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BTX Removal from Polluted Water Through Bioleaching Processes

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Abstract In this study, benzene, toluene, and xylenes (BTX) removal from contaminated water by physical, chemical, and biological processes was studied. Results showed that air sparging in polluted water can reduce monoaromatic compounds from 140,000 to about 5 μg/l in only 1 h process with a gassing rate of 0.33 VVM. This method cannot be considered as a green technology as pollutants are only transferred from the liquid phase to the gas phase The ultimate objective of this research was thus to evaluate the efficiency of a strategy involving BTX adsorption by granular-activated charcoal (GAC) and subsequent regeneration of this support by a bioleaching process. Analysis of such processes requires the building of analytical tools able to accurately determine the contents of the contaminants in samples containing biomass to make possible the calculation of reliable material balances. Current investigation showed that BTX are readily trapped by GAC particles with low further release in the liquid medium whereas they remain at least partially available for in situ biodegradation. BTX adsorption onto the GAC was shown to reach maximum solute retention close to 350, 250, and 150 (as mg/g GAC) for xylenes, toluene, and benzene, respectively. This approach, which could afford efficient biological active carbon regeneration, is very promising for the removal of BTX compounds from water without any further environment damage.

Keywords Monoaromatic · Bioleaching · Contaminated water · Air sparging · GAC · BTX · Adsorption

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Introduction

Benzene, toluene, and xylenes (collectively known as BTX) are monoaromatic hydrocarbon compounds. As they are suspected as being carcinogens, their release in the environment is strictly controlled and they are classified as priority environmental pollutants [1]. BTX compounds do not strongly adsorb to the soil; therefore, they can reach groundwater and are likely to contaminate water supplies as about 50% of drinking water in the world originates from groundwater [2]. Important sources of water contamination by monoaromatics are caused by industrial wastewater and released petroleum products from storage tank, gas work sites, airports, paint manufacturer, chemical industries, and railway yard [3]. BTX compounds may comprise more than 50–60% by weight of the solubilized compounds when gasoline is introduced into water [4]. Permissible limits of BTX given by USEPA in potable water are 0.005, 1, and 10 ppm for benzene, toluene, and mixed xylenes, respectively [5].

There are different methods for monoaromatic compound removal from polluted water such as physical methods (air sparging, carbon adsorption, filtration, adsorption by zeolites) [6, 7], chemical techniques (chemical oxidation, photocatalysis remediation) [8], and biological processes (bioremediation, bioleaching) [4, 9, 10, 11]. Past research has indicated that BTX bioremediation by bioreactors (under aerobic and anaerobic conditions) such as fixed film and moving bed biological reactor appears to be an economical, efficient, fast, and environmentally sound approach [2, 12, 13]. But generally these works do not discuss possible pollutant loss through gas stripping and also the data generated do not take into account the possible solute sorption phenomena by media in fixed film and moving bed bioreactors [14, 15]. The true efficiency of these processes is still to be correctly evaluated as the physical and chemical properties of monoaromatic compounds demonstrate that phenomena such as stripping and volatilization can contribute in a nonnegligible amount to their removal from the liquid phase. It is important to realize that this phenomenon is likely to occur in both aerobic and anaerobic processes [14, 15].

Bioleaching by granular-activated charcoal (GAC) can be defined as a favorable alternative for the treatment of BTX-contaminated waters because at this process monoaromatic hydrocarbon can be adsorbed on the surface of the GAC particles and then stabilized by the biomass at the surface of activated carbon. The bioleaching process provides a combined biological degradation and adsorption–desorption method using activated carbon to deal with a wide variety of pollution problems.

The objective of this work was to study monoaromatic stripping through air sparging, BTX adsorption from synthetically contaminated water on GAC and preliminary studies on the feasibility of subsequent regeneration of this support by a bioleaching process.

Materials and Methods

Chemicals

Benzene (99%) and xylenes (mixture of isomers) were purchased from Sigma-Aldrich (France) and toluene (99.5%) was obtained from Merck (Germany). GAC with particle size 4–8 mm and surface area 950–1,050 m^2/g was prepared from Fluka (France), which was rinsed with distilled water to remove fine powder. Also, mineral salts and other chemical compounds in analytical grade were obtained from Acros Organics (Belgium).

Biological Process

Aerobic sequencing batch reactors (SBR) were incubated with an acclimated biomass obtained from activated sludge. This mixed culture was collected from a domestic wastewater treatment plant and grown on a mineral medium (see below) in the presence of BTX during 3 months duration. The working volumes of SBR bioprocesses in Pyrex-glass bottles were 250 ml and bottle volume were 500 ml. A Gerhardt LABOSHAKE LS 500/RO 500 shaker was used at room temperature with a stirring rate of 150 rpm. The nutrient solution contained KH_2PO_4 85 mg/l, $Na_2HPO_4{\cdot}2H_2O$ 334 mg/l, NH_4Cl 5 mg/l, $CaCl_2{\cdot}2H_2O$ 36.4 mg/l, $MgSO_4{\cdot}7H_2O$ 22.5 mg/l, and $FeCl_3{\cdot}6H_2O$ 0.25 mg/l according to the OECD standard method. Initial BTX and dry biomass concentration used in aerobic bioreactors were in the range of 50–150 and 50–1,000 mg/l, respectively. Hydraulic retention time of bioreactors was between 8 and 30 h, and the pH range was 7.45–7.55.

BTX Analysis

Monoaromatic hydrocarbons were analyzed through high-performance liquid chromatography (HPLC). Liquid chromatography was performed on a Waters system (USA). Chromatographic separation of BTX was carried out on a Supelco Discovery C8 (4.6× 150 mm, 5 μm, Intact) column. Column temperature was kept at 35 °C. The mobile phase reservoirs contained methanol and water with a volume percent of 60/40, and the flow rate was 1 ml/min. Compounds were detected using a UV/Vis detector (Waters 2487 dual λ absorbance detector) at detector set λ=208 nm. The injection loop was 50 μl (Rheodyne, USA). The system also consisted of a Waters 515 high-pressure pump, a solvent degasser (Waters In line model IDL), and a HPLC guard cartridge system (Security Guard Phenomenex, Analytical KJO-4282). Standards were made from the same pure compounds used in the experiments, and sample concentrations were determined from linear regressions on the standards.

OxiTop Test

A manometric respirometric test was carried out with the WTW OxiTop Control system. The respirometric method is based on pressure measurement in a closed bottle under constant temperature. Oxygen was consumed during the degradation of the organic matter and CO_2 gas released was adsorbed from the gas space by caustic soda (NaOH) so that the resulting pressure decline is a measure of the biological oxygen demand. Also, samples in the bottles were sealed with a cap containing an electronic pressure indicator and continuously mixed. The BOD value was calculated from the following equation:

$$\mathrm{BOD(mg/l)} = M(\mathrm{O_2})/RT_\mathrm{m} \times [V_\mathrm{tot} - V_\mathrm{l}/V_\mathrm{l} + \alpha T_\mathrm{m}/T_0] \times \Delta p(\mathrm{O_2})$$

where M (O_2) is the molecular weight of oxygen (32,000 mg/ mol), R is the gas constant (83.144 l hPa/mol K), T_m is the measuring temperature (K), T_0 is 273.15 K, V_{tot} is the bottle volume (ml), V_l is the liquid phase volume (ml), α is the Bunsen absorption coefficient for oxygen (0.03103), and Δp (O_2) is the difference in partial oxygen pressure (hPa) as given by OxiTop.

The nutrient solution used for these assays were in accordance with the OECD standard method (described in the "Biological Process" section). Also, mixed culture biomass after adaptation with BTX compounds was taken from aerobic sequencing batch bioreactor and used as inoculums for OxiTop tests (described in the "Biological Process" section).

Sampling

Five milliliters of the sample containing biomass was added to 15-ml centrifuge glass tubes (Corex, USA) and then centrifuged for 10 min at 10 °C and 10,000×*g* (Sigma type 3K30 centrifuge). Samples were then membrane filtered (0.45 μm polyvinylidene fluoride (PVDF); Millipore, USA). Finally, samples were injected to the HPLC for BTX analysis.

Stripping Experiments

Stripping of monoaromatic hydrocarbons from synthetically polluted water was studied in a mechanically stirred, thermostatted bioreactor of 2 l working volume (Biostat MD, B. Braun, Melsungen, Germany) fitted with an oxygen partial pressure (pO_2) sensor (Mettler-Toledo, Switzerland). The gas flow rate was monitored by a mass flow controller.

Results and Discussion

As depicted in Fig. 1a, air sparging in polluted water could readily reduce its monoaromatic hydrocarbon content through a stripping phenomenon. Results indicated that air sparging in contaminated water can eliminate BTX compounds from 140 ppm to about 5 ppb in only 1 h of processing with a gassing rate of 0.33 VVM. This result was consistent with bibliographical searches which have clearly indicated that air sparging has become a popular tool for the remediation of contaminated water by volatile organic compounds (VOCs), particularly dissolved petroleum hydrocarbons [16, 17]. This approach cannot be considered as a green technology as volatile organic compounds are only transferred from the liquid phase to the gas phase. Also, Fig. 1b showed that a logarithmic plot of the residual concentration in liquid phase vs. time gave a straight line. This feature was characteristic of the so-called dilutor method [18] and allowed the calculation of the activity coefficient of the solute, provided both liquid and gas phases can be considered as diluted and at thermodynamic equilibrium [19, 20]. Hence, the following equation resulted from a mass balance on a solute with the preceding assumptions:

$$\mathrm{Ln}\frac{C_0}{C} = \frac{G\gamma^{\infty}P^0}{C_\mathrm{W}V_\mathrm{L}P}t$$

where C_0 and C are the solute concentrations at time 0 and t, respectively; G is the air molar flow rate, C_W is the water concentration in the liquid (55.6 mol/l), V_L is the liquid volume, P is the total pressure in the vessel, P^0 is the solute vapor pressure, and γ^{∞} the limiting activity coefficient of the solute. If a was the slope of the straight line, then the limiting activity coefficient could be calculated using the equation $\gamma^{\infty} = \frac{aV_\mathrm{L}PC_\mathrm{W}}{GP^0}$. Table 1 shows that the results obtained with these assumptions were close to literature data, which meant that the experimental device used enabled interfacial exchanges to be fast enough to allow the two phases to be always near the thermodynamic equilibrium.

Experiments shown in Fig. 2 were carried out in fully filled bottles to avoid solute gas transfers, as depicted in the preceding paragraph. As a result, the lowering of liquid concentrations was actually because of solute adsorption on the solid adsorbent. The

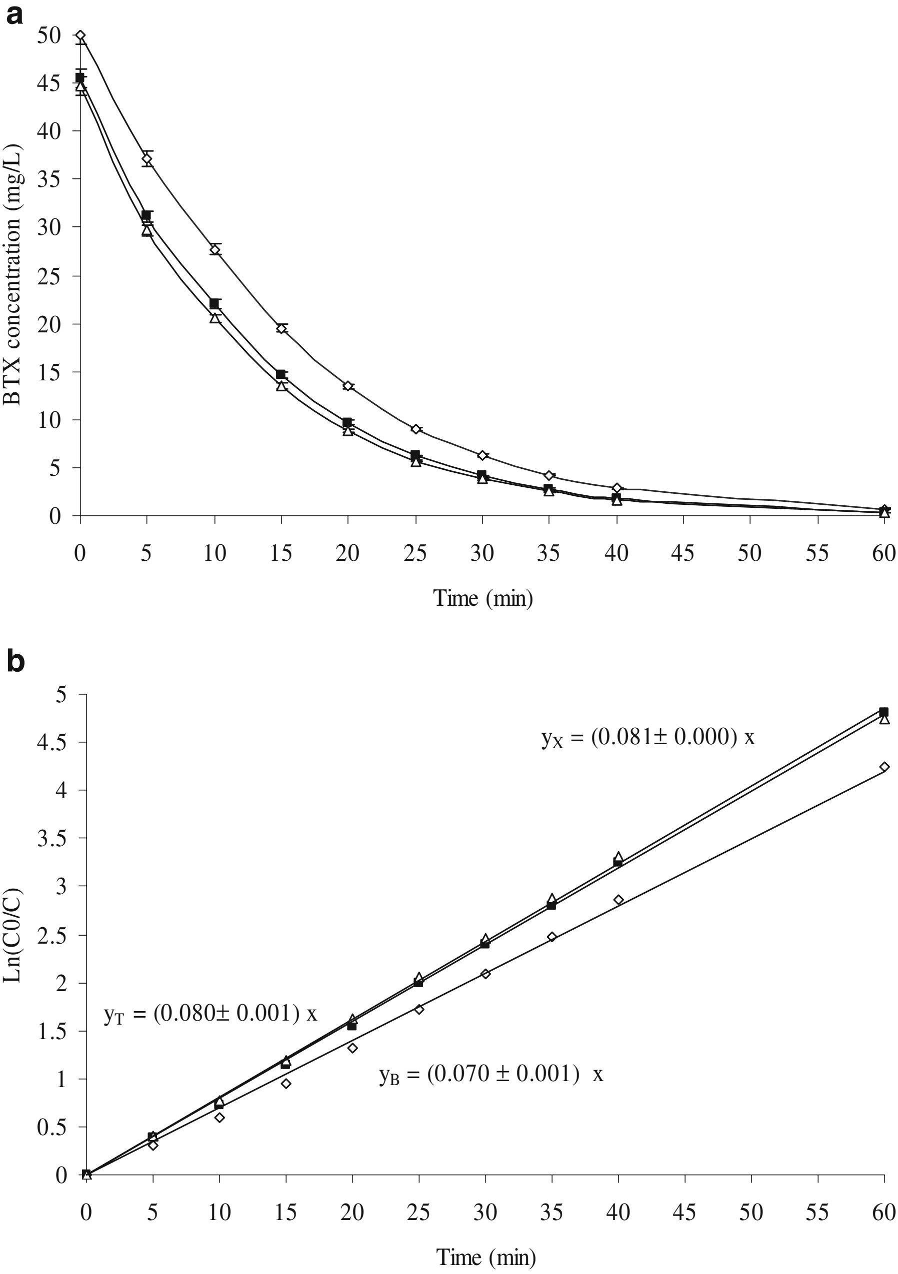


Fig. 1 **a** and **b** Monoaromatic removal from synthetic water contaminated through air sparging (*open diamonds* benzene, *closed squares* toluene, *open triangles* xylenes). Liquid volume 1,500 ml, air flow rate 500 ml/min (0.33 VVM), stirring rate 600 rpm, temperature 20 °C. *VVM* volume of gas per volume of liquid per minute

Table 1 Comparison of literature data and experimental results obtained in this work for limiting activity coefficients of BTX compounds.

Compound	Vapor pressure (mm Hg, 25 °C)	Limiting activity coefficient[a]	Limiting activity coefficient[b]
Benzene	94.8	2,400	2,200
Toluene	28.4	9,700	8,350
Xylenes			
o-xylene	6.61	33,100	
m-xylene	8.29	36,600	
p-xylene	8.84	36,400	
Average[c]	7.9	35,400	30,000

[a] Value at 25 °C calculated from solubility data found in the SRC PhysProp Database (http://esc.syrres.com/interkow/webprop.exe). Calculations were made using the equation $\gamma^{\infty} = \frac{1}{x}$ with $x = \frac{S_W}{MW}$ where S_W is the water solubility (g/l) and MW is the molecular weight (g/mol).

[b] Experimental value at 20 °C, calculated from data in Fig. 1.

[c] Estimated considering an equimolar mixture of isomers, and that there was no interaction between them.s

curves highlighted the fact that the use of activated carbon was effective in the removal of BTX from contaminated water. Activated carbon used in granular form was indeed able to remove BTX down to residual concentrations as low as 5 µg/l. The kinetics of BTX adsorption was observed to be in the order xylenes>toluene>benzene. Favorable adsorption of compounds in this order has been explained as associated with the decrease in solubility and increase in molecular weight. Similar observations have been reported in 2003 by Daifullah and Girgis [6]. It should also be remembered that with a solid adsorbent, the contaminants are retained until its adsorptive capacity. This maximum solute retention could be estimated as being close to 350 mg/g GAC for xylenes, 250 mg/g for toluene, and 150 mg/g for benzene (Fig. 3a). It should be emphasized that an equimolar mixture of these compounds, giving BTX, had a different behavior as the maximal loading could be estimated at a value close to 200 mg/g, instead of the expected value of 145 mg/g (the average of the individual maximal loading capacities). This result indicated that solute interactions were likely to take place in the sorption process.

The curves in Fig. 3b also showed that the Freundlich isotherm could describe BTX adsorption from synthetically polluted water by GAC. It was mathematically expressed as $\frac{x}{m} = KC^{\frac{1}{n}}$ and could be linearized as $\mathrm{Ln}\frac{x}{m} = \mathrm{Ln}K + \frac{1}{n}\mathrm{Ln}\,C$ where x is the mass of the adsorbate (mg BTX), m is the mass of the adsorbent (mg GAC), and C is the equilibrium concentration of adsorbate in solution (mg/l). K and n are dimensionless constants incorporating all factors affecting the sorption process and were close to 14 for K and 2 for n (Fig. 3b). Similar behavior has already been found for BTEX and petroleum adsorption by activated carbon [21, 22].

Solute desorption from the solid adsorbent was also studied. After the adsorption equilibrium was reached, the supernatant was removed and its sorbate concentration was measured. The supernatant was then replaced by clean distilled water. Desorption of BTX from activated carbon was allowed to continue until equilibrium, i.e., at least for 24 h. This process was then repeated, Fig. 4 showed that after eight replicas, <8% of contaminants were released in water. This result demonstrated that BTX retention in GAC particles was not a pure (fully reversible) adsorption phenomenon and that strong interactions were likely to take place between the solutes and the support, in addition to those taking place between solute molecules evidenced above.

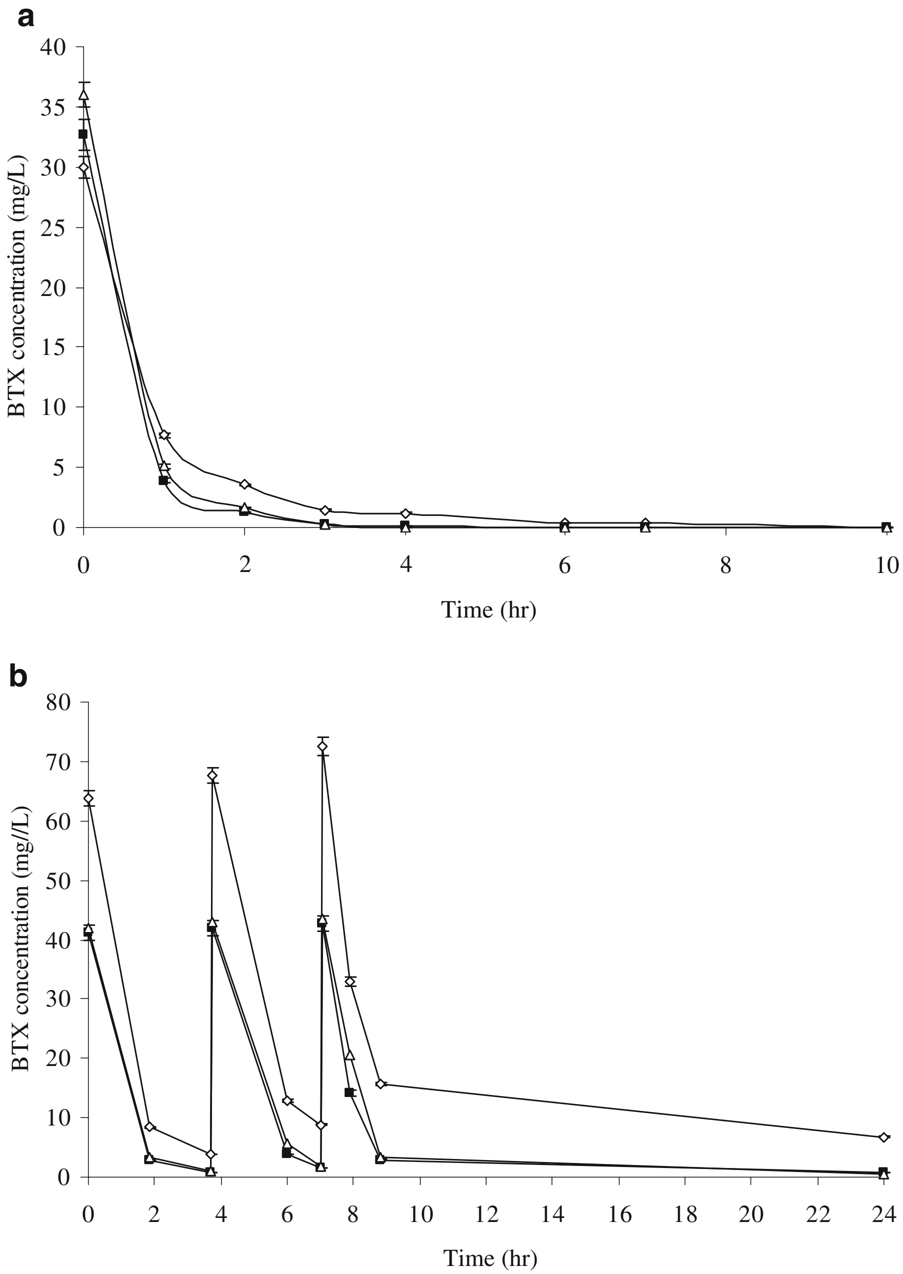
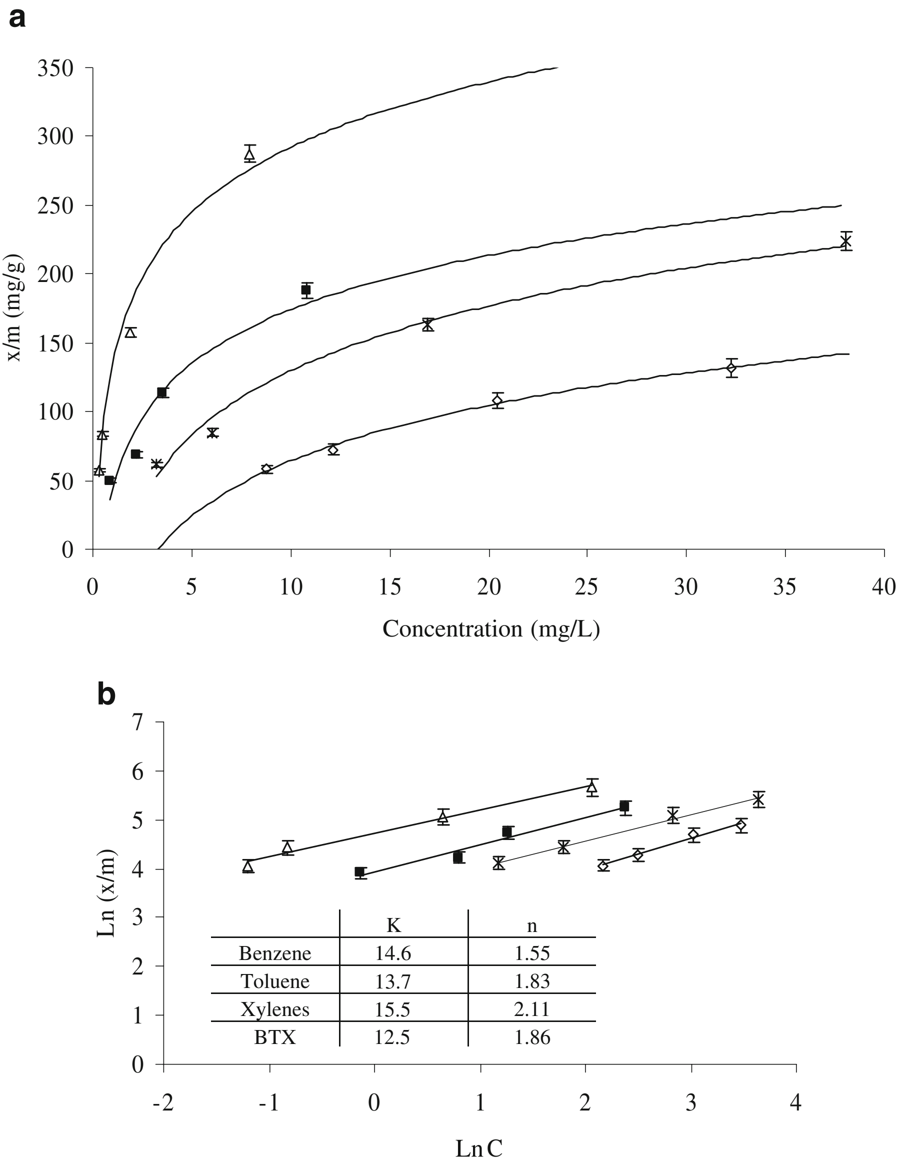


Fig. 2 BTX adsorption from contaminated water by GAC (temperature 24 °C, GAC 2.5 g, working volume 500 ml without air space): **a** BTX adsorption in a single step, **b** BTX adsorption in three steps (*open diamonds* benzene, *closed squares* toluene, *open triangles* xylenes)



	K	n
Benzene	14.6	1.55
Toluene	13.7	1.83
Xylenes	15.5	2.11
BTX	12.5	1.86

Fig. 3 Freundlich isotherm for monoaromatic adsorption from synthetic contaminated water by GAC (working volume 500 ml without air space, temperature 21 °C): **a** Freundlich isotherm, **b** kinetic parameters) (*open diamonds* benzene, *closed squares* toluene, *open triangles* xylenes, *asterisks* BTX)

The results presented in Fig. 5 highlighted the fact that BTX compounds were easily biodegraded by the acclimated biomass used in this study (see the “Materials and Methods” section). Apparent treatment efficiencies up to 99% in terms of monoaromatics disappearance from the liquid could be achieved. However, comparison with a control experiment carried

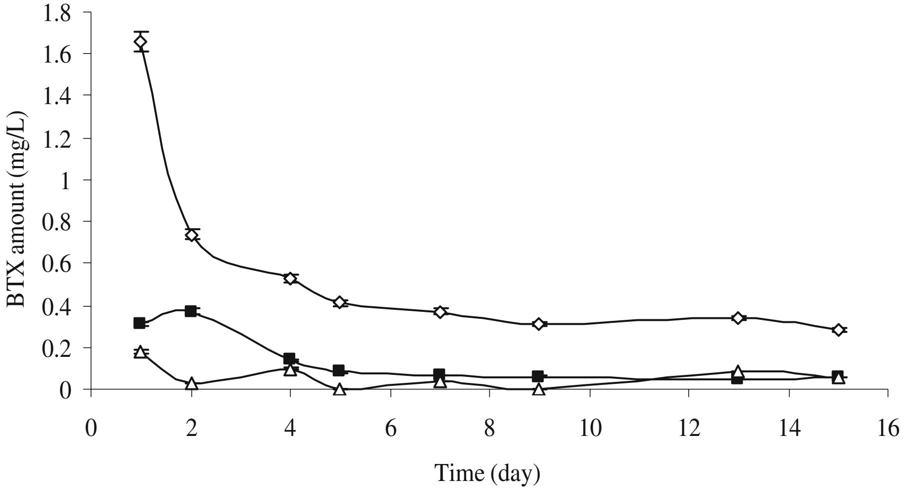


Fig. 4 BTX desorption from GAC in distilled water (working volume 1 l without air space; initial benzene, toluene, and xylenes adsorbed by GAC were 13.1, 14.1, and 12.4 mg/g GAC, respectively; GAC 2 g, temperature 24 °C, pH 6.3) (*open diamonds* benzene, *closed squares* toluene, *open triangles* xylenes). Each point corresponds to an external water change (see text)

out without biomass allowed to demonstrate that a biological process actually took place together with gas–liquid transfers (Fig. 5). This behavior was consistent with the fact that results published up to now have clearly demonstrated that the feasibility of BTX biodegradation through aerobic bioreactors could be considered as well established [23, 24].

When the solid adsorbent was used with a low BTX loading (0.02 g/g), the residual pollutant concentration in the liquid was close to zero, as expected from Fig. 2. Assessment of a bioremediation process could thus be done by indirect metabolic measurements. They were done using OxiTop tests (see the "Materials and Methods" section), based on the measurement of pressure drop as a result of oxygen consumption in a closed vessel where the carbon dioxide produced was trapped by NaOH. Results clearly showed that bioleaching of GAC actually took place, which meant that biomass was able to have an access to BTX retained in the GAC particles (Fig. 6). This process appeared more efficient for benzene, toluene, and mixed xylenes in that order, and up to 35% toluene could be removed after 10 days of process with a very low biomass concentration (46 mg/l) and a significant GAC loading (0.5% *w*/*w*).

Conclusion

Treatment efficiencies of 99% and above in terms of BTX disappearance from polluted water could be achieved by aeration and adsorption processes. These processes are not an environmentally sound approach as VOCs only transferred from the liquid phase to the gas or solid phase. Data indicated that the SBR bioprocess is also a successful method for monoaromatics degradation but VOC stripping and volatilization can contribute in a nonnegligible amount.

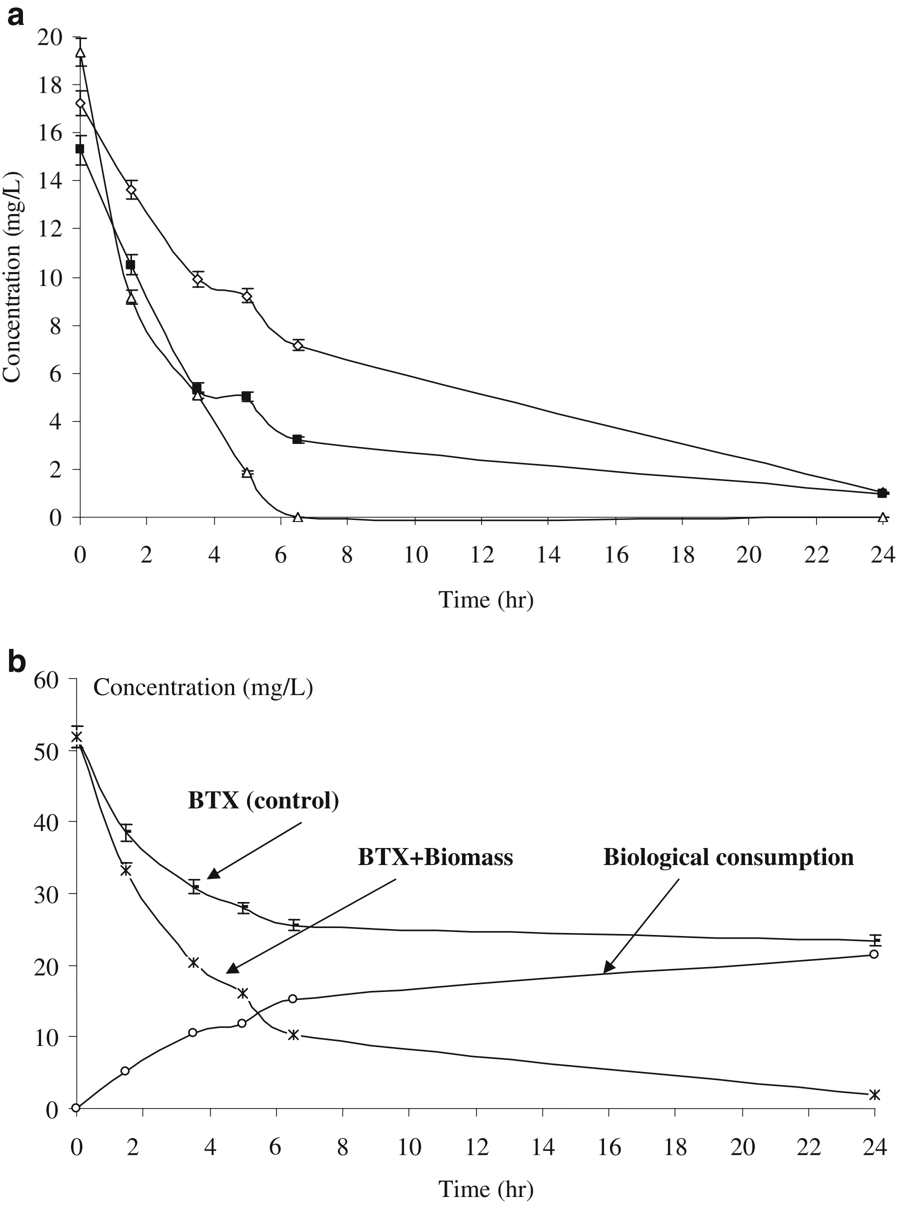


Fig. 5 Monoaromatic removal from polluted water through aerobic batch bioreactor (working volume 250 ml, temperature 23 °C, biomass concentration 65 mg/l, BTX/biomass 1.27 mg/mg): **a** gives the residual concentrations of individual compounds (*open diamonds* benzene, *closed squares* toluene, *open triangles* xylenes), whereas **b** gives the overall residual concentrations and the true biological consumption

Also, this research showed that the strategy of BTX removal from contaminated water by gas stripping and further trapping of solutes in activated carbon particles followed by biodegradation by a bacterial culture in a separate bioreactor could be explored. Current results were very promising for the building of a process enabling the removal of these compounds from polluted water without any further environmental damage.

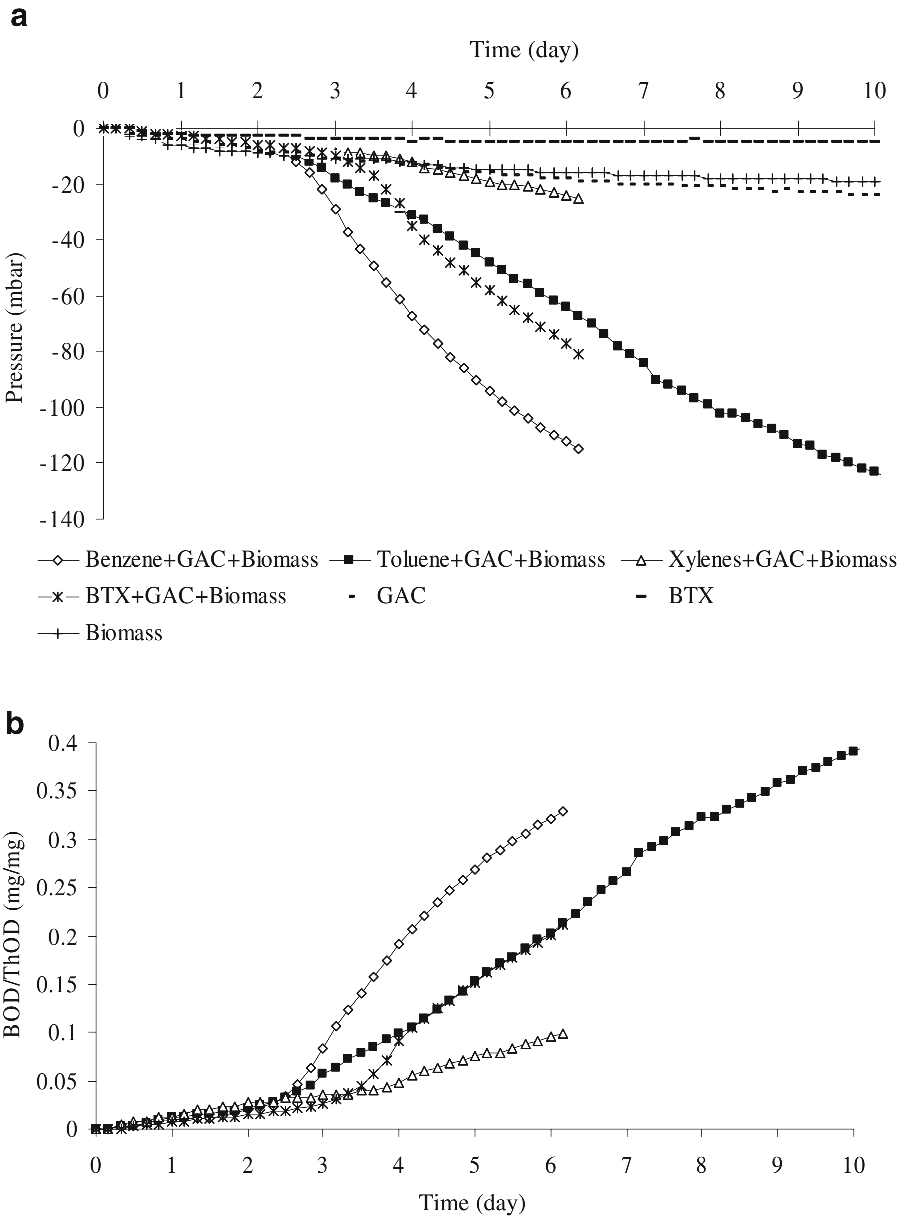


Fig. 6 Bioleaching of activated carbon after monoaromatic adsorption in OxiTop (temperature 30 °C, biomass concentration 46mg/l, contaminants/GAC 22 mg/g, GAC 2.5 g). The theoretical oxygen demand is taken as 3.076, 3.13, and 3.17 g O_2/g for benzene, toluene, and xylenes, respectively. The samples containing GAC and biomass correspond to the bioremediation experiments, whereas the others are controls (GAC, BTX, or biomass alone in water)

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