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Adsorption of toluene, ethylbenzene and xylenes by activated carbon-impact of molecular oxygen

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ABSTRACT

The effect of the presence of molecular oxygen on the adsorption of toluene, ethylbenzene and xylenes in distilled Milli-Q water and in surface water supplemented with background organic matter is evaluated using activated carbon from rice husk. Experiments are conducted under conditions where molecular oxygen is present (oxic adsorption), and where oxygen is absent (anoxic adsorption) from the test environment. Significant increase in the adsorptive capacity had been observed under oxic condition compared to anoxic condition. Molecular oxygen induces polymerization of these compounds on the carbon surface, which resulted in a significant increase in the adsorptive capacity of activated carbon.

Keywords: Oxic and anoxic adsorption; Toluene; Ethylbenzene; Xylenes; Background organic matter

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 dis-charge into the aqueous environment, either through wastewater mismanagement or accidents [4].

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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 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

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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.

Studies of the adsorptive properties of activated carbon have shown that molecular oxygen plays an important role in the adsorption of phenolic compounds [10]. It was found that molecular oxygen induces polymerization of these compounds on the carbon surface, which resulted in a significant increase in the adsorptive capacity of activated carbon. Other investigators have already demonstrated that the presence of background organic matter (BOM) significantly reduces the capacity of activated carbon for a number of target organic compounds [11]. However, the presence of molecular oxygen will cause an increase in the adsorptive capacity of activated carbon for BOM, hence, further reducing adsorptive capacities for the target contaminants. Higher extraction efficiencies of the carbons used in the oxic isotherms (presence of molecular oxygen) were obtained for the carbons that exhibited lower increases in capacities when compared to anoxic isotherms-absence of molecular oxygen [11].

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 [12]. RH is one promising biomass in Egypt because of its large and stable yield (500,000 tons a year) and its low acquisition cost [13]. 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 [14-17]. The present work investigated the importance of the molecular oxygen presence on the adsorption capacity activated carbon from RH for the removal of BTEX in distilled Milli-Q water and in surface water supplemented with BOM.

2. Material and methods

Rice husk activated carbon (RHAC) was prepared according procedures in our previous work with some modification [18]. Briefly, 40gm 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 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 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 2,000 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.

Two different equilibrium isotherm experimental procedures were introduced. In the first experimental runs, the molecular oxygen was present in the test environment "oxic condition" while in the second experimental runs, the molecular oxygen was from the test environment excluded "anoxic condition". For oxic adsorption isotherms, various weighed masses of RHAC (0.5-12 mg) were placed in glass bottles provided with screw caps and purged with air for a short period of time. Bottles are then filled with 5 ml of each single solute of BTEX. The stock BTEX (8 mg/l) solutions were first prepared from oxygenated reagent water (purged with air for 4 h) [19]. The bottles were shaken until equilibrium time was reached at 25 ± 1 °C. For anoxic adsorption isotherms, accurately weighed masses of RHAC (2-12 mg) were placed in the isotherm bottles. ensure maximum displacement of oxygen То entrapped in carbon pores the adsorbent was purged with high purity nitrogen (5 min twice each day for a period of 3 days) prior to the addition of the adsorbate. Dissolved oxygen in the stock solution water (prior to the addition of BTEX) was eliminated by purging with nitrogen gas for a period of 4 h. Then 5 ml (8 mg/l) of each BTEX was added to the bottles. Air from headspace of the isotherm bottles was displaced with nitrogen gas. The isotherm bottles were sealed with rubber stoppers and aluminum caps and placed in thermostatic shaker at $25 \pm 1^{\circ}C$ for 24 h

Table 1 Physical and chemical characterization

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

to reach the equilibrium then the solution was filtered and equilibrium concentration was measured [20]. BTEX compounds concentration before and after adsorption were determined by Purge & Trap (model: HP-7695) Gas chromatography (model: HP-6890) with flame ionization detector (PT-GC-FID) according to US-EPA (524.2) method [21]. Sorption capacity of adsorbent was calculated by:

$$q_{\rm e} = V(C_0 - C_{\rm e})/m \tag{1}$$

where C_0 and C_e are the initial and equilibrium concentration (mg/l) respectively, *m* is the mass of dry carbon sample used (g) and *V* is the volume of solution (ml).

3. Results and discussion

Forty eight hours shaking time was observed as maximum time behind which, there is no further, increases in the BTEX adsorption on RHAC. This time was used for all equilibrium experiments. Figs. 1–3 show the adsorption isotherms for 8 mg/l of toluene, ethylbenzene and P-xylene under oxic and anoxic conditions. 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 were filled and it becomes difficult for the solute molecules to find a site for adsorption.

Data obtained from adsorption isotherms was fitted to linearized forms of Freundlich, Eq. (2):

$$\log q_{\rm e} = \log K_{\rm f} + \frac{1}{n} \log C_{\rm e} \tag{2}$$

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



Fig. 1. Adsorption of toluene in oxic and anoxic conditions.



Fig. 2. Adsorption of ethylbenzene in oxic and anoxic conditions.

Freundlich model suggesting the multilayer adsorption of BTEX compounds on RHAC surface. The Freundlich exponent *n* are greater than unity indicating that the adsorption by RHAC of the solutes studied was favourable [22]. The adsorption parameters given in Table 2 indicates that the adsorption capacities (K_f) followed the order p-xylene>ethylbenzene>toluene. Daifullah and Girgis studied the adsorption of BTEX



Fig. 3. Adsorption of p-xylene in oxic and anoxic conditions.

on activated carbon and obtained similar results regarding the order of adsorption capacities, which were associated with decreases in solubility and increases in molecular weight [23]. It is of great importance to disclose the adsorption mechanism of BTEX on RHAC. It was suggested that the π - π electron-donor-acceptor mechanism involving the carboxylic oxygen-atom of RHAC surface as the electron-donor and the aromatic ring of BTEX as the electron-acceptor is responsible for the uptake of BTEX by RHAC [12]. Similar conclusions have been drawn in the literature for adsorption of BTEX on powdered activated carbon (PAC) [23].

In addition, data in Table 2 indicate that the adsorptive capacity of RHAC increases significantly when molecular oxygen exists in the test environment. Vidic et al. [19], Vidic And Suidan [20], and Karanfil et al. [24] attributed the increase in capacities under oxic condition to polymerization reactions that take place on the surface of carbon. It is therefore, reasonable to believe that these compounds behavior under oxic condition could be due to a polymerization reaction on the surface of RHAC where the methyl groups of BTEX compounds react with molecular oxygen on the carbon surface to form a polymer by losing a molecule of H_2O .

$$-CH_3 + O_2 + H_3C - -H_2O \rightarrow -CH_2 - O - CH_2 -$$

The adsorption parameters of Freundlich isotherm in Table 2 can be used to compare the oxygen sensitivity of different compounds. the Freundlich adsorption capacity determined under oxic $(K_{f,o})$ and anoxic ($K_{f,a}$) condition and the ratio of ($K_{f,o}/K_{f,a}$) which can be used to compare the oxygen sensitivity of various solutes [25]. The adsorption capacity $K_{\rm f}$ of toluene, ethylbenzene, and p-xylene decreased by 35, 43.9 and 75% respectively under anoxic condition. The oxygen sensitivity ratio $K_{f,o}/K_{f,a}$ have the order: (p-xylene >> ethylbenzene > toluene) indicating that as the molecular weight increases the oxygen sensitivity increases [25]. In case of isomers (p-xylene and ethylbenzene which have the same molecular weight) the two methyl groups of p-xylene contribute in polymerization with oxygen and this indicates that molecular oxygen play an important role in adsorption of p-xylene.

The impact of molecular oxygen on adsorption capacity of toluene compound on activated RHAC has been investigated in reagent water (single-component) and in water supplemented with BOM from "Ismailia canal, Egypt" as shown in Fig. 4. Experiments are conducted under conditions where molecular oxygen is present in the test environment (oxic adsorption), and where oxygen is absent from the test environment (anoxic adsorption). As mentioned before, when the isotherms are conducted in reagent water, it was demonstrated that molecular oxygen in the test environment exerts an increase in the adsorptive capacity of activated RHAC for toluene. This can be explained as previously mentioned by the fact that, molecular oxygen induces polymerization of toluene on the carbon surface, which resulted in a significant increase in the adsorptive capacity of activated carbon [11]. However, the presence of molecular oxygen in the test environment further reduces the adsorptive capacity of activated carbon for the target (toluene) isotherm conducted in water supplemented with BOM (Table 3). This is attributed to a reduction in the available surface area of the carbon for the target component, and it is due to a significant increase in the adsorption of BOM under oxic

Table 2 The effect of molecular oxygen on adsorption of BTEX RHAC

| Compound | M. wt | K _{f,o} | K _{f,a} | $K_{\rm f,o}/K_{\rm f,a}$ | n _{f,o} | n _{f,a} |
|--------------|--------|------------------|------------------|---------------------------|------------------|------------------|
| Toluene | 92.14 | 5.7 | 3.7 | 1.54 | 2 | 4.24 |
| Ethylbenzene | 106.17 | 6.7 | 3.76 | 1.78 | 3.25 | 4.56 |
| P-xylene | 106.17 | 10.38 | 2.6 | 4.0 | 2.05 | 1.68 |



Fig. 4. Effect of molecular oxygen on adsorption of toluene in single and multi-component system.

Table 3

Freundlich parameters of toluene in oxic & anoxic conditions on RHAC

| Component | Oxic | | Anoxic | |
|------------------------|-----------------------------|----------------|----------------|----------------|
| | $\overline{K_{\mathrm{f}}}$ | n _f | K _f | n _f |
| Toluene (single) | 5.7 | 2.0 | 3.7 | 4.24 |
| Toluene + BOM (multi-) | 4.2 | 2.2 | 0.61 | 1.0 |

conditions than anoxic conditions. This increase is attributed to a conglomeration of BOM on the carbon surface in the presence of molecular oxygen [11].

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