Isopropyl Alcohol Vapour Removal from Diluted Gaseous Stream by Adsorption: Experimental Results and Dynamic Model

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The gas phase adsorption of isopropyl alcohol (IPA) onto a commercial activated carbon at 30°C was investigated under different operating conditions. Fixed-bed experiments were performed to obtain equilibrium and kinetic data for IPA adsorption. The equilibrium data were fitted by means of the Langmuir equation and isotherm parameters were determined. A dynamic, isothermal, dilute solution adsorption model, based on the linear driving force (LDF) approximation, was developed to describe the kinetic adsorption behavior. A very good agreement between experimental and model results was found when a LDF mass-transfer-rate coefficient dependent on the gas concentration was used.

1. Introduction

Nowadays, in a context of growing attention for the environmental protection, there is an increasing need to reduce the emissions of harmful compounds both in gaseous and liquid effluents. Among them the volatile organic compounds (VOC) represent a very damaging class due to their harmful effects on human health and environment and their widespread use in many industrial processes (Debasish et al., 2004) (Nevers, 2000) Various alternatives for VOC removal are available: condensation, catalytic oxidation, thermal oxidation, membrane separation and adsorption (Khan and Ghoshal, 2000).

Adsorption on porous adsorbent (activated carbon, zeolite, silicalite, etc.) is the most extensively applied method, due to its high selectivity and capacity even at low VOC partial pressure. In particular, activated carbon, which can be produced by a wide variety of raw materials, is a good adsorbent able to remove several polar and non-polar components (Ruhl, 1993). However, its removal efficiency can be negatively affected by the competitive adsorption of different contaminants, gas relative humidity and slow mass transfer rate (Shim, 2006). Indeed, the knowledge of the adsorption equilibrium is not enough to design an efficient adsorption unit, but a dynamic model able to predict the behavior of the adsorption column is required.

In this work, adsorption of isopropyl alcohol (IPA) vapour onto activated carbon was investigated. IPA is a widely used solvent in industrial processes; it is also an important intermediate for pharmaceutical and cosmetic synthesis. Experimental tests were performed on fixed-bed adsorption column, using a conventional activated carbon as adsorbent material and breakthrough curves were analyzed to evaluate the adsorption equilibrium and kinetics. A simple fixed bed adsorption dynamic model, based on the linear driving force (LDF) approximation, is used to describe the column behavior.

2. Materials and Methods

IPA was supplied from Sigma-Aldrich with a purity of 99.5 % while the activated carbon AP4-60 of cylindrical shape, purchased from Chemviron Carbon, was used as adsorbent material. The activated carbon particle had mean length and diameter of 9 and 4 mm respectively and a specific surface area of 1000 m^2/g; in the equilibrium experiments activated carbon was crashed to reduce the particle mean size in the range of 0.7-1 mm. The gas composition was determined by means of gas-chromatographic analysis using an HP5980 gas chromatograph, equipped with a thermal conductivity detector (TCD) and a POROPAK Q 80/100 mesh packed column (SE52) of 1.83 m in length and 0.32 mm in diameter. The oven temperature was kept constant

at 220 °C, while the injector temperature and the detector temperature was set both at 250 °C. The gas chromatograph was calibrated by injecting sample (200 μL) of solutions of different known composition and determining the area associated to each peak. All the experiments were carried out in the linear response range of the detector. The experimental apparatus used to assess the adsorption of IPA (already used in a previous work (Gironi and Piemonte, 2011)) is reported in Figure 1: different mixture of IPA and dry air were realized injecting a fixed flow rate of liquid IPA via a dosing pump in an evaporation chamber, while the air flow rate, supplied by a gas cylinder, was kept constant; the evaporation chamber was kept at 90 °C to obtain the complete vaporization of the solute. The resulting mixture was sent to the adsorption column, made of a stainless steel cylinder (1.4 cm i.d., 27 cm height) and was equipped with a thermostatic jacket in order to work with a fixed column temperature of 30 °C; the adsorbent in the column was supported by a thin layer of glass wool. The outlet of the column was equipped with a six-way sampling and switching valve with a stainless steel sample loop volume (200 μL); at fixed times, usually every 2.5 min, the exhaust stream was diverted to the gas chromatograph, where its composition was determined. The gas flow rate was controlled by mean of a volumetric gas meter placed at the exit of the gas line.
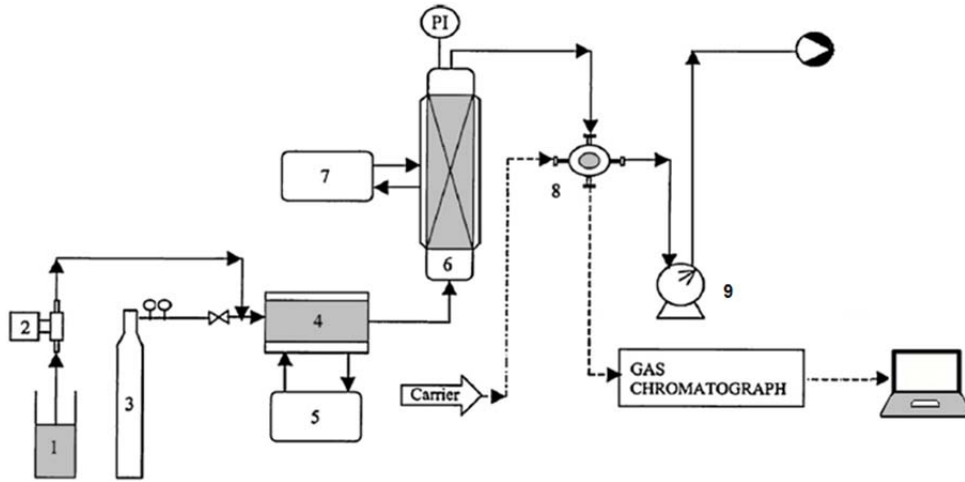

Figure 1: Experimental setup: (1) solute tank; (2) dosing pump; (3) air cylinder; (4) evaporation chamber; (5) hot thermostatic bath; (6) adsorption column; (7) cold thermostatic bath; (8) sampling and switching valve; (9) gas meter.

3. Results and discussions

3.1 Equilibrium data and correlation
The equilibrium data were obtained from breakthrough experiments at 30 °C, with a constant mass of activated carbon and a constant gas flow rate. In details, the amount of adsorbed IPA per unit mass of activated carbon is obtained by means of the solute balance equation:

$$q_{eq} = \frac{FC_0 t_B - \int_0^{t_B} FC(t)dt}{M_{ads}} \qquad (1)$$

where C_0 and $C(t)$ are the inlet and outlet solute concentration respectively, F is the volumetric gas flow rate and M_{ads} is the mass of adsorbent material used for each breakthrough experiments; in Eq(1) t_B is a time sufficient to have an IPA concentration in the outlet gas equal to the influent concentration. In order to have a sharp breakthrough curve and a well-defined t_B value –i.e. to easier assess the adsorption capacity of the bed- powdered activated carbon was used in these experiments.
Examples of breakthrough curves obtained in these experiments are reported in Figure 2a), while the equilibrium adsorption data are reported in Figure 2b).
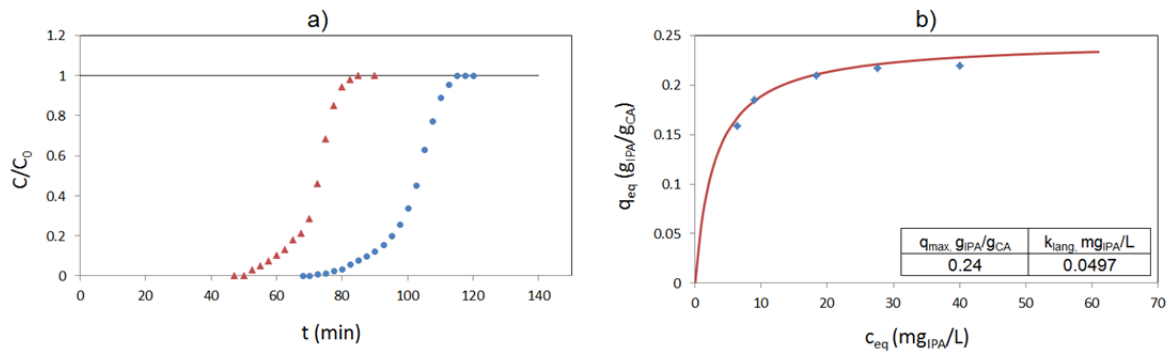
Figure 2: a) Two IPA breakthrough curves by using powered activated carbon. b) Adsorption equilibrium data and Langmuir isotherm of IPA (T=30 °C, M_{ads}=3 g, F=0.49 L/min).

The equilibrium data were correlated by means of Langmuir isotherm (Langmuir, 1918):

$$q_{eq} = q_{max} \frac{\dfrac{c_{eq}}{K_{lang}}}{1 + \dfrac{c_{eq}}{K_{lang}}} \tag{2}$$

and the isotherm parameters, q_{max} and K_{lang}, were evaluated from the fitting of the experimental data, by means of the last square method. The parameter values obtained are reported in Figure 2b), where fitted curves and experimental data are compared. The figure shows that the Langmuir isotherm gives a really satisfactory correlation of the experimental data.

Table 1: Operative conditions of IPA adsorption runs (T=30 °C, F=0.49 L/min)

	C_0 mol/m^3	M_{ads} g	Bed length m	K_{LDF} s^{-1}
A	0.397	8	11.9	2.51E-04
B	0.363	4	6.5	2.34E-04
C	0.554	4	6.1	3.21E-04
D	0.963	8	11.5	5.61E-04

3.2 Adsorption column dynamics

In order to investigate the adsorption kinetics, fixed-bed adsorption runs were performed at different inlet solute concentration and column length (see Table 1), using cylindrical pellet of activated carbon, as usually used in the industrial units. In all the experiments the outlet concentration versus time (breakthrough curves) was determined. The experimental data obtained are shown in Figure 3.
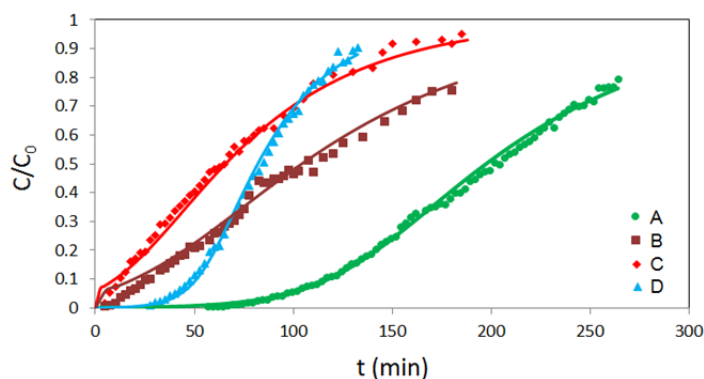

Figure 3: IPA breakthrough curves (the operating conditions for A-D curves are reported in Table 1).

Experimental data were analyzed using a dynamic mathematical model based on the hypothesis of an axially dispersed isothermal plug-flow process with constant gas flow rate; the adsorption equilibrium is described by the Langmuir equation, while the adsorption rate into an adsorbent pellet is described using the linear driving force model with a single lumped mass transfer parameter, K_{LDF} (Glueckauf and Coates, 1947) (Glueckauf, 1955). The fundamental equations of the model are shown in Table 2. The resulting set of algebraic and differential equation was solved using gPROMS software (PSE Enterprise, U. K.); while the adsorption isotherm parameters were already determined and the axial dispersion coefficient D_z was evaluated from Ruthven equation (Ruthven, 1984). The K_{LDF} parameter was considered as an adjustable parameter, determined by fitting the simulations breakthrough curves to experimental data.

Table 2: Model equations for adsorbent fixed-bed model

Solute material balance	Boundary conditions
$$\varepsilon_b \frac{\partial C}{\partial t} + (1-\varepsilon_b)\frac{\partial \overline{q}}{\partial t} = D_z \frac{\partial^2 C}{\partial z^2} - u \frac{\partial C}{\partial z}$$	$$uC\big|_{z=0^+} - D_z \frac{\partial C}{\partial z}\bigg|_{z=0^+} = uC\big|_{z=0^-} \quad \frac{\partial C}{\partial z}\bigg|_{z=L} = 0$$
Linear driving force model	Initial conditions
$$\frac{\partial \overline{q}}{\partial t} = K_{LDF}(q_{eq}(C)-\overline{q})$$	$$\begin{aligned}\overline{q} &= 0 \quad for \quad 0 \le z \le L \\ C &= 0 \quad for \quad 0 < z < L \\ C &= C_0 \quad for \quad z = 0\end{aligned}$$

In details the fitting was based on the minimization of the objective function defined as

$$\phi = \sum [C_{cal}(t,L) - C_{exp}(t,L)]^2 \tag{3}$$

where $C(t,L)$ represents the solute concentration in the gaseous effluent from the adsorption bed and the summation is over all the experimental data of each breakthrough curve. Figure 3 shows the theoretical curves obtained with the proposed model, fitting a K_{LDF} value for each curve: the figure shows that the agreement between experimental data and model results is very satisfactory for all runs. It is worth noting that the values of K_{LDF} obtained are linear function of the inlet IPA concentration C_0 as reported in Figure 4, where the results of the regression is also reported.
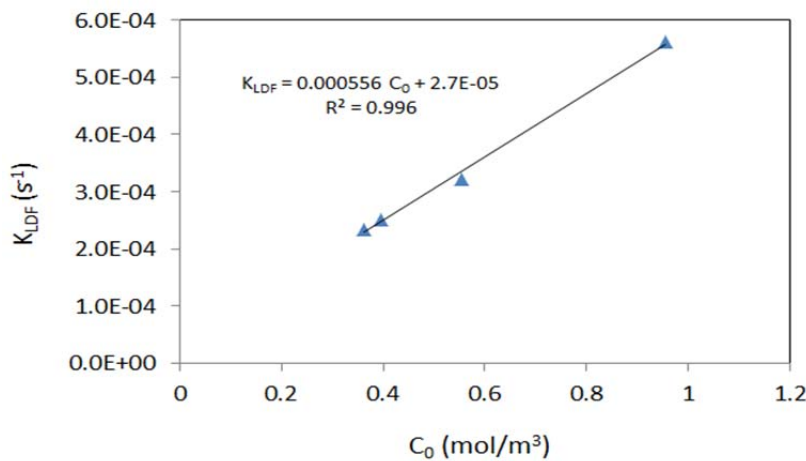

Figure 4: Mass transfer coefficient vs inlet IPA concentration for the different experimental runs

This trend agrees with the theoretical relation proposed by Farooq and Ruthven (Farooq and Ruthven, 1990) simplified to consider only the mass transfer resistance in the macropore

$$K_{LDF} = \frac{8\varepsilon_p D_p}{R_p^2 K_{eq}}$$ (4)

where ε_p is the particle void fraction, D_p is the macropore diffusivity, R_p is the particle radius and $K_{eq}=q_0/C_0$. Indeed, if the adsorption isotherm is described by Langmuir isotherm, the equilibrium constant becomes

$$K_{eq} = \frac{q_{max}}{K_{lang}} \frac{1}{1+\dfrac{C_0}{K_{lang}}}$$ (5)

and by substituting Eq(5) in Eq(4), K_{LDF} becomes

$$K_{LDF} = \frac{8\varepsilon_p D_p}{R_p^2 q_{max}} C_0 + \frac{8\varepsilon_p D_p}{R_p^2} \frac{K_{lang}}{q_{max}}$$ (6)

Eq(6) suggests a linear relation between LDF mass transfer coefficient and the inlet solute concentration, as determined in our experiments. It is also worth noting that the ratio between the slope and the intercept of the regression curve (0.0486 mol/m^3) is actually very close to the value of the Langmuir constant. This value is indicative of the goodness of the findings regarding both equilibrium and kinetic adsorption of IPA onto the activated carbon in the experimental conditions chosen in this work.

4. Conclusions

In the present work experimental and theoretical study on the adsorption process of air streams containing IPA in fixed-bed columns are reported. Breakthrough experiments on activated carbon were carried out in order to obtain information on equilibrium and kinetic conditions. A quite simple model, able to describe the dynamic behavior of the column, was developed on the linear driving force approximation to take into account the IPA adsorption ratio on the carbon pellet. A very good agreement between experimental and numerical results was found by using the LDF coefficient as an adjustable value for each experimental runs. A linear trend between KLDF values and inlet solute concentration was found; this result can be supported by theoretical considerations based on the non-linearity of the Langmuir isotherm used to describe the equilibrium data and on the hypothesis of diffusive transport in macropores as mass transfer controlling resistance. The model has been proved to be suitable to describe the adsorption column behavior in classical breakthrough tests, but it can be used also to evaluate the efficiency of an adsorption-based treatment process in more complex conditions, when gaseous effluent containing different VOCs and/or a time variable VOC content are to be treated.

Nomenclature

C	IPA gas concentration	q_{eq}	equilibrium amount adsorbed
C_{eq}	IPA equilibrium gas concentration	$\bar{q}$	average amount adsorbed
C_0	IPA feed gas concentration	q_{max}	Langmuir isotherm parameter
D_p	macropore diffusivity	R_p	particle radius
D_z	axial dispersion coefficient	t	time
K_{eq}	equilibrium constant	t_B	breakthrough time
K_{lang}	Langmuir isotherm parameter	u	superficial gas velocity
K_{LDF}	LDF mass transfer coefficient	z	axial coordinate in the bed
L	bed length	ε_b	bed void fraction
M_{ads}	mass of adsorbent	ε_p	particle void fraction

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