Full Length Article

Benzene and toluene removal from synthetic automotive gasoline by mono and bicomponent adsorption process

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ABSTRACT

The oil and gas industry produces derivatives with a high content of toxic components, which are already present in crude oil or can be generated during the refinery process, with a negative effect on human health. Thus, the objective of this work was to study benzene and toluene removal from synthetic gasoline, using coconut shell-based activated carbon (18×30 mesh) as adsorbent. From the results, in the monocomponent kinetics, 1.1 mmol/g of benzene and 1.8 mmol/g of toluene removal were obtained at room temperature. The influence of the initial contaminant concentration was evaluated and the adsorption kinetics equilibrium was reached up to 60 min. The maximum adsorption capacity obtained through the isotherms, for the monocomponent system was 2.05 mmol/g for benzene and 2.04 mmol/g for toluene; on the other hand, in the bicomponent system, the adsorption capacity for toluene (1.05 mmol/g) was higher than that of benzene (0.8 mmol/g) due to polarity and molar mass. In addition, for the bicomponent adsorption system, it was observed that the presence of two components reduced adsorption when compared to the monocomponent system. Thus, this process proved to be appropriate for benzene and toluene removal from automotive gasoline.

1. Introduction

Automotive gasoline is one of the major petroleum products, with continuous consumption increase. Gasoline is a complex mixture of volatile and flammable hydrocarbons, which naturally contains benzene, toluene, and xylene-BTX [1]. In this way, BTX is an important component present in the exhaust gases of cars, causing major adverse effects on the heart, lungs and the brain [2]. According to WHO [3] among the pollutants, benzene has been associated with a range of acute and long-term adverse health, and due to the liposoluble characteristic, is rapidly absorbed in the respiratory system, and about 50% of the total absorbed can be stored in fat tissues, such as the central nervous system [4]. Though respiratory and cardiovascular effects of these emissions are well identified, psychological and neurobiological complications of prolonged exposure to vehicle emissions remain unknown [2]. Thus, the development of technologies to reduce the amount of these compounds is necessary.

Adsorption is a separation process in which the components of the fluid phase (liquid or gas) are transferred to the solid surface (adsorbent) by mass transfer [5,6]. The adsorption process is a spontaneous phenomenon, which indicates that Gibb's free energy must be negative ($\Delta G < 0$) and the reduction of the system disorder, when the molecule is adsorbed, leads to an entropy decrease ($\Delta S < 0$) [7].

Thus, chemical, physical and biological methods have been used to remove organic components as benzene and toluene from aqueous effluents. In this sense, activated carbon is by far the most common adsorbent used in wastewater treatment, since, during adsorption, the pollutant is removed by accumulation at the interface between the activated carbon (absorbent) and the liquid phase [6–12]. Activated charcoal has been considered a promising technology for the control of toxic pollutants and recovery of chemicals, and can be manufactured from the carbonaceous material, peat, wood, or nutshells (i.e., coconut) [13]. The manufacturing process consists of two phases, carbonization, and activation. [13–15].

Under this scenario, this work contributes to the literature in the field of adsorption of toxic compounds from automotive gasoline. Then, with the main goal to reduce benzene and toluene contents, a synthetic automotive gasoline was used, and the adsorption capacity of the coconut shell-based activated carbon as adsorbent was studied.

2. Material and methods

2.1. Material

Isooctane (2,2,4-trimethylpentane, Macron Fine Chemicals, 99.8%, 114.3 g/mol). Benzene (Sigma Aldrich, 99.9%) and toluene (Sigma Aldrich, 99.9%) were used as adsorbates. In addition, sodium hydroxide (NaOH, Chromate, 98%), hydrochloric acid (HCl, Labsynth, 38%), sodium chloride (NaCl, Vetec, 99%), and ethanol (Lafan, 99.5, molar mass 46.1 g/mol) were used. For the gas chromatographic analysis, 1,2,3,4-tetrahydronaphthalene (Fluka, 98.5%, 132.2 g/mol) was used as the internal standard. The activated carbon (ACC adsorbent) with specifications 0.9–0.5 mm, 18x30 mesh, moisture content 0.85% (0.17%), volatile material 25.5% (0.06%), ash content 6.77% (0.31%), surface area 758 m^2/g, volume of pores 0.4 cm^3/g, and mean pore diameter 21 Å, obtained from coconut shell used as adsorbent, was donated by Carbomafra S.A.

2.2. Adsorbent preparation and characterization

Initially, the ACC adsorbent was washed 5 times with distilled water and then kept 24 h in the water, the process was repeated three times, and then the adsorbent was dried at 105 °C for 24 h. The pH and adsorbent zero point charge (pzc) was performed at pH range from 2.5 to 11 prepared using 0.01 M NaCl and 0.1 M HCl solution, 0.1 g of ACC adsorbent was kept on an orbital shaker (150 rpm) at room temperature for 24 h. The textural analyses were performed using BET methods (Brunauer, Emmett, and Teller) and BJH (Barrett, Joyner, and Halenda) in order to evaluate the surface area, pore volume and mean diameter pore. Finally, in order to obtain information about the topology and morphology of the adsorbent Scanning Electron Microscope (SEM) analysis was performed.

2.3. Study of adsorbent concentration

The influence of adsorbent concentration was evaluated at a concentration range from 10 to 200 g/L. The experiment was carried out in a monocomponent system for benzene and toluene at 113 mmol/L and 376 mmol/L, respectively using isooctane as solvent. The adsorption capacity at equilibrium (qe) was determined in duplicate (n = 2), as described by Hackbarth et al. (2014) and Luz et al. at 23 ± 2 °C, 110 rpm, pH 6.3 for 24 h.

2.4. Kinetic and adsorption isotherms

The adsorption kinetics was evaluated using 40 g/L of the adsorbent, two benzene concentrations (113 mmol/L and 68 mmol/L in isooctane), and three toluene concentrations (376 mmol/L, 188 mmol/L, and 56 mmol/L in isooctane). The adsorption kinetics were performed in a batch mode (erlenmeyer 125 mL), in an orbital shaker at 110 rpm, pH 6.30, 23 ± 2 °C for 24 h. In order to evaluate the contaminant removal, samples were collected periodically and analyzed by gas chromatography. For the bicomponent assay, a stock solution at 113 mmol/L benzene and 376 mmol/L of toluene in isooctane (commercial gasoline contents) was initially prepared. In order to determine the highest affinity to the ACC adsorbent, the system was evaluated under same initial concentrations of benzene and toluene (113 mmol/L).

The adsorption isotherms (Table 1) were performed in a batch mode (erlenmeyer 125 mL), in an orbital shaker at 180 rpm, pH 6.30, 23 ± 2 °C, 40 g/L with equilibrium time defined in the kinetic study. In all mono and bicomponent assays, samples were analyzed by CG in triplicate (n = 3) at the initial time (C0), before contact with the adsorbent, and at the equilibrium time (Ce). The removed contaminant per gram of adsorbent was calculated by mass conservation balance for batch mode (Eq. (1)) [6,16].

Table 1

Initial concentrations of benzene and toluene used in the monocomponent and bicomponent adsorption isotherm.

Monocomponent system		Bicomponent system		
Benzene C_0 (mmol/L)	Toluene C_0 (mmol/L)	C_0 (mmol/L)	Benzene:toluene C_0 (% v/v)	
0	0	0	0	0
113	47	56	0.5	0.6
135	94	113	1.0	1.2
158	141	169	1.5	1.8
180	188	225	2.0	2.4
203	235	282	2.5	3.0
281	282	338	3.0	3.6
338	329	394	3.5	4.2
394	376	450	4.0	4.8
450	422	–	–	–

$$q_t = \frac{V}{W}(C_0 - C_t) \tag{1}$$

where q_t is the amount of contaminant adsorbed at time t (mmol/g adsorbent), V is the solution volume (L), W is the dry adsorbent (g), C_0 is the initial concentration of adsorbate in the liquid phase (mmol/L), and C_t is the adsorbate concentration in the liquid phase at time t (mmol/L).

The obtained results for the monocomponent assay after adsorption time (t, min) was fitted to the pseudo-first order Eq. (2) and pseudo-second order (Eq. (3)) models [16,17].

$$q_t = q_e[1 - exp(-k_{1,ads}t)] \tag{2}$$

where q_e is equilibrium adsorption capacity (mmol/g de adsorbent), $k_{1,ads}$ constant of the pseudo-first order model (1/min).

$$q_t = \frac{q_e^2 k_{2,ads} t}{1 + k_{2,ads} q_e t} \tag{3}$$

where $k_{2,ads}$ is pseudo-second order constant (1/min).

The experimental results of the equilibrium assays were fitted to Langmuir (Eq. (4)), Freundlich (Eq. (5)), and Langmuir-Freundlich (Eq. (6)) models as shown in Fig. 5. The isotherm parameters are shown in Table 3.

$$q_e = \frac{q_L K_L C_e}{1 + K_L C_e} \tag{4}$$

where q_L is the maximum adsorption capacity (mmol/g), K_L is the constant related to the adsorbent affinity to the adsorbate (L/mmol), and C_e is the adsorbate concentration in the liquid phase in the equilibrium (mmol/L).

$$q_e = K_F(C_e)^{(\frac{1}{n})} \tag{5}$$

where K_F is the indicator of adsorption capacity (mmol$^{1-1/n}$L$^{1/n}$/g) and n is the Freundlich empirical parameter.

$$q_e = \frac{q_{LF} K_{LF}(C_e)^{(\frac{1}{n})}}{1 + K_{LF}(C_e)^{(\frac{1}{n})}} \tag{6}$$

where q_{LF} is the maximum adsorption capacity (mmol/g) and K_{LF} is the Langmuir-Freundlich constant.

The isotherm parameters, correlation coefficient (R^2), and benzene and toluene (RMSE) for the benzene and toluene were obtained by MatLab® software. The adsorption constants were obtained by non-linear regression analysis for each model as listed in Table 3 with the average percentage error. The RMSE was calculated by Eq. (7). The best-fitting models were identified based on the values of correlation coefficient and the best correlations are those with the highest values of R^2 lowest values for RMSE.