# Modelling of Thermal Desorption of Volatile Organic Compounds from Activated Carbon

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*Thermal desorption dynamics of isopropanol and n-hexane from a thin fixed bed of neat and copper impregnated activated carbon was measured and simulated. The influence of operation temperature (80-120 °C), adsorbate and adsorbent type on the desorption performances was experimentally studied. Final desorption efficiency was higher at larger values of operation temperature and adsorbent copper loading as well as for the adsorbate with lower molar mass (isopropanol). A model assuming unsteady heat and mass transfer into a quasi-homogeneous porous plate, whose parameters were regressed based on experimental data, was selected to predict the process dynamics. A good agreement between experimental and predicted results was obtained.*

*Keywords*: *activated carbon, modelling, thermal desorption, volatile organic compound*

Activated carbon (AC) is widely applied to remove pollutants from gaseous and liquid effluents, especially due to its high adsorption capacity, chemical, mechanical, and thermal stability [1-19]. Moreover, AC can be economically prepared from various natural carbonaceous precursors, including coal, wood, agricultural products, and wastes [2,4,5,11,20-23].

Volatile organic compounds (VOCs) are air pollutants mainly emanated from chemical, petrochemical, pharmaceutical, cosmetics, food, electronics industries as well as from the storage, distribution, and use of fossil fuels [1,5,6,17,19]. Because they are hazardous for human and environment, the control of their emissions in the indoor and outdoor air is an important issue. VOCs control techniques are destructive, including thermal, catalytic, and photocatalytic oxidation, bio-filtration, and recuperative, *e.g.*, adsorption, absorption, condensation, membrane separation [1,24,25]. The most frequently applied technique for the removal and recovery of VOCs from air is adsorption [1,14,16,17,25]. The performances of VOCs adsorption onto AC in forms of granules, powder, pellets, monolith, nanotubes, fibers, and cloth of fibers were evaluated in various researches [1,4-6, 8,11,13,14, 16,17,19].

Spent adsorbents can be deposited in landfills, incinerated or regenerated [2,16,17]. Their regeneration is an attractive option taking into account the environmental pollution and energy consumption. Moreover, a recycling of both adsorbent and adsorbate, contributing to a decrease in fresh material demand and production cost, can be achieved by regeneration. Due to its environmental, energy, and economical benefits, the regeneration process has been extensively studied [1-3,7,8,11,13-17,19,25,26]. There are four major regeneration methods which are reported in the related literature, *i.e.*, thermal, chemical, microbiological, and vacuum regeneration [16]. Thermal regeneration at temperatures of 80-300°C using steam (steaming), inert gas (TSA: thermal swing adsorption) or electric field (ESA: electrothermal swing adsorption) as regeneration agents is widely applied to recycle both adsorbent and adsorbate [1,8,11,14,16,17,19,25].

The steaming is commonly employed for recovery of VOCs which are not miscible with water. Regeneration process consists of three steps, *i.e.*, desorption, drying, and cooling. During desorption, the steam transfers heat to the adsorbent bed and the VOC molecules are desorbed. The steam-VOC mixture is further condensed and then divided into a water phase and an organic one. After desorption, the wet and hot adsorbent is dried and cooled in order to be suitable for the next adsorption step. The main drawback of steaming is energy consumption caused by the drying stage. Moreover, if the VOC species are miscible with water, a distillation of the mixture is needed.

An attractive alternative from energy point of view is TSA which implies only two steps, *i.e.*, desorption and cooling. A hot purge gas is commonly used as regeneration agent. Because it is the primary heat source, high gas flow rates are needed for desorption, resulting in a low concentration of desorbed VOC which determines a difficult condensation [1,19]. In order to eliminate this inconvenient, alternative regeneration techniques have been developed, *e.g.*, an adsorbent direct heating with electric current (ESA) or an indirect one using heating jacket, coil or tube bundles [13,14]. ESA technique, implying the bed heating by Joule effect, is unable to regenerate effectively the granular or powder adsorbents but is successfully applied for monoliths and fiber cloths [8,16,19].

A mathematical model describing the thermal desorption of VOC species from a very thin fixed bed of granular activated carbon (GAC) was developed in this paper. Isopropanol (IPA) and n-hexane (HEX) were selected as VOCs representatives. Their adsorption onto fixed bed GAC was reported in a previous study [27].

## Experimental part

### *Materials*

Neat and copper impregnated GAC was employed as adsorbent. CellCarb GAC with a granule mean diameter of about 0.1 cm was supplied by Chemviron Carbon

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Table 1
PHYSICAL PROPERTIES OF VOC SPECIES

| VOC species | Molar mass | Boiling point at 101.325 kPa | Vapour pressure at 20°C |
|---|---|---|---|
| | (g/mol) | (°C) | (kPa) |
| IPA | 60.10 | 82 | 4 |
| HEX | 86.18 | 69 | 16 |

(Belgium). Copper impregnated GAC keeping the shape and dimension of neat GAC was synthesized according to a recommended procedure [28]. The impregnated adsorbents were characterized using a Rigaku Ultima IV X-ray diffractometer (Rigaku, Germany) and a Quanta 250 FEG scanning electron microscope (FEI, Netherlands).

VOCs species consisted of isopropanol (IPA) and n-hexane (HEX) of analytical purity (Sigma Aldrich, Germany) which were used without further purification. Their physical properties are summarized in table 1.

*Experimental set-up and procedure*

Thermal desorption was performed in an Ohaus Sigma MB23 thermobalance (OHAUS, USA). A thin fixed bed consisting of $m_{b0}$ = 10 g of adsorbent saturated with VOC species was placed onto the balance tray (90 mm inner diameter). The VOC mass, $m$ (g), was estimated based on the adsorbent mass, $m_b$ (g), which was continuously measured by the thermobalance and registered by a computer. Atmospheric air was employed as carrier gas for VOC species.

*Experimental variables*

VOC concentration in the adsorbent bed, $c = m/m_{b0}$ (g/g), vs. time was measured for two VOCs species (IPA and HEX), three type of adsorbents, *i.e.*, neat GAC (0 % Cu/GAC) and copper impregnated GAC (4.6 % Cu/GAG and 13.8 % Cu/GAG), and three values of operation temperature (80, 100, and 120 °C). All experiments were carried out at atmospheric pressure.

## Modelling of VOC thermal desorption from fixed bed adsorbent

Species thermal desorption from a spent adsorbent has been simulated using more simple or complex models depending on the simplifying assumptions, equations, and restrictions considered [1,13,16,19,25,26]. A model based on unsteady heat and mass balance into a quasi-homogeneous porous plate was developed in order to describe the VOC species thermal desorption from a very thin fixed bed of adsorbent. Characteristic mathematical model consists of the following system of equations and restrictions:

-equation of unsteady mass balance, where $c_z$ (g/g) is the VOC concentration at the $z$ (m) distance in the fixed bed, $c_\infty$ (g/g) the equilibrium VOC concentration in the fixed bed, $D_{eff}$ (m$^2$/s) the effective diffusivity, $k_d$ (s$^{-1}$) the desorption reaction constant, and $\tau$ (s) the time:

$$\frac{\partial c_z}{\partial \tau} = D_{eff}\frac{\partial^2 c_z}{\partial z^2} - k_d(c_z - c_\infty) \qquad (1)$$

-equation of unsteady heat balance, where $t_z$ (°C) represents the temperature at the $z$ (m) distance in the bed, $a_{eff}$ (m$^2$/s) the thermal diffusivity, $c_s$ (J/kg K) the bed specific heat, and $\Delta H_d$ (J/kg) the VOC desorption heat:

$$\frac{\partial t_z}{\partial \tau} = a_{eff}\frac{\partial^2 t_z}{\partial z^2} - k_d(c_z - c_\infty)\frac{\Delta H_d}{c_s} \qquad (2)$$

-correlation for prediction of $c_\infty$ (g/g), where $k$ (g/g) and $n$ are constants determined based on experimental data, $c_{\infty,exp}$ (g/g), and $t_\infty$(°C) is the operation temperature:

$$c_\infty = k\left(\frac{t_\infty}{80}\right)^n \qquad (3)$$

-relationships for estimation of mean VOC concentration, $c$ (g/g), and temperature, $t$ (°C), where δ (m) is the bed width:

$$c(\tau) = \frac{1}{\delta}\int_0^\delta c_z(z,\tau)dz \qquad (4)$$

$$t(\tau) = \frac{1}{\delta}\int_0^\delta t_z(z,\tau)dz \qquad (5)$$

-initial conditions:

$$\tau = 0,\ 0 \le z \le \delta,\ t_z = t_0,\ c_z = c_0 \qquad (6)$$

-boundary conditions, where $\alpha_\delta$ (W/m$^2$ s) and $\alpha_ä$ (W/m$^2$ s) are the heat transfer coefficients at $z$ = 0 and $z$ = δ, respectively, ρ (kg/m$^3$) is the bed density, and $k_t$ (m/s) the mass transfer coefficient at $z$ = δ:

$$\tau > 0,\ z = 0,\ \alpha_0(t_{z=0} - t_\infty) = a_{eff}\rho c_s\frac{\partial t_z}{\partial z},\ \frac{\partial c_z}{\partial z} = 0 \qquad (7)$$

$$\tau > 0,\ z = \delta,\ \alpha_\delta(t_{z=\delta} - t_\infty) = a_{eff}\rho c_s\frac{\partial t_z}{\partial z},\ -D_{eff}\frac{\partial c_z}{\partial z} = k_t c_{z=\delta} \qquad (8)$$

## Results and discussions

*Adsorbent characterization*

The presence of copper oxide into the impregnated adsorbents was confirmed by XRD experiments conducted on Rigaku Ultima IV X-ray diffractometer. Copper percent mass concentrations of 4.6 and 13.8 % were determined by EDX analysis performed on Quanta 250 FEG scanning electron microscope. Mean diameter of copper oxide particle of 1.12 μm for 4.6 % Cu/GAC and 0.34 μm for 13.8 % Cu/GAC were obtained based on SEM images (fig. 1).

*Experimental data of thermal desorption dynamics*

Characteristic experimental data of desorption dynamics, *i.e.*, VOC concentration in the adsorbent bed, $c = m/m_{b0}$ (g/g), vs. time, τ (min), are illustrated in figures 2-4. Final value of desorption time, $\tau_{\infty,exp}$, equilibrium VOC concentration, $c_{\infty,exp}$, as well as final desorption efficiency (DE), $\eta_{\infty,exp}$, which was calculated using eq. (9), are summarized in table 2. Depicted and tabulated results

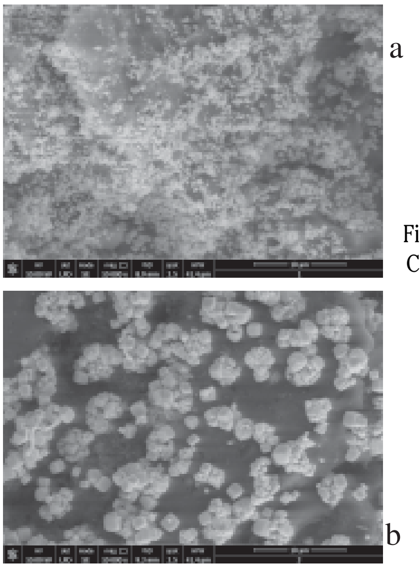

Fig.1. SEM image of 4.6 % Cu (a) and 13.8 % Cu (b) impregnated GAC

**Table 2**

EQUILIBRIUM EXPERIMENTAL DATA

| VOC species | Adsorbent type | $t_\infty$ (°C) | $\tau_{\infty,exp}$ (min) | $c_{\infty,exp}$ (g/g) | $\eta_{\infty,exp}$ (%) |
|---|---|---|---|---|---|
| HEX | 0 % Cu/GAC | 80 | 58 | 0.079 | 63 |
| | | 100 | 44 | 0.059 | 73 |
| | | 120 | 38 | 0.040 | 79 |
| | 4.6 % Cu/GAC | 80 | 46 | 0.067 | 70 |
| | | 100 | 44 | 0.050 | 74 |
| | | 120 | 44 | 0.029 | 83 |
| | 13.8 % Cu/GAC | 80 | 46 | 0.049 | 73 |
| | | 100 | 52 | 0.015 | 87 |
| | | 120 | 44 | 0.002 | 99 |
| IPA | 0 % Cu/GAC | 80 | 72 | 0.037 | 86 |
| | | 100 | 38 | 0.016 | 92 |
| | | 120 | 26 | 0.007 | 93 |
| | 4.6 % Cu/GAC | 80 | 60 | 0.031 | 86 |
| | | 100 | 34 | 0.007 | 97 |
| | | 120 | 24 | 0.001 | 99 |
| | 13.8 % Cu/GAC | 80 | 60 | 0.010 | 95 |
| | | 100 | 40 | 0.006 | 97 |
| | | 120 | 28 | 0.001 | 100 |

**Table 3**

MODEL PARAMETERS IDENTIFIED BASED ON EXPERIMENTAL DATA

| VOC species | Adsorbent type | $t_\infty$ (°C) | $D_{eff}$ ($10^{-9}$ m$^2$/s) | $k_d$ ($10^{-4}$ s$^{-1}$) | $c_\infty$ (g/g) | $k$ (g/g) | $n$ - |
|---|---|---|---|---|---|---|---|
| HEX | 0 % Cu/GAC | 80 | 2.15 | 3.25 | 0.080 | 0.080 | -1.581 |
| | | 100 | 2.20 | 3.98 | 0.056 | | |
| | | 120 | 2.50 | 5.57 | 0.042 | | |
| | 4.6 % Cu/GAC | 80 | 1.92 | 4.60 | 0.070 | 0.070 | -1.772 |
| | | 100 | 2.01 | 5.78 | 0.047 | | |
| | | 120 | 2.40 | 6.53 | 0.034 | | |
| | 13.8 % Cu/GAC | 80 | 1.99 | 3.07 | 0.049 | 0.049 | -5.592 |
| | | 100 | 2.10 | 3.54 | 0.013 | | |
| | | 120 | 2.85 | 5.38 | 0.005 | | |
| IPA | 0 % Cu/GAC | 80 | 1.40 | 2.44 | 0.036 | 0.036 | -3.852 |
| | | 100 | 2.44 | 3.84 | 0.015 | | |
| | | 120 | 2.86 | 4.76 | 0.008 | | |
| | 4.6 % Cu/GAC | 80 | 1.51 | 2.14 | 0.031 | 0.031 | -7.146 |
| | | 100 | 2.54 | 3.14 | 0.006 | | |
| | | 120 | 2.58 | 4.14 | 0.001 | | |
| | 13.8 % Cu/GAC | 80 | 2.00 | 3.20 | 0.010 | 0.01 | -3.478 |
| | | 100 | 2.39 | 4.22 | 0.005 | | |
| | | 120 | 2.83 | 5.21 | 0.002 | | |

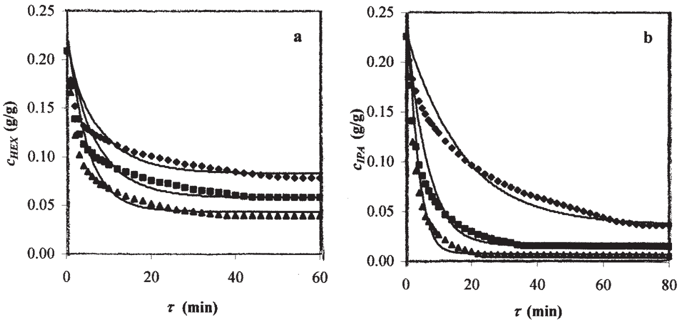

Fig. 2. Experimental (points) and predicted (lines) results of HEX (a) and IPA (b) thermal desorption from neat adsorbent at various temperatures (♦ 80 °C, ■100 °C, ▲120 °C)

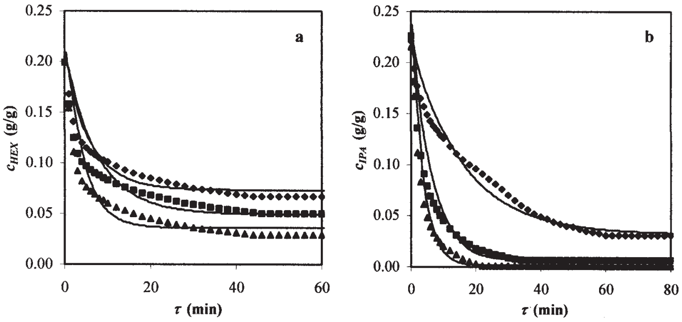

Fig. 3. Experimental (points) and predicted (lines) results of HEX (a) and IPA (b) thermal desorption from 4.6 % Cu impregnated adsorbent at various temperatures (♦ 80 °C, ■100 °C, ▲120 °C)

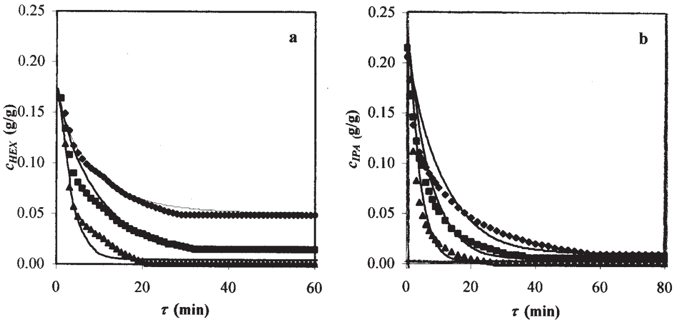

Fig. 4. Experimental (points) and predicted (lines) results of HEX (a) and IPA (b) thermal desorption from 13.8 % Cu impregnated adsorbent at various temperatures (♦ 80 °C, ■ 100 °C, ▲120 °C)

highlight that the desorption process is more rapid at higher values of operation temperature and, excepting the temperature of 80°C, for the adsorbate with lower molar mass (IPA). Moreover, values of $c_{\infty,exp}$ decreases with the temperature and copper loading as well as they are lower for IPA, whereas the DE exhibits an opposite trend.

$$\eta_{\infty,exp} = \frac{c_{0,exp} - c_{\infty,exp}}{c_{0,exp}} \times 100 \qquad (9)$$

*Predicted data of thermal desorption dynamics*

The equations and restrictions system (1)-(8) was numerically solved by an adequate finite difference method. The values of constant parameters were as follows: $a_{eff}$ = 1.5$D_{eff}$ [29], $c_s$ = 800 J/kg K [1], $k_t$ = 8 . 10$^{-3}$ m/s [26], $t_0$ = 25 °C, $\alpha_{\delta'}$ = 4 W/m$^2$s [25], $\alpha_0$ = 34 W/m$^2$s [1], δ= 0.0025 m, $\Delta H_{d,IPA}$ = 9.71 10$^5$ J/kg [13], $\Delta H_{d,HEX}$ = 8.14 x 10$^5$ J/kg [30], ρ = 630 kg/m$^3$. Characteristic values of $D_{eff}$ and $k_d$ adjustable parameters were regressed based on $c_{exp}(\tau)$ and $t_{exp}(\tau)$ experimental data, whereas those of $k$ and $n$ constants were estimated depending on $c_{\infty,exp}$. The values of $D_{eff}$, $k_d$, $k$, and $n$ as well as of $c_\infty$ calculated by correlation (3) are summarized in table 3. Tabulated data emphasize that $D_{eff}$ and $k_d$ increase with the operation temperature, irrespective of VOC species and adsorbent type, whereas $c_\infty$ decreases with the temperature and copper loading as well as its values are lower for IPA. Moreover, a good agreement between $c_{\infty,exp}$ (table 2) and $c_\infty$ is observed. Experimental and predicted desorption curves are compared in figures 2-4. Root mean squared errors less than 0.02 were obtained, consequently the simulated curves fitted well the experimental results.

## Conclusions

Thermal desorption dynamics of VOCs from a thin fixed bed of spent adsorbent was measured and simulated. Isopropanol and n-hexane were selected as VOCs representatives, whereas neat and copper impregnated activated carbon was used as adsorbent. An experimental study highlighting the influence of operation temperature (80-120 °C), adsorbate and adsorbent type on the desorption performances was conducted. Final desorption efficiency was higher for the adsorbate with lower molar mass (isopropanol) and increased with the temperature and adsorbent copper loading.

A model assuming unsteady heat and mass transfer into a quasi-homogeneous porous plate was adopted to predict the process dynamics. The effective diffusivity and desorption reaction constant were selected as adjustable model parameters and regressed based on experimental data. Adjustable parameters values increased with operation temperature. A good agreement between experimental and predicted results was obtained.

*Acknowledgments: This work was supported by the Sectoral Operational Program Human Resources Development (SOP HRD), financed from the European Social Fund and the Romanian Government under the contract number POSDRU/159/1.5/S/137390/.*

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Manuscript received: 8.10.2014