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Adsorption/desorption of BTEX on activated carbon prepared from rice husk

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ABSTRACT

The differences in the adsorption/desorption behavior of benzene, toluene, ethyl-benzene, and p-xylene (BTEX) using rice husk activated carbon (RHAC) were studied. It was proved that RHAC were quite effective in removing BTEX compounds from aqueous solutions. About 48 h was sufficient to attain maximum BTEX adsorption and desorption. Adsorption kinetics data proved a closer fit to the Weber–Morris model, while the isotherm experimental data were better fit to the Freundlich model, producing values of $1/n$ less than one, indicating favorable adsorption. Adsorption isotherms were determined in polluted surface water and it was found that the removal efficiency depends on the initial concentration of BTEX pollutants. Desorption equilibrium is less rapid than the adsorption equilibrium. BTEX adsorption/desorption was affected by chemical structure, solubility, and molecular weight. About 22% benzene, 33% toluene, 58% ethylbenzene, and 18.8% of p-xylene were released from RHAC after contact between the loaded matrix and reagent water. Sorption/desorption of p-xylene in RHAC was found to yield co-incident equilibrium isotherms and no significant hysteresis was observed.

Keywords: Adsorption; BTEX; Activated carbon; Rice husk; Desorption; Reversibility

1. Introduction

The BTEX compounds, namely, benzene (B), toluene (T), ethylbenzene (E), and xylenes (X), are often found in soil and groundwater [1]. The toxicity effect and water solubility of BTEX endowed these compounds with great environmental hazard [2]. They can cause adverse health effects such as chromosome aberrations, cancer, and damage to the liver, kidneys, eyes, and central nervous system [3]. Their frequent use in many industrial applications (e.g. printing and leather industries, rubber manufacture, etc.), as well as their occurrence in petroleum fuels (e.g. gasoline), has led to their extensive discharge into the aqueous environment, either through wastewater mismanagement or accidents [4].

In recent years, different methods such bioremediation/natural attenuation, volatilization (air stripping/air sparging), chemical oxidation, as well as adsorption have been successfully used for removal of BTEX. However, in practice, the utilization of these removal processes on a large scale presents certain

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advantages and disadvantages as far as applicability, site dependence, efficiency, and cost parameters are concerned [4].

Adsorption is a process that can be successfully applied for the removal of these contaminants. It is relatively simple and can achieve high removal efficiencies. Activated carbon is perhaps the most widely used adsorbent for organic compounds, due to its high adsorption capacity. Yet, activated carbon is a relatively expensive material that also has a high regeneration/reactivation cost. Given the constant need to identify new, preferably more natural, more abundant and cheaper materials to prepare activated carbon and/or other efficient, but still expensive, adsorbents, in this study, rice husk (RH) was tested as activated carbon precursor for adsorption potential of BTEX. In the literature, BTEX removal from water by adsorption on resins [5], surfactant modified zeolites [6], organo-clays [7], and carbon nanotubes [8,9] seems to be an interesting perspective.

During any type of treatment, the sites available for adsorption onto activated carbons decrease with adsorbed pollutants resulting in the loss of adsorptive capacity of carbon. Therefore, the carbon must be either replaced or regenerated. Adsorption of organic compounds on activated carbon is relatively simple, the process of regenerating the adsorbent by desorption of the organic compounds poses an important for the present studies, since it has the high affinity of the compounds to the sorbent surface. Currently, techniques, such as thermal regeneration, chemical regeneration, bioregeneration, and ultrasound are used for the desorption of organics from activated carbon [10]. Desorption occurs when (1) adsorbed compounds are displaced by more strongly adsorbing compounds, or (2) when the concentration gradient in the adsorber reverses and adsorbed compounds are driven into the water phase by back diffusion [11]. Displaced desorption is a result of competitive adsorption, has been studied and reported in the literature [12]. Desorption caused by a concentration gradient reversal may be affected by interactions between the desorbing compound and other adsorbed organic species. A few studies have reported experimental concentration gradient reversal desorption results [13,14].

RH is a by-product of the rice milling industry resulting in problems associated with management of solid waste, which if not handled adequately, should attract disease-carrying animals, increasing the risk of fire, or even occupying large spaces in landfill sites [15]. RH is one promising biomass in Egypt because of its large and stable yield (500,000 tons a year) and its low acquisition cost [16]. Activated carbon and porous carbon prepared from RH were used for the adsorption of various dyes and other organic pollutants like malachite green, Rhodamine B, dibenzothiophenes, humic acid, phenol, municipal solid waste landfill leachate, and purification of bio-diesel [17–20]. In this research, BTEX adsorption and desorption kinetics and equilibrium on RHAC were systematically investigated. The reversibility of p-xylene adsorption/desorption on RHAC was studied.

2. Materials and methods

Rice husk activated carbon (RHAC) was prepared according to the procedures in previous work with some modification [21]. Briefly, 40 gm of powdered RH was impregnated with 100 ml of 40% phosphoric acid. This mass was heated gradually up to 700˚C within 2 h in a vertical cylindrical furnace and soaked at this temperature for 3 h. After cooling the carbonized mass was washed several times with bidistilled water until pH 6.5 and dried at 110˚C. Elemental analysis of sorbent materials was performed by CHN Elemental Analyzer (Perkin-Elmer, Norwach, USA). The BET-surface area of RHAC was calculated from N_2-gas adsorption that was obtained by NOVA 3200, V 6.05 gas sorption analyzer, Quantachrome, USA. Elemental analysis and physical characterization concerned with pore volume, and surface area of RHAC are listed in Table 1.

The employed B, T, E, and X were analytical grade with >99% purity and purchased from Merck. A stock solution in methanol (Sigma-Aldrich, puriss p.a. >99.8%-GC) was prepared in 10 ml volumetric flasks containing 2000 ppm from each of the above-mentioned contaminants, using micro-liter syringes. The aqueous standard was prepared by spiking a measured quantity of methanol standard into 100 ml volumetric flask filled with reagent water. These solutions were used for the kinetics and isotherm

Table 1
Physical and chemical characterization RHAC activated carbon

Physical characterization		Chemical characterization	
Inner BET surface area (m^2/g)	446	pH	2.1
Total pore volume (cm^3/g)	0.301	C%	58.5
Mean pore radius (A^o)	15.5	H%	3.4
Micro pore volume (cm^3/g)	0.196	N%	2.9
Density (g/ml)	0.447	Cl%	1.9
Water content (%wt)	9	S%	2.1
		Ash content	3.8

determination batch experiments, in order to explore the adsorbent's capacity and efficiency.

Kinetics experiments were carried out in 5 ml glass vials with gas-tight caps, non-permeable by organic vapors. About 10 ml aliquots of each component of BTEX with an initial concentration of 10 mg/l were shaken with 10 mg of RHAC each mixture was filtered and C_e was measured after 1, 2, 3, 4 … days until the residual concentration remains constant. The minimum contact time was determined and utilized in the remaining tests. Kinetics desorption experiments were started by removing the solution left after the sorption experiments and replaced it by 5 ml of reagent water (Zero concentration). This is followed by shaking at different time intervals up to four days. The aim was to study the effect of shaking time on desorption of each BTEX compound.

Equilibrium experiments for p-xylene were conducted by addition of various weighed masses of RHAC (0.5–12 mg) in glass bottles provided with screw caps. Bottles are then filled with 5 ml of each single solute of BTEX (8 mg/l). The bottles were shaken until equilibrium time was reached at 25 ± 1˚C. To check the adsorption reversibility, after the adsorption equilibrium was attained all the free supernatant was removed and replaced with clean reagent water, the bottles shaked for 48 h (pre-determined desorption equilibrium time). Sampling and analysis of desorption were carried out in the same manner as those for the sorption investigations. BTEX compounds concentration before and after adsorption were determined by Purge and Trap (model: HP-7695) Gas chromatography (model: HP-6890) with flame ionization detector (PT-GC-FID) according to US-EPA (524.2) method [22].

Sorption capacity of adsorbent was calculated by:

$$q_e^{ads} = V(C_o - C_e)/m \tag{1}$$

Desorbable amounts of adsorbat was calculated by

$$q_e^{des} = VC_{des}/m \tag{2}$$

where C_o, C_e, and C_{des} are the initial, equilibrium, and desorbed concentration (mg/l), respectively, m is the mass of dry carbon sample used (g) and V volume of solution (ml).

For the application of RHAC for real water treatment, it was supposed that surface water of Ismailia canal in Egypt was polluted by accident from the fuel station located in front of it. Consequently, unleaded gasoline is mixed with Ismailia surface water. The chemical analysis of collected water samples are shown in Table 2.

Table 2
The chemical analysis of the collected water samples

Item	Concentration (ppm)
Cations	
Na^+	861
K^+	23.7
Ca^{++}	95.9
Mg^{++}	125
Total cations	53.11
Anions	
CO_3^{2-}	44.1
HCO_3^-	179
SO_4^{2-}	342
Cl^-	1474
Total anions	52.95
BTEX	
Benzene	102.4
Toluene	109
Ethylbenzene	19.8
P-Xylene	8.3

The adsorption isotherm of BTEX mixture was carried out by taking each 5 ml of the stock BTEX with various masses of RHAC ranged from 20 to 160 mg in glass bottles provided by screw caps and shaking for 48 h in thermostated shaker/water bath at 25˚C. The residual concentration of BTEX mixture, C_e, was determined.

3. Results and discussion

3.1. Adsorption studies

Fig. 1 shows the variation of the uptake of BTEX on RHAC with time at 25˚C. The amount of BTEX

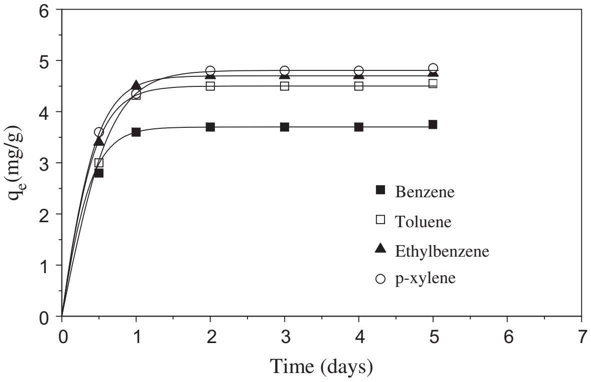

Fig. 1. Effect of contact time on adsorption of BTEX compounds on RHAC.

sorbed on RHAC was found to be greatly affected by contact time. Adsorption capacity increased with increasing the shaking time until reaching saturation where the amount sorbed attains a constant value. The saturation level is specific and depends on the adsorbate, nature of the adsorbent and the chemical composition of medium. Maximum adsorption was observed after two days (48 h) behind, which there is no further, increases in the adsorption. Hence, 48 h shaking time was considered to be sufficient for the adsorption of BTEX compounds on RHAC and was used for all subsequent experiments.

Kinetics of sorption of BTEX on RHAC is currently described by plotting the amount sorbed per unit weight of sorbent, (q) vs. $t^{1/2}$, was described by Weber–Morris intraparticle Eq. (3) [23]:

$$q = k_p t^{1/2} \tag{3}$$

where K_p is the intraparticle diffusion rate constant. The plots covering the initial phase of adsorption (not shown) did not pass through the origin, hinting that pore diffusion may not be the only rate-controlling step in the removal of the adsorbates [24]. The adsorption mechanism can frequently be controlled by multi-diffusion steps, involving film diffusion and intraparticle diffusion [25]. The evaluated sorption rates for intraparticle diffusion, K_p, which are useful for comparative purposes are given in Table 3. It was clear that the molecular configuration has a significant influence on the adsorption rate. A remarkable dependence could be existed between the adsorption rate K_p, and the molecular weight. K_p values for the various BTEX components increase as the molecular weight increases. As the number of methyl group attached to the aromatic ring increases, the adsorption rate increases (from toluene to p-xylene). Also, as the chain length increases, the adsorption rate increases (from toluene to ethylbenzene). As the chain length increased the compound tends to be more hydrophobic and its adsorption increases.

Adsorption isotherms of BTEX on the RHAC have been determined as shown in Fig. 2. Initially, the isotherm rose rapidly over the initial stage of adsorption where low C_e and q_e values existed. This behavior indicates that there were plenty of readily accessible sites available on the adsorbent. Eventually, a slow approach to equilibrium at high concentrations occurred. As more sites are filled, it becomes difficult for the solute molecules to find a site for adsorption and/or the difficulty of molecules in penetrating the layer of adsorbed molecules already covering the surface sites. As result, the rate of adsorption decreases giving a plateau covers a wide range of solution concentrations.

Table 3
The adsorption rates of BTEX on RHAC activated carbon

Compound	K (mg/g h$^{0.5}$) × 10^{-3} (a)	K (mmol/g.h$^{0.5}$) × 10^{-3} (b)
Benzene	20.0	0.256
Toluene	34.0	0.369
Ethylbenzene	40.1	0.3776
P-Xylene	88.7	0.8354

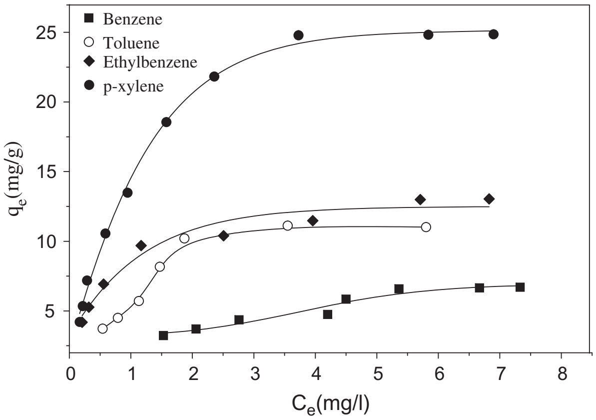

Fig. 2. The adsorption isotherms of BTEX compounds on RHAC.

Data obtained from adsorption isotherms were fitted to linearized forms of Freundlich, Eq. (4) and Langmuir isotherm, Eq. (5):

$$\log q_e = \log K_f + \frac{1}{n_f} \log C_e \tag{4}$$

$$\frac{C_e}{q_e} = \frac{1}{bq^o} + \frac{C_e}{q^o} \tag{5}$$

where q_e is the equilibrium uptake (mg/g), C_e the equilibrium concentration (mg/l); and K_f and n_f are the Freundlich constants, n gives an indication of favorability (adsorption intensity) and k the capacity of adsorbent (adsorption capacity). q_o and b are the Langmuir constants related to the maximum adsorption capacity corresponding to complete monolayer coverage and energy of adsorption respectively. By comparing the calculated correlation coefficients, R^2 in Table 4, for each model it can be concluded that the experimental data fit Freundlich model suggesting the multilayer adsorption of BTEX compounds on RHAC surface. The Freundlich exponent n_f are greater than unity indicating that the adsorption by RHAC of the

Table 4
Langmuir and Freundlich constants of BTEX adsorption isotherms

Solute	Aqueous solubility (mg/l)	M. Wt.	Langmuir			Freundlich		
			q°	b	R	K_f	n_f	R
Benzene	1750	78	9.4	0.33	0.95	2.61	2.02	0.998
Toluene	535	92	17.7	0.48	0.9	5.7	2.0	0.99
Ethylbenzene	175	106	11.6	1.97	0.93	6.7	3.25	0.98
P-Xylene	152	106	27.1	0.83	0.97	10.4	2.05	0.99

Table 5
Adsorption parameters of BTEX compound in reagent and surface water

Compound	Ismailia surface water (mixture)		Reagent water (Single-component)	
	K_f	n_f	K_f	n_f
Benzene	2.54	1.03	2.02	2.6
Toluene	2.26	1.93	2.0	5.7
Ethylbenzene	2.38	0.55	3.25	6.7
P-Xylene	2.0	1.04	2.05	10.38

solutes studied was favorable [26]. It is evident that the K_f increased follows the order: X > E > T > B which is the same order of sorption rates. Favorable adsorption of this order of compounds may be attributed to the decrease in solubility, and the increase in molecular weight and boiling point. Lower solubility compounds have lower affinity towards water and have high affinity for RHAC. Both ethylbenzene and P-xylene have the same molecular weight though the latter compound has higher adsorption capacity. This observation can be explained on the basis of molecular configuration and these results confirm that the adsorption of organic substance was affected by chemical structure, solubility, and molecular weight [27].

The ability of RHAC was tested to remove BTEX from real waste streams. Water sample from Ismailia canal in Egypt was polluted with commercially available unleaded gasoline containing BTEX compounds. Isotherm experiments were carried out by mixing 5 ml of polluted surface water with various masses of RHAC ranged (20–160 mg) at 25°C. It was found that the adsorptive capacity of BTEX is considerably dependent on the initial concentration of each component in the surface water (102.4, 109, 19.8, and 8.3 for BTEX, respectively). The Freundlich parameters, K_f and n_f were calculated and listed in Table 5. It is clear that the adsorptive capacity expressed by K_f values of Freundlich model of each BTEX (single-component) in reagent water is higher than that of Ismailia surface water (mixture). Change in adsorption parameters reflect the competitive effects on the adsorption process and available surface. This behavior can be due to the mixing effects of BTEX components in the mixture and the impact of background organic matter (BOM). The adsorption of one substance will tend to reduce the number of open sites, hence the "concentration" of adsorbent available as a driving force to produce adsorption of the other substance decreased. On the other hand, when both BOM and BTEX are present and adsorbing simultaneously, BOM can compete directly with the BTEX for available adsorption sites on RHAC. RHAC also may bind to BOM materials dispersed in the solution phase and thus effectively enhance the solubility of target compounds and reduce their affinities for adsorption from solution.

3.2. Desorption studies

Desorption of organics from activated carbon in the liquid phase and, especially in aqueous solution has received relatively little attention. The desorption behavior of BTEX on RHAC at different time intervals are shown in Fig. 3. The amount of BTEX desorbed from RHAC was found to be greatly affected by contact time. Desorbed amount increased with increasing the shaking time till reaching saturation where the amount desorbed attains a constant value. In general, the kinetic tests suggested that desorption equilibrium is less rapid than the adsorption equilibrium. Maximum adsorption and desorption was observed after two days (48 h) behind, which there is no further, increases in both adsorption and desorption. As shown in Fig. 1 the adsorption takes the order of X > E > T > B while desorption in Fig. 3 takes the order of E > T > X > B. This observation can be explained on the basis of molecular configuration and these results confirm that the adsorption and desorption of organic substance was affected by chemical structure, solubility, and molecular weight [27].

The kinetic investigations for desorption of BTEX compound from RHAC to the aqueous phase is

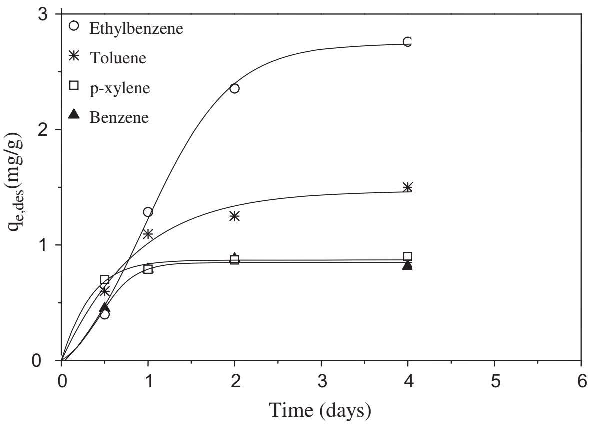

Fig. 3. Effect of contact time on desorption of BTEX compounds from RHAC.

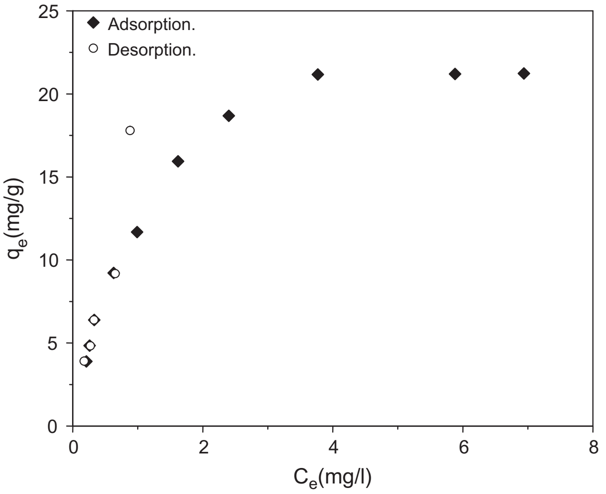

Fig. 4. Adsorption-desorption isotherms for p-xylene on RHAC.

carried out for over four days. It is evident that the equilibrium condition is attained completely after two days of contact between the solution and the RHAC. About 22% benzene, 33% toluene, 58% ethylbenzene, and 18.8% p-xylene were released from the RHAC after four days of contact between the loaded matrix and reagent water.

To check the reversibility of the adsorption process, the adsorption-desorption isotherms for p-xylene has been investigated in Fig. 4. Fig. 4 demonstrates the hysteresis between adsorption and desorption and suggests that small fraction of the p-xylene was irreversibly desorbed. It has been suggested that strong adsorption of aromatics on RHAC can take place through the formation of electron donor-acceptor bonds between aromatic ring and the surface carbonyl groups phosphoric acid activated rice husk carbon [28].

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