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THE EFFECT OF PROCESS FACTORS ON n-HEXANE ADSORPTION ONTO COPPER IMPREGNATED ACTIVATED CARBON

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Fixed bed adsorption dynamics of n-hexane from an air stream onto copper impregnated activated carbon were measured. The effect of air superficial velocity (0.7 cm/s and 1.7 cm/s), operation temperature (30 °C and 40 °C), and adsorbent copper loading (4.6 % and 13.8 %) on process performances was studied. Higher values of saturation adsorption capacity (0.190-0.254 g/g) were obtained at low level of air velocity and copper loading. A mathematical model including mass balance of adsorbed species and Langmuir monolayer adsorption, whose kinetic parameters were regressed based on experimental data, was adopted to predict the adsorption dynamics.

Keywords: activated carbon, adsorption, copper impregnation, Langmuir isotherm, modelling, n-hexane

1. Introduction

Volatile organic compounds (VOCs) are pollutants emitted into the atmosphere from various sources, mainly including the use of solvents in industrial, commercial, and domestic applications as well as the storage, distribution, and use of fossil fuels [1-6]. n-Hexane is a non-polar VOC which is widely used as a solvent in the manufacture of chemical, petrochemical or pharmaceutical reagents, cosmetics, food and also as a cleaning agent and degreaser in the textile, leather, and furniture industries [1,5,7]. Moreover, it is a component of crude oil, natural gas, and their derivative products [7]. Due to its high value of vapour pressure, *i.e.*, 16 kPa at 20 °C, n-hexane evaporates easily into the ambient air. Being a precursor of photochemical oxidants and also a suspected toxicant of respiratory, reproductive, and nervous system, it becomes

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harmful to health and environment at concentration levels higher than permissible exposure limits [7-9]. Accordingly, the control of its emissions in the air is a topical issue.

Adsorption is a non-denaturing, selective, energy efficient, and relatively inexpensive technique which is widely applied to remove VOCs species from air, especially at low concentration [2-5,10,11]. Moreover, because it is a regenerative technique, both adsorbate and adsorbent can be recover, leading to low energy consumptions and production costs [2,3]. Activated carbon and its derivatives [1,2,4,10-13], polymeric resins [3], zeolites [13,14], MCM-14 molecular sieves [13], metal-organic frameworks (MOF) and MOF-based composites [5] have been successfully applied for n-hexane adsorption under various operation conditions. Due to its high adsorption capacity, selectivity, versatility, accessibility, low cost, mechanical, thermal, and chemical stability, the activated carbon is the most used adsorbent for air remediation [1,2,4,10-12,15,16]. Fixed bed activated carbons are frequently employed to remove VOCs species from gas flows [3,4,12,15,16]. Adsorption kinetics and equilibrium (saturation) adsorption capacity are significantly influenced by gas flow rate, operation temperature, characteristics of adsorbate, adsorbent particle and fixed bed.

Adsorption of VOC species (*i.e.*, n-hexane and i-propanol) from air stream onto granular activated carbon (GAC) in a laboratory scale fixed bed column as well as their thermal desorption were studied in our previous works [17,18]. This paper has aimed at measuring and predicting fixed bed saturation curves of n-hexane adsorption from air stream onto copper impregnated GAC (Cu/GAC) under various operation conditions. The effect of process factors (*i.e.*, air superficial velocity, operation temperature, and mass percentage of copper in GAC) on the adsorption performances was established. Activated carbon is usually impregnated with metals in order to increase the adsorption surface and selectivity towards some organic compounds [19,20]. Moreover, electrothermal desorption of n-hexane from Cu/GAC is planned to be studied in a future research.

2. Experimental

Materials and method

n-Hexane of analytical purity was purchased from Sigma-Aldrich Chemie Gmbh (Germany). Atmospheric air was used as carrier gas for n-hexane vapour. Cu/GAC was employed as adsorbent. CELLcarb GAC with a granule mean diameter of 0.1 cm was supplied by Chemviron Carbon (Belgium). Cu/GAC was prepared in our laboratory according to a procedure reported in the related literature [21]. An amount of 100 g of GAC was added in an impregnation solution consisting of 30 g $CuSO_4{\cdot}5H_2O$, 100 g Rochelle salt ($KNaC_4H_4O_6{\cdot}4H_2O$), 30 g Na_2CO_2, and 50 g NaOH, which were sequentially dissolved in 1 L of distillated water. The impregnation was performed under the following conditions: magnetic stirring, ambient temperature, atmospheric pressure, and 11.5 pH. After 3 hours, 50 mL of 37 wt.% formaldehyde (HCHO) aqueous solution was slowly added in the GAC suspension in order to reduce Cu^{2+} to Cu^0. The suspension was further stirred for 1 hr and then filtered. The obtained copper impregnated GAC (Cu/GAC I) was washed with distillated water, further washed with 5 vol.% H_2SO_4 solution, filtered, and washed with distillated water until a neutral pH. The procedure was repeated once again, but after HCHO adding, GAC suspension was stirred for 1.5 hr (to obtain Cu/GAC II). Prior to each adsorption test, the adsorbents were dried for 12 hr at 120 °C to remove all adsorbed gases and moisture content.

Impregnated adsorbents were characterized using a Quanta 250 FEG scanning electron microscope (FEI, Netherlands). Copper mass percentages of 4.6 % (Cu/GAC I) and 13.8 % (Cu/GAC II) were obtained, respectively. The mean diameters of copper oxidized microparticle of 1.12 μm for 4.6 % Cu/GAC and 0.34 μm for 13.8 % Cu/GAC were determined [22]. The characteristics of adsorbent granule and fixed bed adsorbent used for n-hexane removal study are summarized in Tables 1 and 2.

Table 1

Physical properties of adsorbent granule

Property \ Adsorbent	4.6 % Cu/GAC	13.8 % Cu/GAC
Mean diameter, d_g (cm)	0.10	0.11
Density, ρ_g (g/cm^3)	0.85	0.88
Porosity, ε_g	0.64	0.62
Specific surface area, σ_g (cm^2/g)	1.11×10^7	1.10×10^7

Table 2

Physical properties of fixed bed adsorbent

Property \ Adsorbent	4.6 % Cu/GAC	13.8 % Cu/GAC
Height, H (cm)	22	22
Mass, m_{b0} (g)	21	22
Density, ρ_b (g/cm^3)	0.42	0.44
Void fraction, ε_b	0.21	0.20

Experimental set-up and procedure

Experimental set-up and adsorption procedure were described in our previous papers [17,18]. Dried Cu/GAC was packed into a glass adsorption column (d_c=1.7 cm internal diameter and H_c=29 cm height) set onto a digital balance. The carrier gas (air) was fed by a compressor into a bubbler containing liquid n-hexane. The mixture of air and n-hexane vapour leaving the bubbler was fed into the adsorption column and up-flowed through the fixed bed adsorbent. The amount of adsorbed n-hexane was determined from the increase in adsorption column mass. The process was stopped 10 minutes after the bed saturation. The bubbler was weighed before (m_1) and after (m_2) each adsorption test and total n-hexane mass picked-up by the carrier gas (m_{tot}) was calculated with by Eq. (1).

$$m_{tot} = m_1 - m_2 \tag{1}$$

Experimental variables

Dynamic adsorption capacity of fixed bed adsorbent for n-hexane ($q=m/m_{b0}$) *vs.* time (τ) was measured for two levels of each independent variable (factor), *i.e.*, air superficial velocity (w), operation temperature (t), and mass percentage of Cu in GAC (c_{Cu}). All experiments were carried out at atmospheric pressure.

3. Modelling of adsorption dynamics

Fixed bed dynamics of VOCs adsorption have been predicted using complex or simpler mathematical models. Typically, the complex ones include characteristic equations of mass and heat balance for the bed voids, mass and heat balance for the adsorbent particle, pressure drop across the bed, overall adsorption rate, and equilibrium relationship [4,17,18,23]. Aiming at simplifying these models, some assumptions may be adopted, *e.g.*, no axial and radial dispersion, negligible pressure drop across the bed, negligible external or/and internal diffusion resistance, instantaneous surface reaction, linear overall adsorption rate, linear equilibrium relationship, isothermal conditions [4, 15, 17, 18, 23].

A model of dynamics of n-hexane adsorption from air stream onto fixed bed Cu/GAC was developed on the basis of the following simplifying assumptions:

- axially dispersed plug flow of gas phase occurs along the column;
- radial dispersion and pressure drop across the fixed bed are negligible;
- Langmuir monolayer adsorption of n-hexane molecules takes place onto the surface of adsorbent granules and copper oxidized microparticles;
- surface reaction is the process rate-limiting step;
- the process is conducted under isothermal conditions.

Characteristic mathematical model of fixed bed adsorption of n-hexane from gas phase consists of the following system of equations and restrictions:

- equation of unsteady mass balance in bulk gas phase in the fixed bed voids, where c (g/cm^3) is n-hexane concentration in the gas phase,

D_l=(wd_g)/2 (cm^2/s) axial dispersion coefficient [23], x (cm) axial distance along the column, and τ (s) time:

$$\varepsilon_b \frac{\partial c}{\partial \tau} + w \frac{\partial c}{\partial x} - \varepsilon_b D_l \frac{\partial^2 c}{\partial x^2} + \rho_b \frac{\partial q}{\partial \tau} = 0 \qquad (2)$$

- equation of overall adsorption rate, where k_a (s^{-1}) is adsorption rate coefficient, k_d (s^{-1}) desorption rate coefficient, and Q maximum adsorption capacity of adsorbent:

$$\rho_b \frac{\partial q}{\partial \tau} = k_a \varepsilon_b \left(1 - \frac{q}{Q}\right) c - k_d \rho_b q \qquad (3)$$

- equation of estimation of mean adsorption capacity:

$$q_{mn}(\tau) = \frac{1}{H} \int_0^H q(x,\tau) dx \qquad (4)$$

- initial conditions:

$$\begin{array}{llll} \tau = 0, & 0 < x \le H, & c = 0, & q = 0 \\ \tau = 0, & x = 0, & c = c_0, & q = 0 \end{array} \qquad (5)$$

- boundary conditions:

$$\begin{array}{lll} \tau > 0, & x = 0, & \dfrac{\partial c(0,\tau)}{\partial x} = \dfrac{w}{D_l}(c_0 - c) \\ \tau > 0, & x = H, & \dfrac{\partial c(H,\tau)}{\partial x} = 0 \end{array} \qquad (6)$$

4. Results and discussion

Experimental data of fixed bed saturation dynamics

Experimental saturation curves, expressed as adsorption capacity of fixed bed adsorbent for n-hexane (q) *vs.* time (τ) at two levels of air superficial velocity (w), operation temperature (t), and copper loading (c_{Cu}) are shown in Fig. 1. Steeper saturation curves, indicating lower values of saturation time (τ_{sat}), were obtained at high levels of w, whereas higher values of saturation (equilibrium) adsorption capacity (q_{sat}) were observed at low levels of w and c_{Cu}. Moreover, for 13.8 % Cu/GAG adsorbent, values of q_{sat} and τ_{sat} were invariant with t.

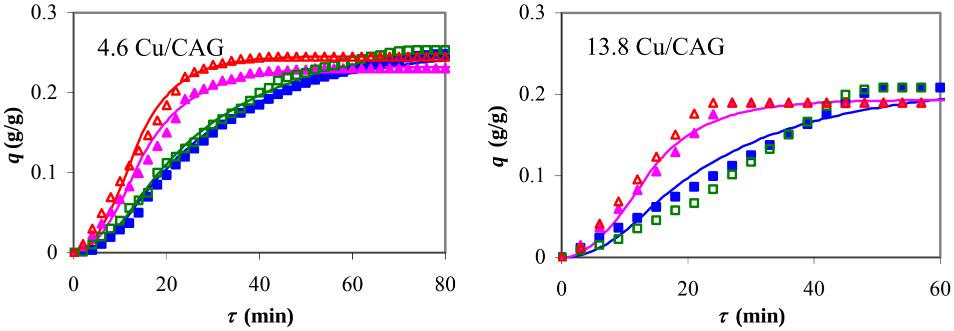

Fig. 1. Experimental (bullet) and predicted (line) saturation curves for n-hexane adsorption onto Cu/GAC: □ 0.7 cm/s, 30 °C; □ 1.7 cm/s, 30 °C; □ 0.7 cm/s, 40 °C; □ 1.7 cm/s, 40 °C

Influence of process factors on adsorption performances, evaluated in terms of q_{sat} and mean adsorption rate ($v=q_{sat}/\tau_{sat}$), is emphasized in Table 3.

Table 3

Effect of factors on adsorption parameters

Factors			**Experimental parameters**			**Calculated parameters**				
c_{Cu} (%)	w (cm/s)	t (°C)	q_{sat} (g/g)	v (g/g·hr)	$c_{sat}\times10^3$ (g/cm^3)	Q (g/g)	K_L	$k_a\times10$ (s^{-1})	$k_d\times10^4$ (s^{-1})	K_{Lc}
4.6	0.7	30	0.248	0.219	1.251	0.47	857	2.76	2.92	945
	1.7		0.231	0.365	1.082			7.07	7.48	
	0.7	40	0.254	0.224	1.291	0.39	1042	3.53	2.94	1201
	1.7		0.245	0.432	1.168			9.07	7.55	
13.8	0.7	30	0.208	0.245	0.980	0.44	886	3.89	3.88	1003
	1.7	40	0.190	0.422	0.831			10.25	10.22	

Tabulated data reveal the following aspects:

- v increases significantly (1.67-1.93 times) with w, whereas q_{sat} has a slight decrease (1.04-1.09 times);
- q_{sat} decreases (1.19-1.29 times) as c_{Cu} increases;
- for 4.6 % Cu/CAG adsorbent, q_{sat} and v increase with t (up to 1.06 times and 1.18 times, respectively), whereas for 13.8 % Cu/CAG adsorbent, the process performances are invariant with t.

Moreover, the process performances (q_{sat}=0.190-0.254 g/g and v=0.219-0.432 g/g·hr) are in a good agreement with those obtained in a previous study referring to n-hexane adsorption onto commercial Calgon CPG® LF 12x40 GAC (d_g=0.14 cm) at identical levels of w and t (q_{sat}=0.217-0.260 g/g and v=0.223-0.527 g/g·hr) [17]. Values of q_{sat} are higher or close to data reported in other studies performed under similar conditions using various fixed bed adsorbents, e.g., q_{sat}=0.067-0.126 g/g for phosphoric acid-impregnated GAC derived from almond shell wastes [12], q_{sat}=0.122-0.250 g/g for polymeric resins [3].

Modelling of adsorption equilibrium

A Langmuir monolayer adsorption of n-hexane molecules onto the adsorbent surface was selected to describe the adsorption equilibrium. Experimental values of n-hexane equilibrium (saturation) concentration in the solid (q_{sat}) and gas (c_{sat}) phase are summarized in Table 3. The values of c_{sat} were calculated using Eq. (7), where c_0 (g/cm^3) is n-hexane initial concentration in the gas phase and $\tau_{fin}=\tau_{sat}+600$ (s) final operation time.

$$c_{sat} = c_0 = \frac{m_{tot}}{w\tau_{fin}\frac{\pi d_c^{\,2}}{4}} \tag{7}$$

Experimental saturation concentrations were correlated based on a linearized form of Langmuir isotherm expressed by Eq. (8), where Q is maximum adsorption capacity of adsorbent and K_L Langmuir equilibrium constant. Aiming at estimating Q and K_L parameters, additional experiments were performed at w=1.2 cm/s. Characteristic values of Langmuir parameters, estimated with high accuracy (root mean squared errors less than 0.1) from the intercept and the slope of the straight line given by a plot of $1/q_{sat}$ *vs.* $1/c_{sat}$, are listed in Table 3.

$$\frac{1}{q_{sat}} = \frac{1}{Q} + \frac{\rho_b}{\varepsilon_b c_{sat} Q K_L} \tag{8}$$

Modelling of adsorption dynamics

The system of equations and restrictions (2)-(6) was numerically solved based on an adequate finite difference method. Values of kinetic parameters k_a and k_d were fitted by minimizing the root mean squared error, δ, defined by Eq. (9), where $q_{exp}(j)$ is experimental adsorption capacity at dimensionless time $j=\tau/\Delta\tau$ (j=0, 1, …, M), $\Delta\tau=\tau_{fin}/M$ (s) time increment, and M a positive integer number.

$$\delta(k_a,k_d)=\sqrt{\frac{\sum\limits_{j=0}^{M}\left[q_{mn}(j)-q_{\exp}(j)\right]^2}{M+1}} \tag{9}$$

Values of k_a and k_d regressed under various operation conditions are summarized in Table 3. Tabulated results highlight that both kinetic parameters increase with w (about 2.6 times) and c_{Cu} (1.10-1.45 times for k_a and 1.32-1.37 times for k_d). Moreover, for 4.6 % Cu/CAG adsorbent, k_a increases with t (about 1.3 times) and k_d is almost invariant with t, whereas for 13.8 % Cu/CAG adsorbent, both kinetic parameters are invariant with t. Characteristic values of k_{ai} and k_{di} are consistent with data obtained in other studies [15,17,18]. Table 3 contains also the values of Langmuir equilibrium constant (K_{Lc}) defined by Eq. (10) as a ratio between the rate coefficients. Values of K_{Lc} are 10-15 % larger than those of K_L estimated based on experimental equilibrium data. Experimental and predicted saturation curves under various operation conditions, which are compared in Fig. 1, are in a good agreement ($\delta < 0.1$).

$$K_{Lc}=\frac{k_a}{k_d} \tag{10}$$

5. Conclusions

Copper impregnated granular activated carbon (Cu/GAC) was used as adsorbent for removal of n-hexane from air streams. Fixed bed adsorption dynamics were measured and predicted at two levels of air superficial velocity (w=0.7, 1.7 cm/s), operation temperature (t=30, 40 °C), and mass percentage of copper in GAC (c_{Cu}=4.6, 13.8 %).

The adsorption performances, evaluated in terms of saturation adsorption capacity (q_{sat}=0.190-0.254 g/g) and mean adsorption rate (v=0.219-0.432 g/g·hr), have been consistent with data existed in the related literature. Experimental data emphasized a significant effect of c_{Cu} on q_{sat} as well as of w on v. Accordingly, values of q_{sat} were up to 29 % lower at high level of c_{Cu}, whereas those of v were up to 93 % larger at high level of w. Moreover, for 13.8 % Cu/GAG adsorbent, adsorption performances were invariant with t.

A mathematical model assuming axially dispersed plug flow of gas phase, Langmuir monolayer adsorption, surface reaction as a rate-limiting step, and isothermal conditions was developed to predict the adsorption dynamics. The model kinetic parameters, *i.e.*, adsorption rate coefficient (k_a) and desorption rate coefficient (k_d), were fitted based on experimental data. Values of Langmuir equilibrium constant calculated as a ratio between k_a and k_d were in a good agreement with those estimated based on experimental equilibrium data. The model simulated well the real conditions and could be used in applications referring to adsorption of VOCs from gas streams onto fixed bed adsorbent.

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