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Study on Granular Activated Carbon Adsorption of Volatile Organic Compounds (VOCS) From Aqueous Solution

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Abstract – The most volatile organic compounds contaminating ground water and agricultural waste waters are chlorinated hydrocarbons and aromatic substances. It's better to recover the dissolved compounds in the water to resolve the issue. The equilibrium adsorption was studied in order to determine the capacity for recovery with volatile organic water compounds of granular activated carbon (GAC). This research focuses on the adsorption of dichloromethane in a commercial GAC as a conventional chlorinated organic volatile compound, and toluene as an aromatic organic fluid compound representative. Together with toluene in 293, 303 and 313 K and dichloromethane in 298, 303 and 313 K inside the solubility spectrum, the two volatile organic compounds on GAC were assessed at 3 separate temperatures. GAC adsorption was 4 and 0,2 mol/Kg-1 respectively, with a combined adsorption capacity of dichloromethane and toluene. The collected experimental results were correlated to many models of isothermal adsorption. At all three temperatures the Langmuir models were modified to characterize the GAC adsorbing dichloromethane while the adsorptions of toluene to GAC were well-defined at all three temperatures by the Langmuir-BET hybrid model. Thermodynamic equation of Clausius–Clapeyron showing that the adsorption mechanism for both substances is endothermic was determined as well.

Keywords – Granular Activated Carbon, Volatile Organic Compounds, Aqueous Solution

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INTRODUCTION

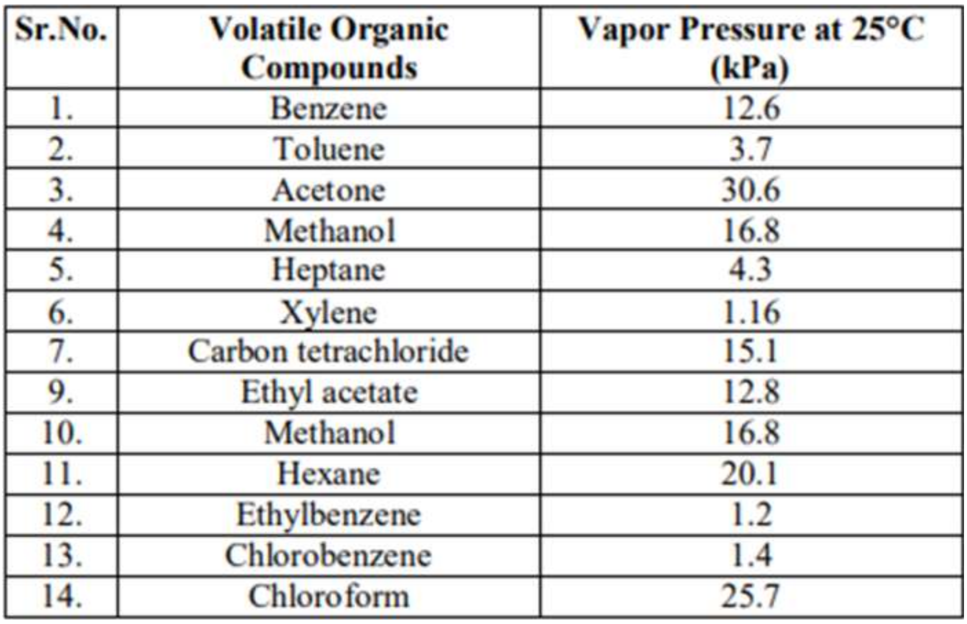
Most volatile organically compounds (VOCs) present a serious challenge to human health and to the climate, both poisonous, mutagenic and carcinogenic. The constant growth in VOC applications and the strict rules governing their usage produces an increasing and lasting need to reduce VOC pollution. The pollution of VOCs may either be anthropogenic or naturally occurring pollutants. The continued industrial advances have recently led to a substantial rise in anthropogenic VOC pollution. In China, for example, the volume of VOCs produced by manufacturing operations has risen by 8.5% since 1980 on average per annum; more growth is from 1.15 to 13.35 Tg by 2010. (Zhang et al. 2017).

VOCs are extracted more from human activities, including manufacturing operations, building, indoor production and transport (Massolo et al. 2010). The petrochemical sector has, Yen and Horng (2009), listed benzene, toluene, xylene, propene, isobutene butane, alcohol, ketones, chlorinated substances and polycyclic aromatic carbons as the most popular VOC. VOC is the primary industrial source of VOC pollution. VOC concentration however is normally higher in close proximity to petrochemical plants compared to urban and industrial areas that can adversely affect health in close proximity.

In the current research, two main VOC toxins in water have studied the equilibrium adsorption of dichloromethane and toluene. The experimental data were associated at three distinct temperatures for various adsorption isothermic models. An adsorption heat which provides an insight into the heat nature of the adsorption was also analyzed.

Volatile Organic Compounds

The volatile organic compound, abbreviated as VOC, is one of the most general terminology used in the solvents industry. VOCs are an extensive collection of organic chemicals that evaporate easily at room temperature. The vapor pressure of more than 0,5 kPa at 25°C is characterizing (Magureanu et al., 2005). VOCs are organic carbon liquid or solid (carbon, hydrogen, sulfur or nitrogen but not carbonated carbon such as in CaCO3 nor carbide as in CaC2, CO or CO2) (Chavadej et al., 2007). Some solvent thinners, grazers, cleaners, lubricants and liquid fuels are organic compounds that are volatile. Table 1.1, which contains methane, ethane, tetrachloroethane, methyl chloride, and numerous chloro hydrocarbons and perfluorocarbons, presents a short list of several typical VOC and its 25°C steam strain.



Sr.No.	Volatile Organic Compounds	Vapor Pressure at 25°C (kPa)
1.	Benzene	12.6
2.	Toluene	3.7
3.	Acetone	30.6
4.	Methanol	16.8
5.	Heptane	4.3
6.	Xylene	1.16
7.	Carbon tetrachloride	15.1
9.	Ethyl acetate	12.8
10.	Methanol	16.8
11.	Hexane	20.1
12.	Ethylbenzene	1.2
13.	Chlorobenzene	1.4
14.	Chloroform	25.7

Impact of VOC on Health and Environment

Both main and secondary adverse effects on soil air quality and human wellbeing have to do with VOC emissions. VOCs have an immediate health impact of irritation, irritation of the nose, irritation of the lungs, fever, nausea, dizziness, exacerbation of asthma, etc. The lifelong health consequences of VOCs are cancer, liver injury, renal damage, damage to the central nervous system, etc. Chemical solvents can induce intermittent symptoms at low to moderate concentrations in the environment, including euphoria, headache and dizziness, whereas higher amounts could contribute to anesthesia, cardiovascular, respiratory and even death. Damage to the central nervous system from long-term exposure may involve cognitive and emotional disorders and persistent encephalopathy. The toxic effects of liver and skin have been identified. The prevalence of cancer caused by VOC pollution in Indiana counties and the significant associations between VOC emissions and brain and nervous system tumors, thyroid and other endocrine systems and skin, have been studied by Boeglin et al. (2005). Kabir et al., (2010) have tested constantly at hourly intervals from the online odor detection station in Korea seven odor-volatile organic compounds including styrene, methyl ethyl ketone, isobutyl alcohol, methyl isobutyl ketone, which butyl acetate and should not be overlooked in terms of human health.

Adsorption

VOC-packed gas may travel through a packaged bed with adsorbent material on which VOCs are adsorbed. This technique allows VOCs adsorbed by a desorption procedure may be retrieved. Commercially accessible adsorbents include carbon fiber enabled, alumina, silica gel, zeolites, etc. This method is generally restricted to origins with organic compounds of more than 50 and less than roughly 200 molecular weights. It is suitable for a variety of VOCs from less than 10 ppm to less than 10,000 ppm. At a low degree of concentration, the most common way of removing VOCs is adsorption by activated charcoal. If the gross VOC concentration approaches 25 percent of LEL, the upper limit is attributed to the possible risk of explosion. For gas streams that produce particulates and/or high humidity concentrations, adsorption systems are not advised. The usage of granular packaged beds, however, is seriously impaired by high pressure decline, such as the flux of gas into the packaged media, grain attrition, channeling and gas by passage, etc. The use of low density activated carbon fiber monoliths will prevent these drawbacks (ACFMs). Furthermore, it is low weight and mechanically resistant. Adsorption beds are commonly used where the VOC-powered gas stream comprises (a) one to three or significant amount of organic compounds in low concentration, and before thermal or catalytic oxidation, these organic compounds must be pre-concentrated.

LITERATURE REVIEW

Different Types of Adsorbents Used in the VOC Adsorption

Anfruns et al. (2011) Pyrolusite sewage-sludge adsorbents prepared using two separate methods: acid washing and alkaline hydroxide activation. Dynamic adsorption/desorption tests were conducted using air streams filled with lower consents (<100ppm v/v) of the three odor episodes associated with odor episodes in wastewater treatment plants (toluene, methylketone, and limonene). Adsorption per g of alkaline active sludges is acquired up to 350, 220 and 640 mg toluene, methylketone and limonene. Signified that large proportions of the pre-adsorbed VOC were irreversibly absorbed, desorption tests under comparable circumstances (293 K, 250 ml min-1 air with 20 percent relative humidity). It has also been shown to be comparable to highly poreous products, like commercial acidic composites, by means of a quick acid washing of the pyrolyzed buckets.

Singh et al. (2012) Recognized carbon fiber adsorption as one of the feasible regenerative control methods for separation and reuse of VOCs. The hexane and benzene adsorption conduct on the active carbon cloth in one part and a mixing method was studied. The information was applied to the isotherm’s adsorption by Langmuir and Freundlich. In addition to benzene, adsorption of n-hexane was observed to be higher. In the benzene-hexane blend too the activated carbon fabric performed well. Studies in kinetics to establish different rate constants have been performed. The internal diffusion control adsorption of benzene and n-hexane to the activated carbon fabric has been shown to be dependent on the experiment design.

Sone et al. (2018) demonstrated strongly crystalline carbon nanotubes able to adsorb aromatic VOCs selectively. Cis- 1,1,1-trichloroethane, carbon tetrachloride, 1.2-dichloethane, benzene, tichloroethylene,12-dichloroethylene, bromodychloromethane, cis-1,3-dichloropropene, toluene, to-1,3-dricloropropene, 1,1,2-trichloroethene, tetrachloroethane, di-chloromochloroethane, m— Tetrachloroethane, tetrachloride-ethylene, m- Air contains 23 added VOCs. Air samples were passed through a cardboard lined with HC- MWCNTs to perform adsorptive testing. Both their LUMO and HOMO levels were used for the affinity of the VOC compound for MWCNTs. The molecular orbital view can be called a kind of "soft-chemical bonding" relationship between the adsorption of aromatic VOCs by HC- MWCNTs.

Hodar et al. (2017) Uses 13 monolithic aerogels for toluene adsorption, with distinct pore textures. Both static and dynamic adsorption is performed. Both meso-s and micropore were interested in toluene adsorption under stagnant conditions at 25°C and after saturation. Adsorption potential up to 1,36 cm3/g or 1180 mg/g was reached under these conditions. In all carbon aerogels, toluene adsorption was reversible and heated up fully to a temperature of 400°C. Regenerated adsorption indicated that there were no polar blocks and that the surface and micropore diameter of the samples were greater than the initial. Adsorption under 100°C complex conditions after a minimum of three successive adsorption-desorption periods was also entirely reversible. For use in thermal swing adsorption or pressure swing adsorption equipment the ability of these aerogels to reversibly adsorb toluene may be helpful.

Demeestere et al. (2013) Concentration on the adsorption on photocatalyst TiO2 Degussa P25 of gaseous trichloroethylene, toluene and chlorobenzene. To research balance partitioning, an integrated EPICS technique (Equilibrium Partitioning in Closed Systems) was applied. Equilibrium adsorption was achieved within 60 minutes of incubation for the three compounds studied. Adsorption isotherms, measured at 298.2 K temperature (T) and relative humidifies (RH) of 0.0% to 57.8%, were observed to be linear, indicates that the concentration of the analyzed monolayer surface was not covered (0.02 mg/l <= Cg <=10.45 mg/l). The effect of both relative humidity and temperature was studied systematically within the longitudinal component of the isotherm and examined from a thermodynamic perspective.

Various Mathematical Models Used in the Adsorption

Zhang et al. (2011) Carbon fixed beds found an economical and extremely efficient means of reducing pollution of chlorofluorocarbon (CFCs). In this project, the breakthrough comportment of trichlorofluoromethane (CFC-11) adsorption into a fixed bed packed with active carbon fibers was predicted in a complex model with constant wave conditions (ACFs). The analytical solution of a constant pattern wave method built on a dynamic model was based on the dynamics obtained by the adjustment of the breakthrough curves with the Langmuir Isotherm. The results on the breakthrough curves were experimentally studied by the packaged bed, gas flow rate and initial CFC-11 concentration. The findings showed that the Langmuir isothermal analysis model in deep beds (> 120 mm) was able to explain the adsorption dynamics well based on external mass transfer. By curving the model to the experimental progress results, the characteristic time of breakthrough, t0, and extra part transfer coefficient, kf, were calculated. The mass transfer from fluid to fiber surface was seen to dominate CFC-11, as CFC11 molecules do not need to go through the macroforms or mesopores to the adsorption locations in the micropores. The progress made shows that t0 decreased as the rate of gas flow and feed concentration increased, and bed height increased.

Chuang et al. (2013) To evaluate the temperature effects on adsorption and desorption of three VOCs, a BDR model was used. The BDR model was consistent with both Langmuir Isotherm and LDF (Langmuir) as 42, because CCl4 was greater ka/kd (BDR) and KL (Langmuir Isotherm) and KL (LDF with Langmuir) than C6H6 and CHCl3 and ka/kd of CCl4 and C6H6 values. Adsorption isotherms and break-through curves were predicted under different operating conditions based on these parameters. Experimental and model forecast results show that both constants of adsorption and desorption have risen while the constants of balance adsorption have fallen at high reaction temperatures.

Xiang et al. (2018) Research was conducted to compare the adsorption equilibrium and kinetic with the morphologic features of active carbons in three industrial granular activating carbons (GAC) with dibenzofuran adsorption. The isothermal and kinetic isotherms of dibenzofuran in the activated carbons have been assessed in a breakthrough test. Both test runs have been conducted on a fixed bed at 368 K process temperature. There were investigations of the impact of adsorbent morphological properties on the kinetics of the adsorption. The balance data fitted to the Langmuir isotherm were considered to be sufficient. To predict the fixed bed adsorption of dibenzofuran, an intraparticle diffusion model using the Langmuir isotherm has been created. The findings showed that the model is well suited to all breakthrough curves. Dibenzofuran's surface diffusion coefficients were measured and connections with micro porosity were noticed on the activated charcoal. In the case of certain carbons with reduced pore diameter, the dibenzofuran molecule found further kinetic limitations.

EXPERIMENTAL SETUP

Materials and methods

Toluene (mass fraction of 0.99 purity) and dichloromethane were the VOCs chosen in this analysis (mass fraction 0.998 purity). They've been bought by Merck. Apply Chem Co was purchased from Apply Chem Co, which had a size range of 1-3 mm and a bulk density of 0.4 g cm-3 (Germany).

Equilibrium experiment

GAC was dried in an oven at 115°C until the procedure started to eliminate all the gases and moisture still adsorbed. After drying for 48 hours in an oven at 388 K, the dry weight of the adsorbent was weighed. The adsorption tests were carried out by touching an adsorbent volume (3 g) of various original amounts of adsorbing solutions in an incubator shaker (weighted by an accurate balance Sartorius model GE 412, Germany of 0.01 g) at constant temperature. For each experimental phase, a temperature-controlled shaker at a constant speed of 190 rpm agitated 100 ml of toluene and dichloromethane solution of established initial concentration, (c0) and adsorbent dose (3 gr) in a 250 ml of conical bottle with a stopper. Samples were collected regularly every 15 minutes and spectrophotometer concentrations calculated so far as the balance was achieved (normally after 2 hours). Three separate temperatures have been tested to assess the temperature effect on toluene and dichloromethane adsorption.

The adsorption potential was calculated by the following equation for granular activated carbon:

$$q_e = \frac{V\left(C_0 - C_e\right)}{w}$$

When the initial concentrations of C0 and Ce are liquid phases (molm-3), V corresponds to the volume of a solution (m3) and w to the weight of dry sorbents, respectively (kg).

RESULTS AND DISCUSSION

Adsorption equilibrium

The most basic and informative information on an adsorption mechanism is adsorption isotherm. It is also essential to analyze and develop an adsorption mechanism in model prediction. The strength scattered between the adsorptive and adsorbent usually drives adsorption to a sorbent. Thus, both the sorbate and the sorbent have their adsorption potential. The adsorption of toluene and dichloromethane was found to be rapid within the first 30 minutes by studying the impact of touch time, and the removal of toluene and dichloromethane became quite sluggish afterwards. Fig. 1 shows toluene adsorption isotherms at 3 different temperatures on the GAC, that is 293,303 and 313 K; Fig. 2 shows adsorption GAC isotherms at 298, 303 and 313 K. Several isothermal equations of the equilibrium, like Langmuir, Freundlich, Redlich–Peterson and LangmuirBET, were checked to describe the data of the test isothermal sorption. The following equation should explain the Langmuir model:

$$q_e = \frac{q_m \, b \, C_e}{1 + b \, C_e}$$

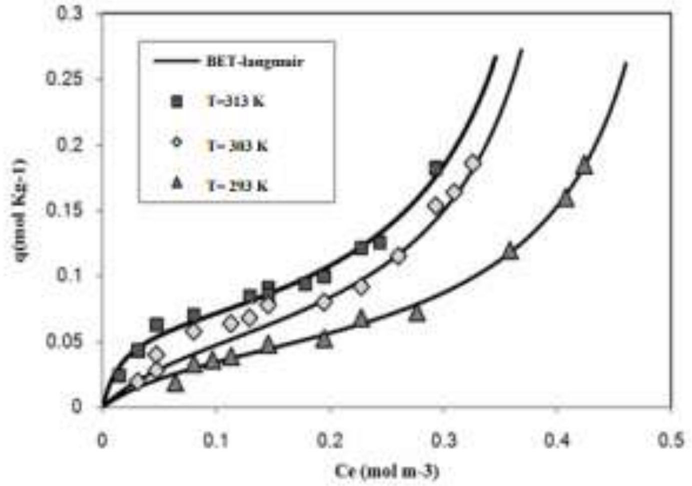


Figure 1. Toluene Adsorption to T= 298, 303, and 313 K on the GAC. Experimental information symbols, line=model

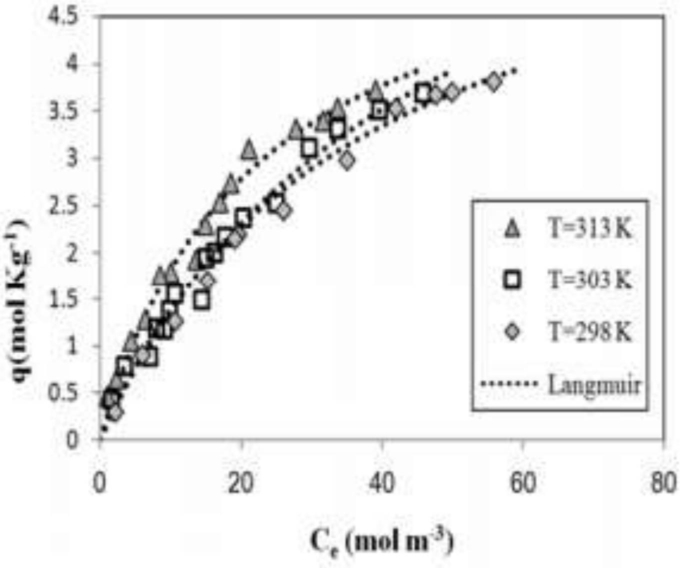


Figure 2. T= 298, 303, and 313 K Dichloromethane adsorption isotherms on GAC, symbols=an exploratory data, line=model.

Whenever Ce is the adsorbed equilibrium (molm-3), qe is the adsorbed sum per unit weight adsorbed by adsorbent (molkg-1), and Langmuir isothermal constants are qm and b, respectively, linked to the maximal adsorbed potential and adsorption power. The equation describes the Langmuir BET model:

$$q_e = \frac{q_m b C_e}{1 + b C_e} + \frac{q_m K_{BET} C_s C_e}{(C_s - C_e)\left[C_s + (K_{BET} - 1) C_s\right]}$$

Where KBET is the model parameter for the BET isotherm and Cs the compound has saturated solubility in water. A non-linear fit to the experimental information is used to recover parameters of the isothermal equation in MATLAB 7.5 (2007). When relating the test results to the balancing isotherm, the toluene-GAC data is found for Langmuir-BET hybrid isotherm, while Langmuir isotherm reflects the dichloromethane-GAC data better. Freundlich's model was not satisfactory and Redlich- Peterson's.

The isothermal model parameters for the adsorption to activated carbon (GAC) of dichloromethane and toluene at three temperatures are described in Table1.

Table 1. The conditions for dichloromethane and toluene at three separate temperatures for Langmuir and Langmuir–BET equations.

Isotherms	Constants	Dichloromethane			Toluene		
		Temperature(K)					
		298	303	313	293	303	313
Langmuir	B	7.12	7.3382	5.8510	–	–	–
	q_m	0.02166	0.0230	0.04565	–	–	–
	R^2	0.9821	0.9849	0.9881	–	–	–
Langmuir-BET	B	–	–	–	13.03	22.98	58.01
	q_m	–	–	–	0.04391	0.05631	0.06287
	K_{BET}	–	–	–	0.2444	0.4614	0.2763
	R^2				0.9956	0.9856	0.9869

Estimation of heat of adsorption

An apparent isosteric heat (never Hst,a) of the toluene and qe = 1.5 mol kg-1, 2.5 mol kg-1, 3 mol kg-1, and 3.95 mol kg-1 of the dichloromethane were computed using the Clausian-Clapeyrone ecological equation (Qe = 0.05 mol kg-1, 0.5 mol kg-1, and 0.15 mol kg-1, and 0.18 mol kg-1).

$$\frac{d \ln C_e}{dT} = \frac{-\Delta H_{st,a}}{RT^2}$$

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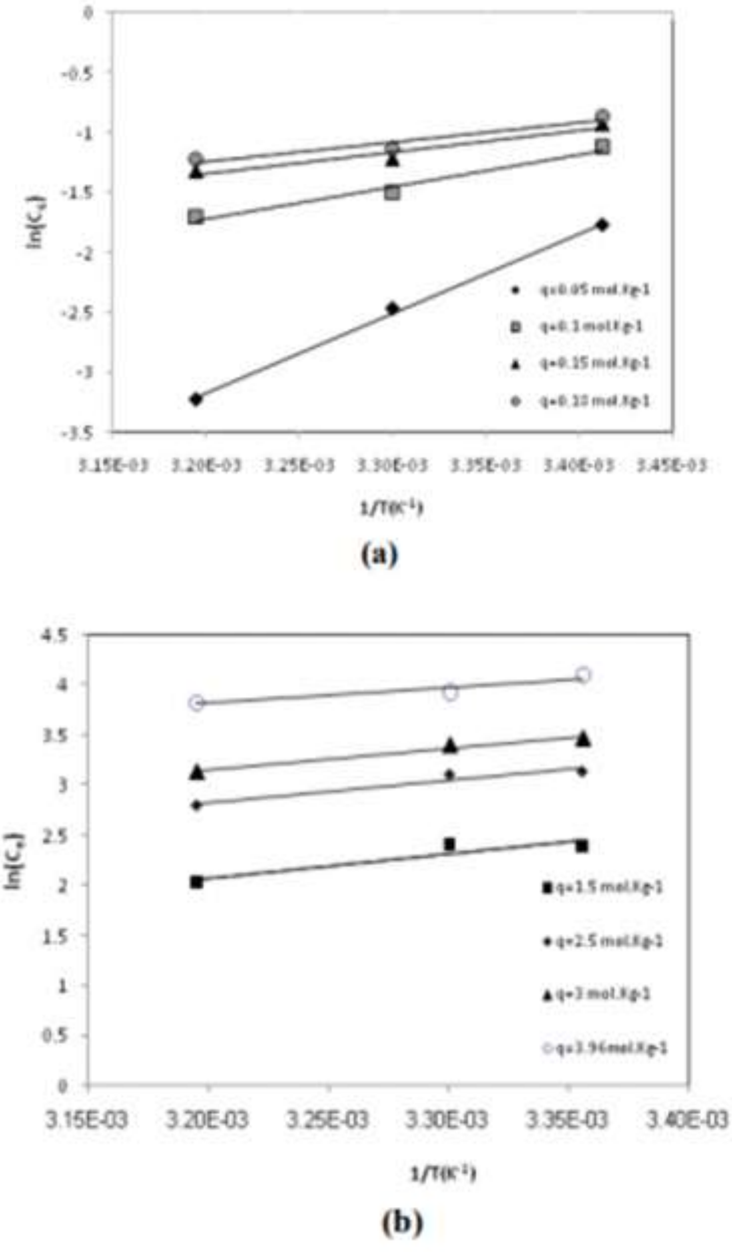
In this sense, Ce at constant qe was obtained from the toluene isothermic adsorption equation Langmuir-BET and from the dichloromethane isothermic adsorption equation at different temperatures. The lin(Ce) slope versus (1/T) plot an is determined from the slope (Fig. 3a and 3b).

Fig. 3(a) and (b) illustrate that as the balance uptake rises, a decrease. The favorable value for thermal adsorption (positive slope) proved again the endothermically mechanism of sobbing toluene and dichloromethane on GAC. Tables 2 and 3 for toluene and dichloromethane respectively demonstrate the measured heat of adsorption at various constant balance uptakes. The low values obtained for ostehst and for these components (Table 2 shows that physisorption controlled the adsorting into the adsorbent GAC for both components (maximum 6.64 KJ.mol-1).



(a)

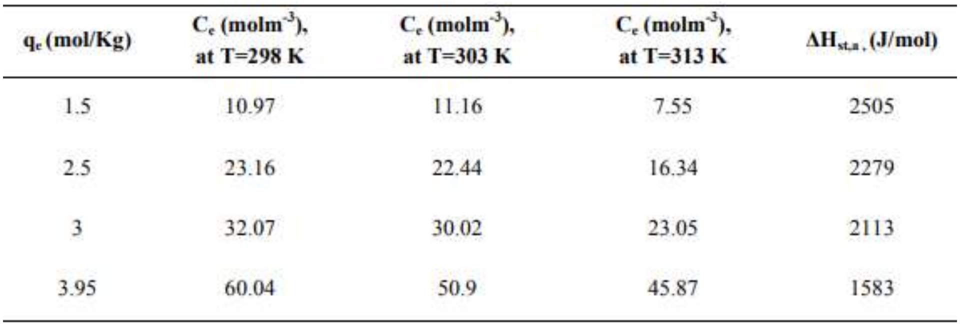
(b)

Figure 3. Isotherm for adsorption heat determination on the toluene GAC for (a). Adsorption isotherm. (b) GAC dichloromethane.

Table 2. ΔHst, a estimated at various temperatures for toluene from the slope ln(Ce) vs(1/T) and the Ce values

q_e (mol. Kg^{-1})	C_e (mol. m^{-3}), at T=293 K	C_e (mol. m^{-3}), at T=303 K	C_e (mol. m^{-3}), at T=313 K	$\Delta H_{st,a}$ (J. mol^{-1})
0.05	0.17	0.085	0.0399	6640
0.1	0.327	0.223	0.182	2694
0.15	0.396	0.295	0.266	1833
0.18	0.42	0.321	0.296	1628

Table 3. ·At various temperatures for dichloromethane /Hst from the ln(Ce) to (1/T) and Ce values measured



q_e (mol/Kg)	C_e ($molm^{-3}$), at T=298 K	C_e ($molm^{-3}$), at T=303 K	C_e ($molm^{-3}$), at T=313 K	$\Delta H_{st,a}$, (J/mol)
1.5	10.97	11.16	7.55	2505
2.5	23.16	22.44	16.34	2279
3	32.07	30.02	23.05	2113
3.95	60.04	50.9	45.87	1583

CONCLUSIONS

Dichloromethane and toluene were examined in this analysis in three separate temperatures for adsorption of the industrial carbon granular activated carbon dependent on coal. GAC adsorption balance data is equipped with Langmuir isotherm, while Langmuir-BET defines isotherms of toluene adsorption by GAC at all three temperatures in a satisfactory manner. Toluene and dichloromethane sobbing rise with an increment in temperature, indicating that all adsorbates are sorted by endothermic treatment (toluene and dichloromethane). From the ln(c) slope to (1/T) at constant qe a was measured. The positive value of the toluene and dichloromethane adsorption by GAC is an endothermic operation. But the low measured heat of adsorption for both components showed that both components are physiosorbed by the main mechanism of GAC adsorption.

REFERENCES

1. Anfruns, A., Martin, M.J. and Mones-Moran, M.A. (2011). “Removal of odourous VOCs using sludge-based adsorbents”, Chemical Engineering Journal, 166, pp. 1022-1031.

2. Singh, K.P., Mohan, D., Tandon, G.S. and Gupta, G.S.D. (2012). “Vapor-Phase adsorption of hexane and benzene on activated carbon fabric cloth: Equilibria and Rate Studies”, Industrial & Engineering Chemistry Research, 41, pp. 2480-2486.

3. Sone, H., Fugestu, B., Tsukada, T. and Endo, M. (2018). “Affinity-based elimination of aromatic VOCs by highly crystalline multi-walled carbon nanotubes”, Talanta, 74, pp. 1265-1270.

4. Hodar, F.J.M., Castilla, C.M., Marin, F.C. and Cadenas, A.F.P. (2017). “Reversible toluene adsorption on monolithic carbon aerogels”, Journal of Hazardous Materials, 148, pp. 548- 552.

5. Demeestere, K., Dewulf, J., Langenhove, H.V. and Sercu, B. (2013). “Gas-solid adsorption of selected volatile organic compounds on titanium dioxide Degussa P25”, Chemical Engineering Science, 58, pp. 2255-2267.

6. Zhang, X., Zhao, X., Hu, J., Wei, C. and Bi, H.T. (2011). “Adsorption dynamics of trichlorofluoromethane in activated carbon fiber beds”, Journal of Hazardous Materials, 186, pp. 1816-1822

7. Chuang, C.L., Chiang, P.C. and Chang, E.E. (2013). “Modeling VOCs adsorption onto activated carbon”, Chemosphere, 53, pp. 17-27.

8. Xiang, L.I., Zhong, L.I. and Lingai, L.U.O. (2018). “Adsorption kinetics of dibenzofuran in activated carbon packed bed”, Chinese Journal of Chemical Engineering, 16, pp. 203-208.

9. Zaitan, H., Bianchi, D., Achak, O. and Chafik, T. (2018). “A comparative study of the adsorption and desorption of o-xylene onto bentonite clay and alumina”, Journal of Hazardous Materials, 153, pp. 852-859.

10. Zhao, Z., Li, X. and Li, Z. (2011). “Adsorption equilibrium and kinetics of p-xylene on chromium-based metal organic framework MIL-101”, Chemical Engineering Journal, 173, pp. 150-157.

11. Sinquin, G., Petit, C., Libs, S., Hindermann, J.P. and Kiennemann A. (2010). “Catalytic destruction of chlorinated C1 volatile organic compounds (CVOCs) reactivity, oxidation and hydrolysis mechanisms”, Applied catalysis B: Environmental, 27, pp. 105-115.

12. Shim, W.G. and Kim, S.C. (2016). “Heterogeneous adsorption and catalytic oxidation of benzene, toluene and xylene over spent and chemically regenerated platinum catalyst supported on activated carbon”, Applied Surface Science, 256, pp. 5566-5571.

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