



# Simultaneous adsorption of selected VOCs in the gas environment by low-cost adsorbent from *Ricinus communis*

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## Abstract

Benzene, toluene, ethylbenzene, and xylenes are commonly known as (BTEX) and include volatile organic compounds (VOCs) in ambient air. Exposure to some BTEX has been associated with health risks. This study aimed to reduce BTEX on the environment and human health dramatically. This research targeted decreasing the BTEX in an air environment by producing high surface area activated carbon (KA-AC) under optimized synthesis conditions from *Ricinus communis* as lignocellulosic waste using ZnCl<sub>2</sub> solution, respectively. The influence of several activation parameters was investigated on the surface area, such as impregnation ratio, carbonization time, and carbonization temperature. The KA5-AC prepared under optimized conditions showed BET surface area and total pore volume of 1225 m<sup>2</sup>/g, and 0.72 cm<sup>3</sup>/g, respectively. The optimized synthesis conditions were as follows: 0.1, 0.5, 1, 2, and 5 M impregnation ratio, 450–950 °C carbonization temperature, and 100 min carbonization time. The characteristics of the optimized KA-AC were analyzed using nitrogen adsorption–desorption isotherm, scanning electron microscopy, and pore structural analysis. The results confirmed that the VOCs adsorption on KA-AC followed a monolayer adsorption isotherm over a homogeneous adsorbent surface. It showed the removal efficiency of benzene, toluene, ethylbenzene, and m, p-xylene ( $R^2 =$  from 0.991 to 0.997). Moreover, the KA-AC exhibited good performance without considerable loss of efficacy throughout the experiments. Accordingly, it is concluded that developing low-cost activated carbon to use BTEX vapor adsorption research could be practical and developments to overcome for utilization in air pollution control.

**Keywords** Air pollution control · Carbonaceous material · Gas-phase · Lignocellulosic material · VOCs

## 1 Introduction

Many definitions of volatile organic compounds (VOCs) from major human activities and naturally occurring emissions in urban areas constitute air pollution [1, 2]. The VOCs have released any carbon compound from various sources under different conditions which boiling points are between 50 and 260 °C [3–6]. Although the number of VOCs is very high, in recent years, due to their carcinogenic and non-carcinogenic properties, they have been the subject of interest and at the beginning of trend research [7, 8]. They form secondary pollutants such as Ozone (O<sub>3</sub>) and proxy acetyl nitrate (PAN) after they create various photochemical

reactions depending on the conditions of the environment [9–11]. Toxic hydrocarbons such as benzene, toluene, ethylbenzene, meta (m), ortho (o), and para (p)-xylene are defined as BTEX in VOCs [12–14]. They are carcinogenic substances according to their amount and existing conditions [15, 16].

The ratio of toluene and benzene gas (T/B) is used as the pollutant index of BTEX gases [17–19]. Benzene is the most dangerous and is defined as a Group 1 carcinogen, ethylbenzene has occurred potential carcinogenic risk in Group 2B, toluene and xylene are defined as Group 3 by the International Agency for Research on Cancer (IARC) [20]. As a result of exposure to BTEX, first irritation of the skin, eyes, and nose, followed by drowsiness, severe headache, and seizures, are observed [21]. In addition, it is known that it causes neurological disorders and damage, negativities in the reproductive system, damage to the respiratory tract, and various types of cancer at advanced levels [22, 23]. However, there is no information about where

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these pollutants are released into the environment. Their sources have been determined according to the excess concentrations in the studies which is a high amount of each volatile has been released in many areas such as gas stations [24, 25], photocopy centers [26–28], restaurant kitchens and foods [29, 30], beauty salons [31, 32], heating system [33], small scale industries [34], indoor tobacco-related [35], automotive [36], paint places [37], solid waste storage facilities [38], wastewater treatment facilities [39], and some biogenic source [40]. BTEX gases formed due to the release of chemicals used and secondary pollutants created due to their reactions have been observed in several places. However, excessive amounts of BTEX have been found in indoor air, especially with periodic and insufficient ventilation. They could not reach a high concentration in open areas because ambient air quickly dispersed them [41–43].

In the Council directive, which is in force for the evaluation and management of air quality, there is an obligation to reduce BTEX gases as well as other pollutants [44–46]. In this context, various removal methods and even recovery studies have been applied in closed areas or industries where it is impossible to ventilate or periodically open windows [47, 48]. The need to purify industrial gases is a fundamental problem for human health in the environment [49, 50]. Biological methods used in studies conducted in this context (biofiltration, bioscrubbers, biotrickling filtration, membrane bioreactors), thermal oxidation, catalytic oxidation, catalytic reverse flow reactor, plasma methods, condensation, membrane techniques, absorption, and adsorption (especially carbon-based adsorbents) [51–55]. Although these methods have advantages and disadvantages, they have obtained favorable results in BTEX removal. Considering the cost-performance and application relationship, adsorption and carbon-based adsorbents, which are preferred in environmental engineering, come to the fore. With the adsorbents with the high surface area used in the adsorption method, the removal efficiency reached 90% on average in the laboratory environment. Due to the many advantages of this method, although it is widely preferred as a BTEX filter, the search for more economical and practical approaches has accelerated on an industrial scale [56–58].

The aim of this study is the efficient production of carbon-based adsorbent to be used to remove BTEX gases, which are common in indoor spaces. It is planned to examine the behavior of BTEX gases, which are intended to be released in different concentration ranges and under other conditions. In this context, it is aimed to play an active role in reducing the adsorbent cost of *Ricinus communis*, which is used to produce activated carbon found as waste in nature. Furthermore, obtaining high porosity and efficiency with the chemical activation process is foreseen to improve the pore structure of the produced activated carbon.

## 2 Materials and methods

### 2.1 Materials and chemical reagents

*Ricinus communis* (*Rc*) was collected from the local forest around Kastamonu, Türkiye. Zinc chloride (% assay,  $ZnCl_2$ ) was purchased from Merck, Germany. All other chemicals were used in analytical grade and obtained from Sigma–Aldrich.

### 2.2 Preparation of adsorbent

Raw materials were washed with distilled water to remove undesired surface compounds such as phenolic groups soluble in water. They were dried in an oven at 55 °C for 48 h. The dried lignocellulosic precursor was ground in a grinder and sieved to the desired size of 300 mesh. It used a sieve of different sizes, ensuring that the particles were classified according to their sizes. The preferred particle size was chosen to be < 75 mesh size so that it was not too small to avoid increased loss in the process. For the chemical activation process, samples were impregnated with activating agents at an impregnation ratio of 0.1, 0.5, 1, 2, and 5 M. 8 g of *Rc* powder was mixed with  $ZnCl_2$  solutions (25% distilled water and 75% stock), respectively. According to previous studies, all mixture was logged for 120 min [59]. The activating process was prepared in a muffle furnace at 450, 550, 650, 750, 850, and 950 °C for 100 min. After the carbonization, the obtained several carbons were cooled overnight. The final step was washed several times with boiling distilled water to remove any acid or base (to neutral pH) and dried. Afterward, the outcome carbons are labeled as KA-AC and stored in a desiccator for standby during BTEX adsorption experiments.

### 2.3 Adsorption studies

All adsorption experiments were performed in triplicate using a batch system at 25 °C until 60 min. The initial concentration of benzene, toluene, ethylbenzene, m,p-xylene, and o-xylene (as BTEX mixture) was used in a stock solution of 1000 µg/L for removal studies. An effort was made to increase the adsorption capacity by changing the initial gas concentration, contact time, and temperature at the main point of the adsorption experiments. The initial concentrations for adsorption were chosen to obtain levels in natural indoor air. When equilibrium attains, the concentrations of each compound in the batch reactor were determined using US EPA Method TO-17. TENAX tubes were collected for each sample and analyzed TD-GC/MS (Thermal Desorber, Markes Unity)—(Gas chromatography, Thermo Scientific

Trace 1300)/(Mass detector, Thermo Scientific ISQ QD) and capillary column (TG-624; 30.0 m × 0.25 mm × 1.4 μm). Temperature programming was maintained from 65 to 170 °C with a constant rise of 5 °C/min, and further, the temperature was increased by 10 °C/min up to 220 °C and again held isothermal at 220 °C for 5 min. Mass spectra were taken at 70 eV; interface temperature at 230 °C, and ion source temperature at 150 °C. Interpretation of the mass spectrum of GC–MS was made using the National Institute Standard and Technology (NIST) database having more than 62,000 patterns. Equilibrium studies were carried out to determine the adsorption behavior with 0.3 g KA-ACs. A blank sample without any KA-ACs was tested as a control. The removal of BTEX % and adsorbed amount of BTEX at equilibrium were determined by following Eqs. 1 and 2, respectively.

$$\text{Removal} = [(C_0 - C_e)/C_0] \times 100, \quad (1)$$

where  $C_0$  ( $\mu\text{g}/\text{m}^3$ ) is the initial concentration of benzene, toluene, ethylbenzene, m,p-xylene, and o-xylene, while  $C_e$  ( $\mu\text{g}/\text{m}^3$ ) is the equilibrium concentration of benzene, toluene, ethylbenzene, m,p-xylene, and o-xylene, where  $q_e$  is the equilibrium adsorbate concentration in the solid phase ( $\mu\text{g}/\text{g}$ ),  $V$  is the solution volume (L),  $m$  is the adsorbent mass ( $\mu\text{g}/\text{m}^3$ ), and  $C_0$  and  $C_e$  are the initial and equilibrium adsorbate concentrations in the liquid phase ( $\mu$ ), respectively.

$$q_e = (C_0 - C_e) \frac{V}{W}. \quad (2)$$

### 3 Results and discussion

#### 3.1 Optimal pore diameters

The physicochemical properties investigated surface functionality of both lignocellulosic biomass and KA-ACs. The surface area and porosity were compared to reveal discrepancies after activating process in Table 1. The significant change in the KA-ACs was determined with SEM images. Furthermore, the pore structure accompanied the  $\text{N}_2$  adsorption–desorption at 77 K in the pore fractions (micro, meso, macro size), and type I isotherms were shown by micropore structure with the Barrett–Joyner–Halenda (BJH) equation from desorption curves [60].

The elemental analysis of adsorbents is listed in Table 2. The carbon content of KA-AC increased obviously from 62.35% to 79.87% with different chemicals. It is seen that  $\text{ZnCl}_2$  was used to obtain high carbon to enrich. The produced activated carbon content with carbon, which is the main target of the experiment. KA5-AC's nitrogen content was 0.47% due to nitrogenous compounds clinging to the

pores. Oxygen content is higher than other elements due to the formation of groups such as hydroxyl and carboxyl.

Meanwhile, other elements were detected in structures where undesired compounds might occur and replaced by several responsible groups. The surface properties show the maximum concentration of  $\text{ZnCl}_2$  measured in BET surface area were 258  $\text{m}^2/\text{g}$  with 0.1 M at 850 °C, 337  $\text{m}^2/\text{g}$  with 0.5 M at 750 °C, 611  $\text{m}^2/\text{g}$  with 1 M at 850 °C, 1033  $\text{m}^2/\text{g}$  with 2 M at 850 °C, and 1225  $\text{m}^2/\text{g}$  with 5 M at 850 °C. The maximum value of all impregnation ratios was determined at 850 °C in the BET surface area.

The SEM images of samples shown in Fig. 1 show the large porosity and structure destroyed by the  $\text{ZnCl}_2$ . Previous studies reported that the corrosive effect of chemicals on pore structure could be similar to this investigation [61–63].

The development in the morphology of the structure has been revealed, which can be considered almost at the mint level. It has been observed that the design variations result from the activation chemical used in each of them. Maneerung et al. [64] investigated wood chips as feedstock for preparing activated carbon. They used physical activation ( $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) at 700–900 °C under  $\text{N}_2$  atmosphere. Carbon content was found at 84.5% due to the activating duration being fixed at 3 h. Compared with other adsorbents, it was observed that the carbon structure increased and expanded as the activation time grew. Similar to this study, Ioannidou et al. [65] used agricultural materials including olive kernels, corn cobs, soya stalks, and rapeseed stalks to produce activated carbon. They found several surface areas ranging from 490 to 650  $\text{m}^2/\text{g}$  and performed SEM analyses by JEOL JSM-840A. The morphological characteristics of samples were examined; lignin structure is seen to dominate, such as numerous pores on its surface and cross-interconnected pores spongy. Generally, the heterogeneous features in constructing of materials collected from nature are very similar to other materials [66–68].

#### 3.2 Removal efficiency

The experimental setup carried out the equilibrium adsorption for the steady-state conditions, without adsorbate and including KA-ACs. Experiments were applied to the adsorption mechanism and the best data fitting parameters. The values of the initial concentrations (5, 20, 50, 200, 500, 800, and 1000  $\mu\text{g}/\text{m}^3$ ) for each compound of adsorption equilibrium were chosen to be close to its presence in real indoor air in the balance and to determine the type of behavior of adsorption process. The adsorption isotherm, empirical equality, supposes that the sorption reaction occurs on heterogeneous surfaces and that the number of sites is non-constant [69, 70] (Fig. 2).

The removal efficiency of BTEX mixture vapor obtained a minimum value of 51.69% with KA0.1-AC, while the

**Table 1** Production of adsorbents and their surface areas

Thermal activation temperature °C	Chemical activation agent concentration	BET surface area (m <sup>2</sup> /g)	R <sup>2</sup>	V <sub>Total</sub> (cm <sup>3</sup> /g)	V <sub>Meso</sub> (cm <sup>3</sup> /g)	V <sub>Micro</sub> (cm <sup>3</sup> /g)
450	0.1 M	29	0.881	0.12	0.09	0.03
550		83	0.914	0.16	0.11	0.05
650		181	0.959	0.26	0.17	0.09
750		227	0.966	0.33	0.19	0.14
850		258	0.970	0.39	0.24	0.15
950	0.5 M	221	0.958	0.29	0.20	0.09
450		37	0.901	0.14	0.08	0.06
550		88	0.924	0.19	0.11	0.08
650		198	0.932	0.31	0.19	0.12
750		337	0.950	0.39	0.24	0.15
850	1 M	268	0.964	0.47	0.29	0.18
950		306	0.958	0.31	0.17	0.14
450		43	0.903	0.19	0.11	0.08
550		91	0.911	0.29	0.16	0.13
650		312	0.923	0.33	0.19	0.14
750	2 M	596	0.955	0.43	0.24	0.19
850		611	0.969	0.53	0.32	0.21
950		588	0.962	0.48	0.27	0.21
450		103	0.898	0.22	0.14	0.08
550		286	0.906	0.35	0.22	0.13
650	5 M	443	0.957	0.53	0.39	0.14
750		894	0.977	0.64	0.44	0.20
850		1033	0.989	0.73	0.52	0.21
950		991	0.987	0.68	0.37	0.31
450		225	0.906	0.25	0.14	0.11
550		556	0.919	0.36	0.23	0.13
650		891	0.958	0.53	0.35	0.18
750		1183	0.989	0.73	0.44	0.29
850		1225	0.999	0.72	0.49	0.23
950		981	0.977	0.41	0.30	0.11

**Table 2** Elemental analysis (wt %) of *Rc* and adsorbents

Samples	ID	C	O	Zn	Cl	Si	K	N	Others
<i>Ricinus communis</i> biomass	<i>Rc</i>	51.37	38.99	–	–	0.18	2.12	0.88	6.46
0.1 M ZnCl <sub>2</sub> at 850 °C	KA0.1-AC	62.35	31.18	1.87	1.37	0.16	–	–	3.07
0.5 M ZnCl <sub>2</sub> at 750 °C	KA0.5-AC	67.71	24.83	1.08	1.35	1.43	–	–	3.60
1 M ZnCl <sub>2</sub> at 850 °C	KA1-AC	79.87	17.93	1.09	0.05	0.63	–	–	0.43
2 M ZnCl <sub>2</sub> at 850 °C	KA2-AC	78.04	19.01	0.87	0.41	0.38	–	0.50	0.79
5 M ZnCl <sub>2</sub> at 850 °C	KA5-AC	77.72	18.09	0.99	0.71	0.52	–	0.47	1.50

maximum value was acquired as 94.13% with KA5-AC. It was more successful at the end of all the experiments. Figure 3 demonstrates the adsorption capacity (μg/g) of KA5-AC according to several contact time until 5 min/h in BTEX mixture vapor. It was analyzed that the adsorptive capacity increased rapidly for the first time. Still, the adsorptive capacity decreased significantly after the 35th minute and was stable after the 40th minute. It has been

determined that the adsorption capacity of the studies with activated carbons decreases as the initial concentration is kept constant and increased by some scholars [71–73]. Gebreegziabher et al. [74] endeavored to remove NH<sub>3</sub> from indoor air with a low-cost adsorbent derived from corncob. The high surface area was found as 1618.703 m<sup>2</sup>/g and 65% of removal succeeded at 2400 ppm. In the studies, the

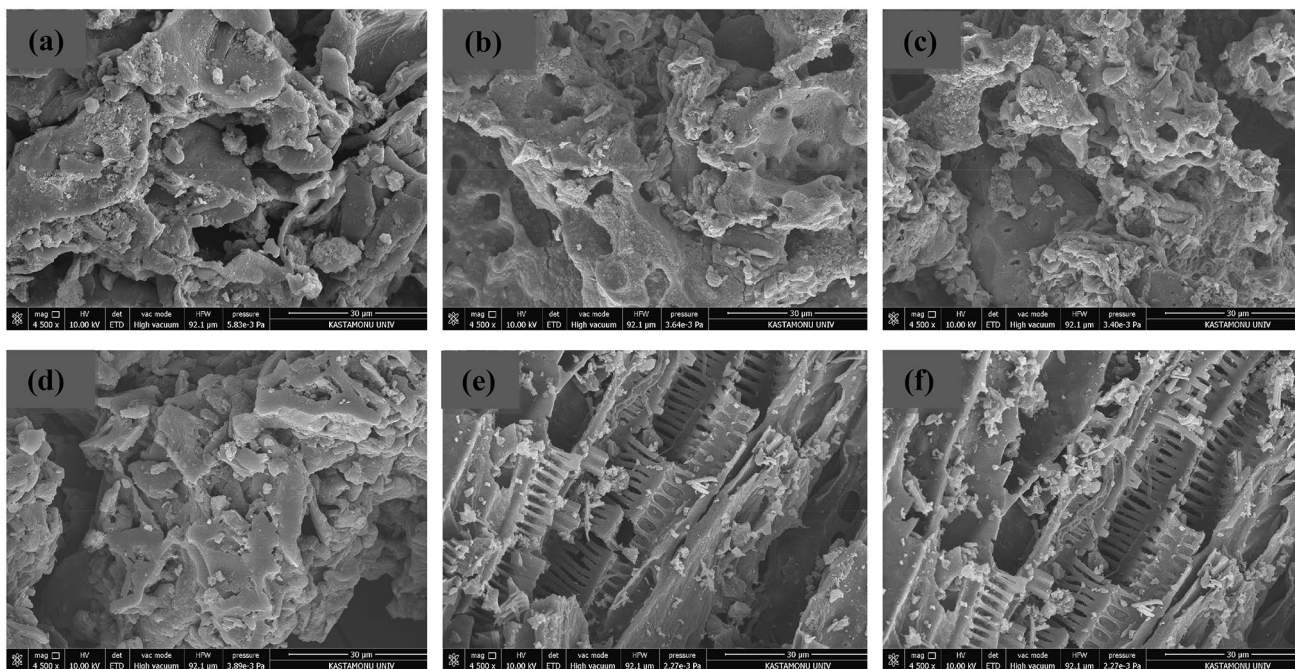
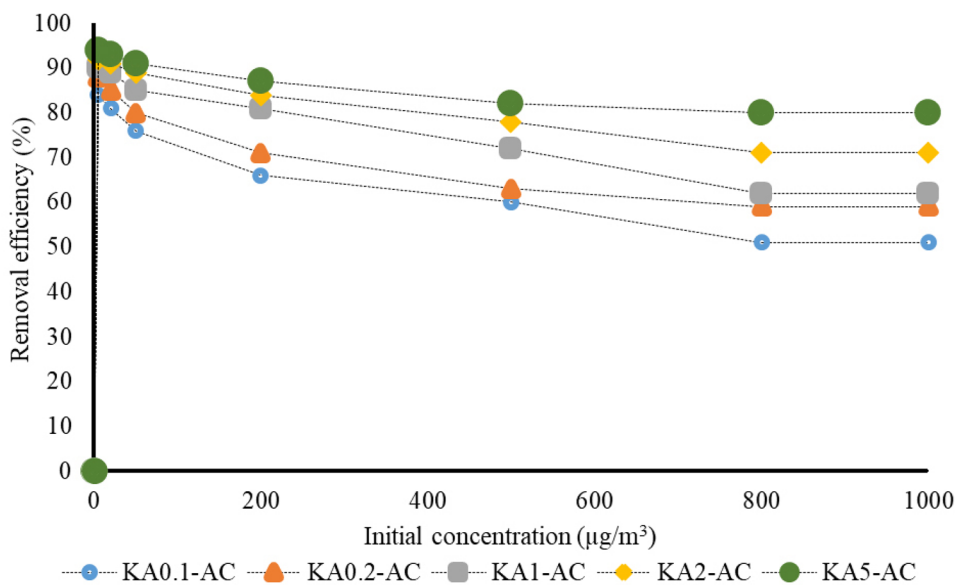


Fig. 1 The SEM images of adsorbents at 30 nm a *Ricinus communis* biomass, b KA0.1-AC, c KA0.5-AC, d KA1-AC, e KA2-AC, f KA5-AC

Fig. 2 The performance of selected adsorbents for the BTEX mixture in equilibrium

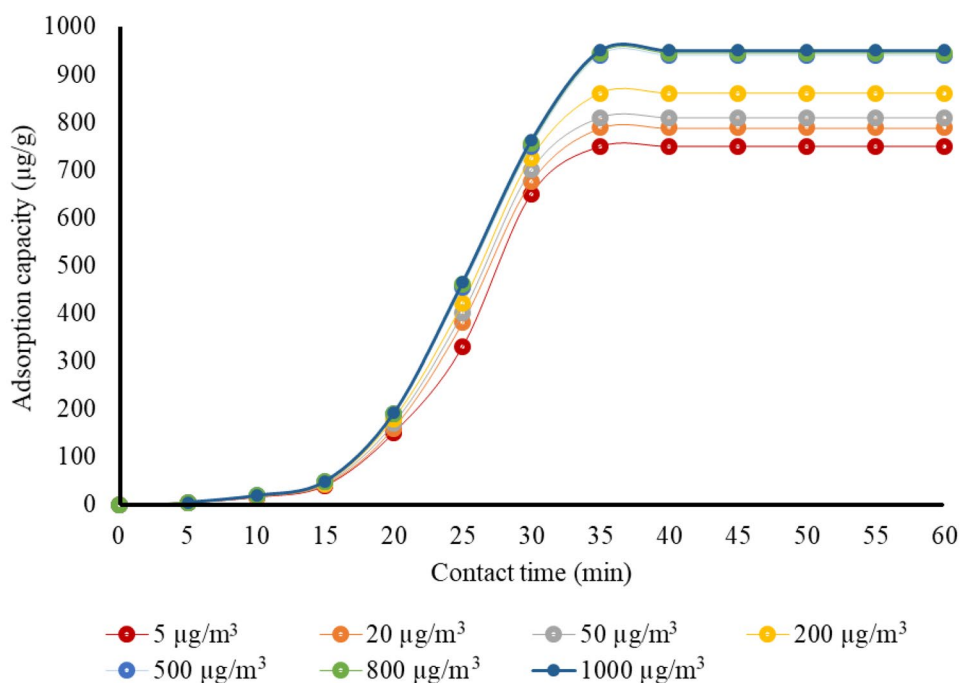


removal efficiency at high initial concentration values is lower than the lower initial concentration efficiency [75].

Several research studies studied the simultaneous removal of VOCs to eliminate from gas environment [76, 77]. However, adsorption is the most effective way of using activated carbon for VOCs removal. Liu et al. [78] prepared activated carbon from *Sargassum* and *Enteromorpha* with ZnCl<sub>2</sub> solution. The study targeted to the removal of gaseous Hg<sup>0</sup> at 80 °C, 120 °C and 160 °C. The adsorption results show that Hg<sup>0</sup> removal efficiency ranged from 74.1 to 92.8%. The

efficiency change here varied according to the morphological characteristics of the adsorbents. Due to the differentiation of the physicochemical properties of the adsorbents produced within the scope of the literature studies, differences were noted in the yields in the areas where they are used in adsorption experiments by studies [79–81]. Ma et al. [82] aimed to research the removal of VOCs (selected benzene, toluene, and chlorobenzene) from coal-fired power plants by commercially activated carbon. Contrary to our study, the adsorption temperature of 120 °C and VOCs concentration

**Fig. 3** The BTEX mixture adsorption capacity for KA5-AC



of 40–50 mg/m<sup>3</sup> were chosen for experiments. In addition, their equilibrium adsorption capacities were detected between 12.3 and 52.7 mg/g higher than in this work.

## 4 Conclusion

In summary, KA-ACs were prepared successfully from the *Ricinus communis* biomass as a novel adsorbent, agricultural waste and abundantly available in nature for BTEX in an air environment. BTEX adsorption has been deemed to be an efficient and economical method. Differences examined the BTEX adsorption process in the reaction of various activating chemicals, impregnated ratio, initial BTEX concentrations and contact time. The physical and chemical characteristics of KA-AC and *Ricinus communis* biomass were also analyzed for a better adsorbent. The vapor BTEX mixture found that monolayer surface adsorption as the maximum value was 951 µg/g. The sustainability and reusability of the KA5-ACs were established as more than 64% BTEX mixture adsorption efficiency was maintained after three successive regeneration cycles. The overall findings indicate that KA5-AC with a low-cost and high surface area of about 1225 m<sup>2</sup>/g suggests the effectiveness of removing BTEX gases and successful operation with single-component sorption systems into the ambient air. Finally, it was concluded that KA5-AC could be utilized as an effective, sustainable material that avoids many VOCs and can be easily used for future work in large-scale carbon-based other VOCs removal.

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**Data availability** The data will be provided by corresponding author under reasonable requests.

## Declarations

**Conflict of interest** The author declares no competing interests.

**Ethical approval** Not applicable.

**Consent to publish** Not applicable.

**Consent to participate** Not applicable.

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