



Multi-Component Adsorption of Benzene, Toluene, Ethylbenzene and Xylenes from Aqueous Solution by Activated Carbon from Rice Husk

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Experimental studies were done on the adsorption of benzene, toluene, ethyl benzene, xylenes and their binary mixtures by rice husk activated carbon in an isothermal condition of 25 °C. The results showed that the uptake of each compound was considerably reduced in the presence of other component. The adsorptive orders of these four volatile organic compounds were same in single- and binary-solute system: toluene > benzene > and *p*-xylene > ethyl benzene. This reflects the effect of molecular configuration chemical structure, solubility and molecular weight on the adsorption process. Presence of background organic matter adversely affected the adsorption capacity of toluene, onto rice husk activated carbon.

Keywords: Adsorption. BTEX. Multi-component. Activated carbon.

INTRODUCTION

The BTEX compounds, namely, benzene (B), toluene (T), ethyl benzene (E) and xylenes (X), are often found in soil and groundwater¹. The toxicity effect and water solubility of BTEX endowed these compounds with great environmental hazard². They can cause adverse health effects such as chromosome aberrations, cancer and damage to the liver, kidneys, eyes and central nervous system³. 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 accidents⁴.

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 advantages and disadvantages as far as applicability, site dependence, efficiency and cost parameters are concerned⁴. 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 low cost 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 resins⁵, surfactant modified zeolites⁶, organo-clays⁷ and carbon nanotubes⁸ seems to be an interesting perspective.

In general, research on removal of volatile organic compounds has focused on pure component⁹. However, most adsorption problems appearing in engineering practice involve mixture adsorption. In this study, experiments were taken to investigate the adsorption of multicomponent BTEX on rice husk carbon. The multicomponent systems are representative of the most common real situations as many industrial discharges contain a mixture of several pollutants.

A major factor that affects the adsorptive capacity of activated carbon for volatile organic chemicals in natural water is the presence of background organic matter (BOM)¹⁰. A reduction in the capacity of activated carbon for target volatile organic compounds results from the competition between background organic matter and the volatile organic compounds for limited surface area available for adsorption.

Rice husk 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 sites¹¹. Rice husk is one promising biomass in Egypt because of its large and stable yield (500,000 tons a year) and its low acquisition cost¹². Activated carbon and porous carbon prepared from rice husk 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 biodiesel¹³. Motivated by these studies, we carried out a series of batch experiments to evaluate the adsorption behavior of rice husk activated carbon to BTEX compounds from aqueous solution. Evaluations were performed considering kinetic and equilibrium approaches.

The present work evaluated rice husk activated carbon for the removal of BTEX, by adsorption process. Evaluations were performed considering equilibrium approaches in single- and multi-component systems. Efficiency of rice husk activated carbon was tested in natural water to see the effect of background organic matter on adsorption process.

EXPERIMENTAL

Rice husk activated carbon (RHAC) was prepared according procedures in previous work with some modification¹⁴. Briefly, 40 g of powdered rice husk 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, Norwath, USA). The BET-surface area of rice husk activated carbon was calculated from N₂-gas adsorption that was obtained by NOVA 3200; V 6.05 gas sorption analyzer, Quantachrome, U.S.A. Elemental analysis and physical characterization concerned with pore volume and surface area of rice husk activated carbon are listed in Table-1.

TABLE-1
PHYSICAL AND CHEMICAL CHARACTERIZATION
RICE HUSK ACTIVATED CARBON

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

The employed benzene, toluene, ethyl benzene and *p*-xylene 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 microliter 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 determination batch experiments, in order to explore the adsorbent's capacity and efficiency.

Equilibrium experiments were conducted by addition of various weighed masses of rice husk activated carbon (0.5 mg to 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.

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) method¹⁵. Sorption capacity of adsorbent was calculated by:

$$q_e = V(C_o - C_e)/m \quad (1)$$

where C_o and C_e are the initial and equilibrium concentration (mg/L), respectively, M is the mass of dry carbon sample used (g) and V volume of solution (mL).

In order to investigate the competitive effect on the adsorptive capacity of each component of BTEX in presence of another, isotherm was done in binary mixtures. For this purpose, various quantities of rice husk activated carbon (RHAC) ranged from 0.1 to 6 mg were added to the isotherm bottles. Each contains 5 mL of equal initial concentration, (8 mg/L) of benzene/toluene or ethyl benzene/*p*-xylene using the reagent water. Then the bottles were shaken for 2 days till equilibration. The equilibrium concentration of residual constituents in the filtrate was measured.

In order to gain better insight on the effect of background natural organic matters (BOM) on the adsorption capacity of BTEX. The experimental design was directed to investigate this effect on the adsorption isotherm of toluene. The same procedures described above were carried out by using surface water obtained from Ismailia canal in Egypt instead of the reagent water.

RESULTS AND DISCUSSION

The shaking time (48 h) was observed as maximum time behind which, there is no further, increases in the BTEX adsorption on Rice Husk activated carbon. This time was used for all equilibrium experiments. Adsorption isotherms of BTEX on the Rice Husk activated carbon in single and binary system have been determined as shown in Figs. 1-4. Isotherm tests for binary system were performed by mixing equal amounts of benzene/toluene and ethyl benzene/*p*-xylene. Initially there were plenty of readily accessible sites available on the adsorbent then isotherms rose rapidly over the initial stage of adsorption. However a plateau was formed at latter adsorption stage due to more sites are filled and it becomes difficult for the solute molecules to find a site for adsorption. The isotherm of each compound in mixture reached the plateau-like region at lower q_e values than of single compound isotherms.

Data obtained from adsorption isotherms was fitted to linearized forms of Freundlich, eqn. 3:

$$\log q_e = \log K + \frac{1}{n} \log C_e \quad (3)$$

where q_e is the equilibrium uptake (mg/g), C_e the equilibrium concentration (mg/L); and K and n are the Freundlich constants, n gives an indication of favorability (adsorption intensity) and k the capacity of adsorbent (adsorption capacity). Experimental data fit Freundlich model suggesting the multi-layer

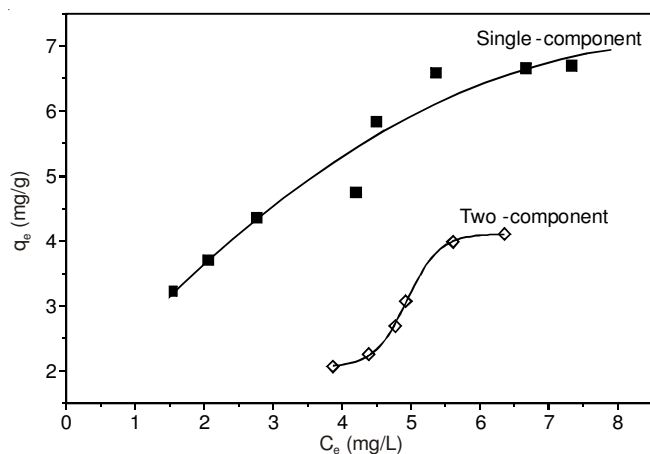


Fig. 1. Adsorption isotherms of benzene in single and two-component system

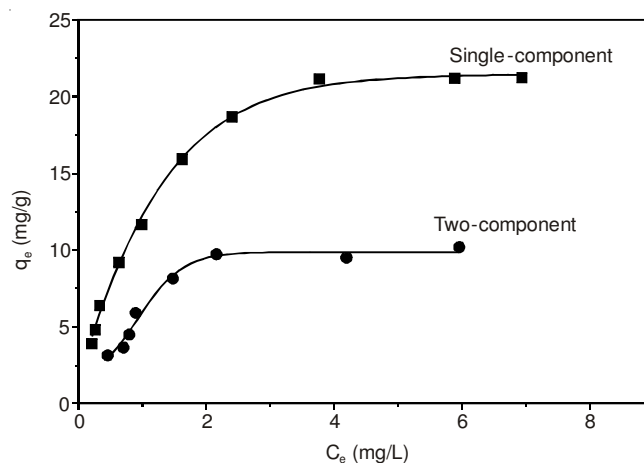
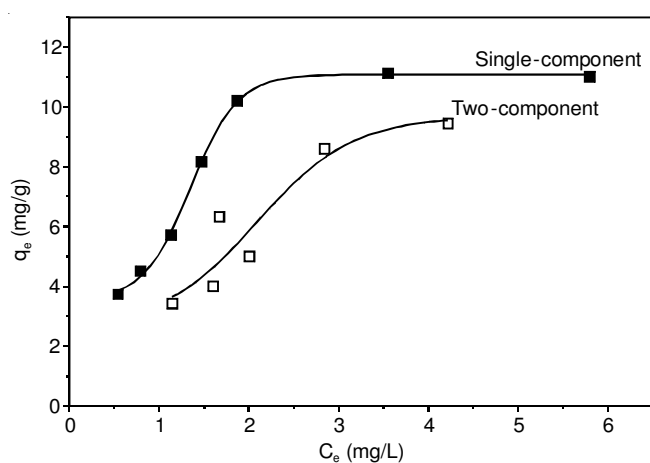
Fig. 4. Adsorption isotherms of *p*-xylene in single and two-component system

Fig. 2. Adsorption isotherms of toluene in single and two-component system

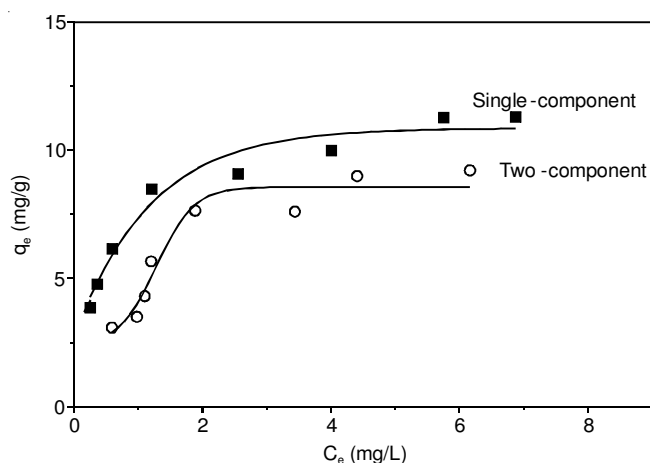


Fig. 3. Adsorption isotherms of ethyl benzene in single and two-component system

adsorption of BTEX compounds on rice husk activated carbon surface. The Freundlich exponent n are greater than unity indicating that the adsorption by rice husk activated carbon of the solutes studied was favourable¹⁶. The adsorption parameters given in Table-2 indicate that the uptake of each compound was considerably reduced in the presence of other component (binary system). However, the order of adsorption capacity, K_f , was the same as for the single-solute system *i.e.* toluene >

Compound	Single-component systems		Two-component systems	
	K_f	n_f	K_f	n_f
Benzene	2.60	2.02	0.24	0.63
Toluene	5.70	2.00	3.21	1.24
Ethyl benzene	6.70	3.25	4.31	2.05
<i>p</i> -Xylene	10.38	2.05	5.27	2.10

benzene > and *p*-xylene > ethyl benzene. This order 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 weight¹⁷. In binary system, 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 will be less. Change in adsorption parameters reflect the competitive effects on the adsorption process and available surface. This behavior can be related to different factors;¹⁸ (i) Solute-solute interactions: in solutions and at the sorption sites, (ii) sorbent affinity (or capacity) change, (iii) non-equal competition. This is attributed to the heterogeneity of the carbon surface. This implies that species have non-equal chances to be adsorbed, (iv) the effect of molecular sieving: carbon particles have wide pore-size ranges and molecular sieving is the exclusion of some sorbates from reaching the micropores in the particle interior due to their relatively large molecular sizes, (v) irreversibility: some functional groups on the carbon surface form bonds that resist desorption and cause hysteresis effects.

Waste water treatment occur in the presence of background organic matter (BOM) which is one of the main factors affecting the equilibrium capacity of activated carbon in water treatment¹⁰. Therefore, we study the effect of background organic matter on the adsorption of BTEX compounds by rice husk activated carbon. We use for this purpose the surface water of Ismailia canal, Egypt. Natural water isotherm tests of the adsorption of toluene on rice husk activated carbon compared to reagent water in Fig. 5 shows a significant reduction in adsorption capacity as results of competition with background organic matter. It is known that background organic matter

adversely affected the adsorption of trace organic compounds, onto activated carbons through two major competitive mechanisms: direct site competition and pore constriction/blockage¹⁹. When background organic matter (BOM) was present during activated carbon treatment of water containing trace organic compounds, background organic matter would compete for adsorption sites with the target compounds. As a consequence, the adsorption of trace organic compounds would usually be reduced²⁰. In addition, preloaded background organic matter was found to reduce adsorption capacity primarily through direct site competition and decrease adsorption kinetics primarily by pore blockage²¹.

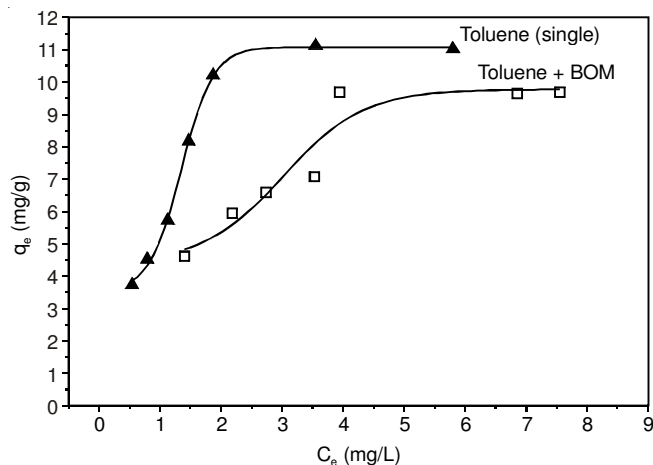


Fig. 5. Effect of background organic matter on adsorption of toluene

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