min ^{-1/2})	R^2
Benzene	0.033 ± 0.003	0.969 ± 0.051	23 ± 1	0.993 ± 0.004
Toluene	0.030 ± 0.002	0.981 ± 0.036	20 ± 0.8	0.994 ± 0.004
Ethylbenzene	0.029 ± 0.002	0.983 ± 0.032	18 ± 0.7	0.994 ± 0.003
Cumene	0.027 ± 0.002	0.986 ± 0.028	16 ± 0.5	0.995 ± 0.002

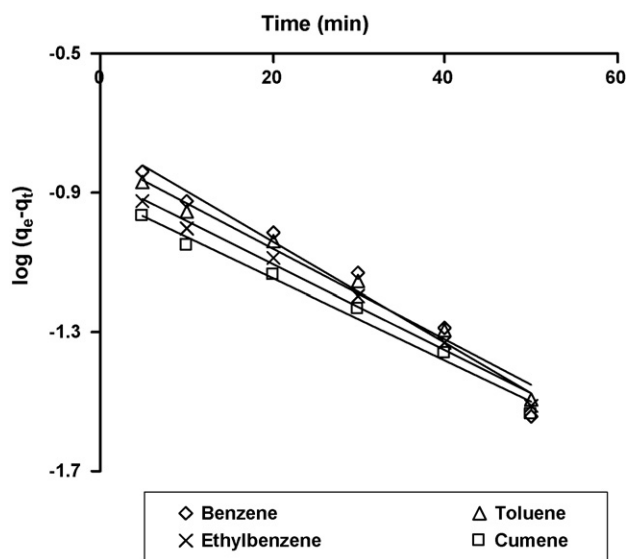


Fig. 9. Lagergren plots of BTEC onto 0.1 g MOP, 25 cm³ of 1.3×10^{-3} , 1.1×10^{-3} , 0.9×10^{-3} , 0.8×10^{-3} mol dm⁻³ sorbate concentration, 60 min agitation time at pH 6 and 303 K.

Table 5, which are in the range $0.027 < k < 0.033$ min⁻¹. The results of k , for benzene, toluene, ethylbenzene and cumene onto rice bran estimated earlier [20] were 0.03 ± 0.002 , 0.04 ± 0.003 , 0.04 ± 0.003 and 0.05 ± 0.004 which are also in agreement with the values found in present study onto MOP.

Film resistance plays an important role in the overall transport of the solute. In order to estimate the intraparticle diffusion rate Morris–Weber equation was also subjected to sorption kinetic data in the following form:

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

where q_t is the amount sorbed at time t , and R_{id} is the intraparticle diffusion rate constant. If q_t is plotted against $t^{1/2}$, the sorption data yields a straight line. This observation indicates that kinetics of BTEC components sorption computed from the slope of linear plots onto MOP surface follows linearity in the range of 5–60 min as shown in Fig. 10, revealing partial intraparticle diffusion. The results of R_{id} are presented in Table 5.

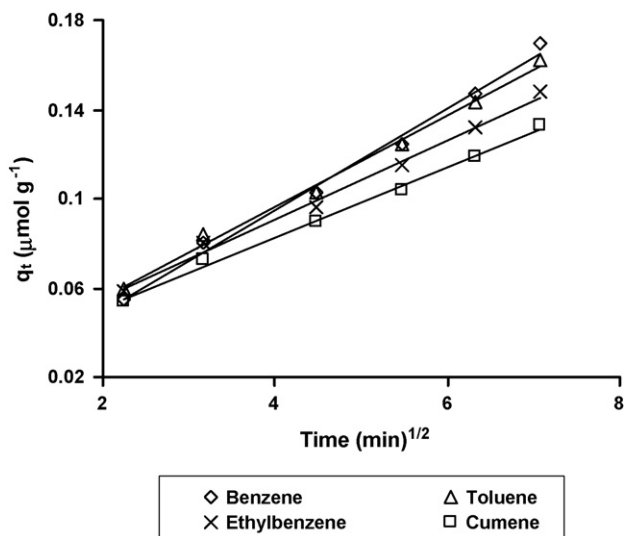


Fig. 10. Validation of Morris–Weber equation for BTEC onto 0.1 g MOP, 25 cm³ of 1.3×10^{-3} , 1.1×10^{-3} , 0.9×10^{-3} , 0.8×10^{-3} mol dm⁻³ sorbate concentration, 60 min agitation time at pH 6 and 303 K.

The results obtained with MOP are almost same as obtained for BTEC onto rice bran which were 17 ± 1 , 14 ± 0.9 , 13 ± 0.6 and 13 ± 0.5 nmol g⁻¹ [20]. This before shows that intraparticle diffusion rate is slightly higher onto *Moringa* pods rather than onto rice bran for same sorbates studied.

3.8. Thermodynamic studies

The variation in temperature, a major factor influencing the distribution of sorbate between solid and liquid phases is monitored in the range of 283–308 K under the optimized conditions chosen to evaluate the effect of temperature on the sorption of BTEC components. The dependence of the equilibration constant $K_c = F_e / (1 - F_e)$, where F_e is the fraction of % sorption at equilibrium, with temperature is indicated by the relationship [33]:

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

where ΔH is the enthalpy (kJ mol⁻¹) and ΔS is the entropy (J mol⁻¹ K⁻¹). The plots of $\ln K_c$ vs. $1/T$ (K⁻¹) are linear in the entire range of temperature investigated for all the sorbate molecules (Fig. 11). The computed values of ΔH and ΔS from the respective slope and intercept of the plots are listed in Table 6. Another thermodynamic parameter ΔG (kJ mol⁻¹) Gibbs free

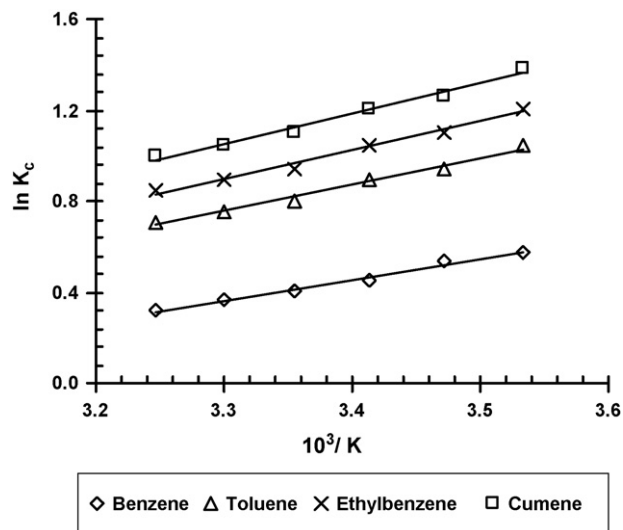


Fig. 11. Variation of sorption equilibrium of BTEC onto 0.1 g MOP with temperature, 25 cm³ of 1.3×10^{-3} , 1.1×10^{-3} , 0.9×10^{-3} , 0.8×10^{-3} mol dm⁻³ sorbate concentration, 60 min agitation time at pH 6 and 303 K.

energy, was estimated using following equation:

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

where R is a gas constant in kJ mol⁻¹ K⁻¹ and T is the temperature in Kelvin and the estimated values of ΔG at 303 K are recorded in Table 6. The negative values of ΔH and ΔG exhibit the exothermic and spontaneous nature of the sorption respectively. As the sorbed molecules have at the most two degrees transitional freedom on the surface and in view of this fact, the rotational freedom of sorbed species must always be less than that of gas phase molecules, the entropy change on sorption $\Delta S = S_{\text{ads}} - S_{\text{gas}}$ is inevitably negative. In order for significant adsorption to occur the free energy change on adsorption (ΔG) must also be negative and since $\Delta G = \Delta H - T\Delta S$, that requires ΔH negative or exothermic adsorption. This is generally true for sorption from liquid phase also, although exceptions are possible [33]. This is in conformity with the observation of negative ΔH , ΔS and ΔG values of BTEC components onto MOP in the present investigation. The results of ΔH , ΔS and ΔG obtained at 303 K onto rice bran for BTEC were -10.7 ± 0.4 , -11.1 ± 0.4 , -9.5 ± 0.3 , -12.4 ± 0.5 kJ mol⁻¹, -31.8 ± 1.3 , -28.5 ± 1.3 , -18.5 ± 1.1 , -25.9 ± 1.6 J mol⁻¹ K⁻¹ and -0.4 ± 0.01 , -1.0 ± 0.04 , -1.7 ± 0.05 , -1.9 ± 0.05 kJ mol⁻¹ respectively [20].

Table 6
Thermodynamic parameters of BTEC onto MOP

Analyte	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	$\Delta G_{303 \text{ K}}$ (kJ mol ⁻¹)	R^2
Benzene	-8 ± 0.4	-22 ± 2	-0.9 ± 0.2	0.987 ± 0.013
Toluene	-10 ± 0.6	-26 ± 2	-1.9 ± 0.2	0.986 ± 0.017
Ethylbenzene	-11 ± 0.7	-27 ± 2	-2.3 ± 0.1	0.985 ± 0.019
Cumene	-11 ± 0.7	-29 ± 3	-2.6 ± 0.2	0.984 ± 0.029

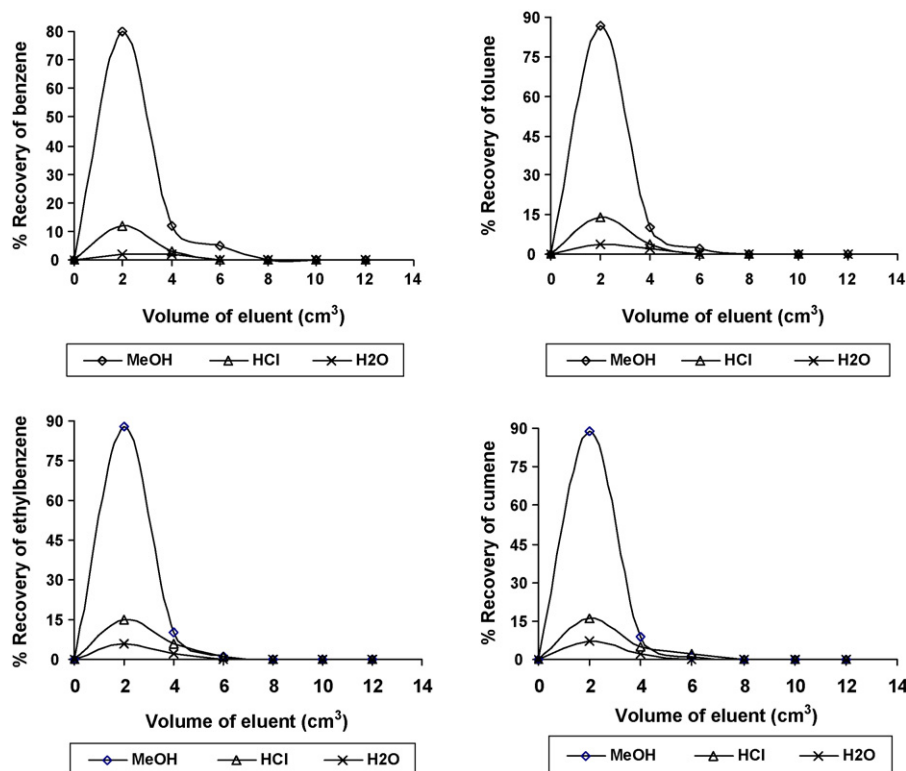


Fig. 12. % recoveries of BTEC from 0.1 g MOP, using 2 ml of MeOH, 0.1 M HCl and H₂O at 1.3×10^{-3} , 1.1×10^{-3} , 0.9×10^{-3} , 0.8×10^{-3} mol dm⁻³ sorbate concentration, pH 6 and 303 K.

3.9. Column investigation

Fig. 12 shows the feasibility of MOP for the removal of BTEC as a function of elution profile. For determining the suitability of adsorbent and eluting solvent, the % recovery of the BTEC was investigated using glass column ($\varnothing 30$ cm \times 0.7 cm) containing 0.1 g of MOP on a glass wool support. The column was loaded with 500 ml of 10 μ g/ml BTEC solution for 2 h at a flow rate of 4.2 ml/min; $\geq 98\%$ of BTEC were sorbed onto the sorbent. The elution of sorbed amount of BTEC was carried out with 2 ml each of methanol, 0.1 M HCl solution and doubly distilled deionized water by sonication in an ultrasonic bath for 10 min. The elution capacity as % recovery of benzene, toluene, ethylbenzene and cumene respectively followed the order:

MeOH($96 \pm 0.5\%$) > 0.1 M HCl($15 \pm 2\%$) > H₂O($4 \pm 2\%$)

MeOH($98 \pm 0.5\%$) > 0.1 M HCl($18 \pm 1\%$) > H₂O($6 \pm 2\%$)

MeOH($98 \pm 0.3\%$) > 0.1 M HCl($22 \pm 2\%$) > H₂O($8 \pm 1.5\%$)

MeOH($98 \pm 0.3\%$) > 0.1 M HCl($22 \pm 2\%$) > H₂O($9 \pm 1\%$)

The % recovery of BTEC in methanol is much better than cited for the same compounds in dichloromethane [1].

3.10. Application to wastewater sample

Contaminated water sample of the Phulaili canal, Hyderabad, from the top of water surface close to the right bank was col-

lected in a rinsed dark glass 5 l capacity bottle and transferred immediately to an air conditioned vehicle for transportation to the laboratory, to be placed in a refrigerator at 4 °C until analyzed. The characteristics of contaminated water are listed in Table 7. The water sample was spiked with 10 μ g/ml of the each analyte (BTEC), 10 μ l from spiked sample water was then injected to HPLC for quantitative determination of BTEC compounds. Amount of benzene (0.45 ± 0.02 μ g/ml), toluene (0.34 ± 0.02 μ g/ml) and ethylbenzene (0.22 ± 0.03 μ g/ml) in wastewater sample was estimated by comparing the retention time and peak heights (mV) of individual organic compounds with synthetic sample solution, as per procedure in the literature [34], while cumene was not detected in the sample. 500 ml aliquot of the spiked wastewater was passed through the column discussed above, containing 0.1 g MOP under the conditions as mentioned earlier. 10 μ l was injected to HPLC for the analysis. *M. oleifera* pods effectively sorb benzene, toluene and ethylbenzene from wastewater and the elution of sorbed amounts of BTE were recovered with 2 ml of methanol. The results of the analysis along with % sorption onto MOP and % recovery with

Table 7
Characteristics of contaminated water

Characteristics	Values
pH	7.1
EC (μ S cm ⁻¹)	281
TDS (mg l ⁻¹)	230
COD (mg l ⁻¹)	495
BOD (mg l ⁻¹)	56

Table 8

% Sorption and % recovery of benzene, toluene and ethylbenzene from contaminated wastewater onto MOP

Analyte	Concentration of analyte determined in spiked contaminated sample ($\mu\text{g/ml}$) \pm SD		% Sorption	% recovery with 2 ml methanol
	Before sorption	After sorption		
Benzene	10.45 \pm 0.002	0.2 \pm 0.001	98 \pm 0.1	96 \pm 0.3
Toluene	10.34 \pm 0.003	0.1 \pm 0.001	99 \pm 0.2	98 \pm 0.4
Ethylbenzene	10.22 \pm 0.002	0.1 \pm 0.001	99 \pm 0.06	98 \pm 0.3
Cumene	ND	ND	ND	ND

Spiked sample (BTE) = 10 $\mu\text{g/ml}$.

2 ml of methanol are listed in Table 8. The results of BTE in contaminated water samples are in the same order of magnitude as reported in river water samples (benzene 0.35, toluene 0.23 and ethylbenzene 0.15 $\mu\text{g/ml}$) [1].

4. Conclusion

Results exhibit overall sorption order of organic contaminants onto MOP, i.e., cumene > ethylbenzene > toluene > benzene which may be correlated, with their solubility, as more soluble substances in alcohol and water prefer to remain in solution relative to sorbent material. Langmuir model fitted well to the sorption data with higher values of coefficient of determination. The values of $1/n$ and R_L from Freundlich and Langmuir isotherms reveal better sorption at low concentrations. The results of sorption energy obtained from D–R isotherms indicate the ion-exchange mechanism 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 on the surface of MOP. Results of Lagergren plots follow first order rate equation. Methanol was found to be more suitable solvent for desorption of the BTEC compounds. The recovered amount of benzene, toluene, ethylbenzene and cumene can be used as a raw material in different industries. *M. oleifera* pods an inexpensive, indigestible and easily available raw material in large quantities may be used for different industrial applications to lower the cost of wastewater treatment and has potential applications for the removal of BTE from wastewater.

References

- [1] M.A. Mottaleb, M.Z. Abedin, M.S. Islam, Determination of benzene, toluene, ethylbenzene and xylene in river water by solid-phase extraction and gas chromatography, *Anal. Sci.* 19 (2003) 1365–1369.
- [2] A. Adachi, C. Ikeda, S. Takagi, N. Fukao, E. Yoshie, T. Okano, Efficiency of rice bran for removal of organochlorine compounds and benzene from industrial wastewater, *J. Agric. Food. Chem.* 49 (2001) 1309–1314.
- [3] C.J. Quigley, R.L. Corsi, Emissions of VOCs from a municipal sewer, *J. Air Waste Manage. Assoc.* 45 (1995) 395–403.
- [4] H.A. Hattemer-Frey, C.C. Travis, M.L. Land, Benzene: Environmental partitioning and human exposure, *Environ. Res.* 53 (1990) 221–232.
- [5] Toxicological Profile for, Toluene, Agency for Toxic Substances and Disease Registry, US Department of Health and Human Services, Atlanta, Georgia, USA, 2000, pp. 73–100.
- [6] I.A. Kaipper, A.S. Madureira, H.X. Corseuil, Use of activated charcoal in a solid-phase extraction technique for analysis of pesticide residues in tomatoes, *J. Braz. Chem. Soc.* 12 (2001) 514–518.
- [7] S. Jomaa, A. Shanableh, W. Khalil, B. Trebilco, Hydrothermal decomposition and oxidation of the organic component of municipal and industrial waste products, *J. Adv. Environ. Res.* 7 (2003) 647–653.
- [8] T. Okuda, A.U. Baes, W. Nishijima, M. Okada, Isolation and characterization of coagulant extracted from *Moringa oleifera* seed by salt solution, *Water Res.* 35 (2001) 405–410.
- [9] G. Xia, W.P. Ball, Adsorption-partitioning uptake of nine low-polarity organic chemicals on a natural sorbent, *J. Environ. Sci. Technol.* 33 (1999) 262–269.
- [10] P. Kumari, P. Sharma, S. Srivastava, M.M. Srivastava, Biosorption studies on shelled *Moringa oleifera* Lamarck seed powder: Removal and recovery of arsenic from aqueous system, *Int. J. Miner. Process.* 78 (2006) 131–139.
- [11] A. Adachi, T. Tanaka, M. Nakatani, R. Muguruma, T. Okano, Removal efficiency of defatted seed for organochlorine compounds, *J. Health Sci.* 47 (2001) 54–59.
- [12] N.M. Damaris, M.S. Paul, M.N. Rachel, N.K. Geoffrey, Adsorption and detection of some phenolic compounds by rice husk ash of Kenyan origin, *J. Environ. Monit.* 4 (2002) 978–984.
- [13] L. Hui, S. Guangyao, J.T. Brian, T.J. Cliff, A.B. Stephen, Sorption and desorption of pesticides by clay minerals and humic acid-clay complexes, *J. Am. Soil Sci. Soc.* 67 (2003) 122–131.
- [14] J. Megat, *Moringa oleifera* seeds as a flocculant in waste sludge treatment, *Int. J. Environ. Stud.* 58 (2001) 185–195, and references therein.
- [15] S. Iqbal, M.I. Bhangar, Effect of season and production location on antioxidant activity of *Moringa oleifera* leaves grown in Pakistan, *J. Food Comp. Anal.* 19 (2006) 544–551, and references therein.
- [16] M.P. Steven, F.G. Donald, Volatile organic analysis by direct aqueous injection, *Talanta* 41 (1994) 1845–1852.
- [17] D.R. Lide (Editor-in-Chief), CRC Handbook of Chemistry and Physics, 83rd ed. CRC Press, Boca Raton, Florida, 2002.
- [18] D. Perrin, B. Dempsey, Buffers for pH and Metal Ion Control, John Wiley and Sons, Inc., New York, 1974.
- [19] R. Sivaraj, C. Namawsivayam, K. Kadirvelu, Orange peel as an adsorbent in the removal of acid violet 17 (acid dye) from aqueous solutions, *Waste Manage.* 21 (2001) 105–110.
- [20] M. Akhtar, M.I. Bhangar, S. Iqbal, S.M. Hasany, Efficiency of rice bran for the removal of selected organics from water: kinetic and thermodynamic investigations, *J. Agric. Food Chem.* 53 (2005) 8655–8662.
- [21] S.J.T. Pollard, F.E. Thompson, G.L. McConnachie, Microporous carbons from *Moringa oleifera* husks for water purification in less developed countries, *Water Res.* 29 (1995) 337–347.
- [22] P. Sharma, P. Kumari, M.M. Srivastava, S. Srivastava, Removal of cadmium from aqueous system by shelled *Moringa oleifera* Lam. seed powder, *Biosource Technol.* 97 (2006) 299–305.
- [23] L.G. Morrill, B.C. Mahilum, S.H. Mohiuddin, Organic compounds in soils: sorption, degradation and persistence, *Ann Arbor Science, Collingwood, Ann Arbor, MI*, 1982, pp. 56–57.
- [24] H. Freundlich, *Colloid and Capillary Chemistry*, Methuen, London, 1926, pp. 397–414.
- [25] I. Langmuir, The adsorption of gases on plane surface of glass, mica and platinum, *J. Chem. Soc.* 40 (1918) 1361–1403.
- [26] G. McKay, H. Blair, J.R. Gardiner, The adsorption of dyes onto chitin in fixed bed column and batch adsorbers, *J. Appl. Polym. Sci.* 28 (1989) 1499–1544.

- [27] M.M. Dubinin, L.V. Radushkevich, The equation of the characteristic curve of the activated charcoal, *Proc. Acad. Sci. USSR. Phys. Chem. Sec.* 55 (1947) 331.
- [28] J. Li, C.J. Werth, Modeling sorption isotherms of volatile organic chemical mixtures in model and natural solids, *Environ. Toxicol. Chem.* 21 (2002) 1377–1383.
- [29] J.P. Hobson, Physical adsorption isotherms extending from ultra-high vacuum to vapor pressure, *J. Phys. Chem.* 73 (1969) 2720–2727.
- [30] F. Helfferich, *Ion Exchange*, McGraw-Hill, New York, USA, 1962, p. 166.
- [31] S. Lagergren, Zur theorie der sorption geloster stoffe, *Handlingar* 24 (1898) 1.
- [32] W.J. Morris, J.C. Weber, Kinetics of adsorption on carbon from solutions, *J. Saint. Eng. Div. ASCE* 89 (1963) 31.
- [33] U.R. Malik, S.M. Hasany, M.S. Subhani, Sorptive potential of sunflower stem for Cr(III) ions from aqueous solutions and its kinetic and thermodynamic profile, *Talanta* 66 (2005) 166–173.
- [34] APHA, *Standard Methods for the Examination of Water and Wastewater*, 17th ed., American Water Works Association, New York, 1989.