

Assessment of the multi-compound non-equilibrium dissolution behaviour of a coal tar containing PAHs and phenols into water

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Abstract

Herein, an experimental study coupled with a model in order to assess the non-equilibrium and multi-compound dissolution behaviour of a coal tar containing PAHs and phenols into water, is presented.

For this aim, two experimental studies has been carried out: (1) coal tar–water partition equilibrium and (2) dissolution dynamics of coal tar under controlled hydrodynamic conditions in percolation columns packed with glass beads.

The dissolution amount of the three target constituents (i.e. phenol, naphthalene and phenanthrene) was monitored by UV detection. The dissolution behaviour was modelled using a predictive fraction approach.

The partition coefficients have been estimated from experimental data and the obtained results show that the partition coefficient of each constituent between the aqueous phase and the tar depends on the activities of the constituent in both phases and cannot be estimated only from the solubility of the pure compound in water.

The non-equilibrium dissolution model was established, applied for the experimental conditions and validated for three target compounds adjusting the effective interfacial area between tar and water. This parameter is specific of the experimental set-up. The global behaviour of coal tar has been modelled taking into account four categories of compounds according to their water solubility and volatilities. The mass transfer parameters have been estimated using available correlations. The results of this paper indicate that a model based on component fractions can be used to assess the non-equilibrium dissolution behaviour of a coal tar.

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1. Introduction

Non-aqueous phase liquids (NAPLs) are among the most common groundwater contaminants. Due to their low solubilities in water, NAPLs travel through the subsurface as separate liquid phases, resulting complex multi-phase clean-up problems [1–3]. Once this type of hazardous chemical is released into the subsurface environment, its low solubility (and still lower effective solubility within a multi-component mixture) renders it a long-term source of groundwater pollution [4–7].

Many studies have shown that the dissolution of NAPL phases in underground water is a non-equilibrium process [7–10], the main physico-chemical phenomena determining the dissolution behaviour being: (i) the partition of organic compounds between the NAPL and aqueous phases; (ii) a limited mass transfer rate between the phases in contact; (iii) the convective transport with the water flow. The importance of evaluating and remediating contaminated soils and aquifers still raises many questions linked to each of these three dissolution steps and at different scales [3,4]. One of the recent research goals is the understanding and modelling of the long time dissolution behaviour of real multi-component NAPL [3,4,11–13]. This objective needs elucidation of some behavioural aspects as: (i) how to account for NAPL compositional changes over time and for the NAPL–water equilibria evolution; (ii) what is the role

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Nomenclature

a_s	specific interfacial area (m^2/m^3 aqueous phase)
a_{sb}	maximum specific interfacial area of glass beds (m^2/m^3 aqueous phase)
A	total UV absorbency of solution (dimensionless)
A_0	total UV absorbency of solution at dissolution equilibrium (dimensionless)
A_k	specific UV absorbency of compounds (mol^{-1})
c_c	concentration of a compound in coal tar (mol/m^3)
c_w	concentration of a compound in water (mol/m^3)
d	glass beds diameter (m)
D_c	diffusion coefficient in coal tar (m^2/s)
D_w	diffusion coefficient in water (m^2/s)
f^0	standard state fugacity coefficient
f_s	effective interfacial area fraction
h	thickness of coal tar phase (m)
k_t	mass transfer coefficient (m/s)
K	equilibrium partition coefficient (m^3 coal tar/ m^3 water)
K_t	mass transfer rate coefficient (s^{-1})
K_x	equilibrium partition coefficient
M_c	molar masse of coal tar (g/mol)
M_w	molar masse of water (g/mol)
n	number of stirred reactors in series
Q	volumetric flow rate of water (m^3/s)
Re	Reynolds number
s_w	solubility in water of a pure compound (mol/m^3)
S_b	total surface area of glass beds (m)
Sc	Schmidt number
Sh	Sherwood number
t	time (s)
t_{dif}	characteristic diffusion time in coal tar (s)
t_{ext}	characteristic external mass transfer time in interfacial film layer (s)
t_m	characteristic convection time of water (s)
u	Darcy velocity (m/s)
v	pore velocity of aqueous phase (m/s)
V_c	coal tar volume (m^3)
V_o	aqueous phase volume (m^3)
V_p	total pore volume in column (m^3)
V_t	total volume of the column (m^3)
x	molar fraction in water
y	molar fraction in coal tar
z	space coordinate (m)

Greek letters

δ	thickness of interfacial aqueous film (m)
ε	volume fraction of water in column
γ_c	activity coefficient of a compound in coal tar
γ_w	activity coefficient of a compound in water
μ_w	dynamic viscosity of water ($\text{kg}/\text{m s}$)
ρ_c	coal tar density (kg/m^3)
ρ_w	water density (kg/m^3)
τ	coal tar saturation in column

Subscripts

i	compound
j	reactor number
h	at the interface

Superscripts

eq	equilibrium
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of non-ideal behaviour of the NAPL mixtures; and (iii) how the mass transfer process and their parameters change in time.

Coal tar is composed of hundreds of aromatic compounds (including PAH) exhibiting a wide range of chemical, physical and toxicological properties. For that reason it is difficult to characterize and predict its behaviour. The theory of the pseudo-compound, which considers that the dissolution of coal tar in water can be described as that of a single compound according to Raoult's law was often used [14,15], as well as the lumped metrics approach, which considers parameters such as total petroleum hydrocarbons to specify the remediation goals. These pseudo-compound or lumped parameter approaches are unable to taken into account the variation in NAPL composition and then the variation of risk over time. On the other hand, numerical models were developed for the simulation of the individual behaviour of each compound in a NAPL by coupling equilibrium, transport laws and material balances [1,9,11–14,16,17]. The importance of the non-ideal behaviour of the both aqueous and NAPL phases and it's modelling is argued [9,13,16,18]. Because the most of the published models consider time invariant transfer parameters, the long-term behaviour prediction needs to consider the ageing of the NAPL–water interfacial film as done in [9,16,17]. Validation of such elaborated models needs experimental data obtained by detailed analysis procedures, which are time-consuming and costly.

As an alternative, an approach based on component fractions was proposed by [19]. The aromatic compounds were grouped following their normal boiling points and each group was described by an estimated solubility, volatility, etc. and was assimilated with an hypothetic compound. Simulations were done in the case of two hypothetic PAH NAPLs without experimental validation.

The aim of this study is the experimental investigation and the modelling of the release of organic compounds (PAH and phenols) contained in a coal tar in contact with water. The scenario considered here is the dissolution of the coal tar dispersed at the surface of soil particles. A simple monitoring method was used in order to quantify the dissolved amount and then the dissolution behaviour was modelled using a predictive compound fractions approach. The main stages of the present study are:

- (1) Determination of the phase partition equilibrium.
- (2) Non-equilibrium dissolution assays in percolation column under different operating conditions; the coal tar was dispersed as thin layer coating on an inert granular support.

Three target pollutants as well as the tar global release were monitored.

- (3) Modelling of the non-equilibrium dissolution process taking into account the phase partition equilibrium, the tar–water mass transfer and the dispersive convection; adjustment of the ill characterized interphase surface area.
- (4) Using the model and a fraction approach to assess the tar global dissolution behaviour.

2. Materials and methods

2.1. Coal tar

The coal tar used comes from a reservoir situated on an old manufactured-gas plant site in France. It contains monocyclic aromatic hydrocarbons, phenols, polycyclic aromatic hydrocarbons and an important residue fraction (no identified compounds). The concentrations of the identified compounds are listed in Table 1. The very low content of benzene, toluene and xylene (BTX) are characteristic of quite an old coal tar. The HAP amount is characteristic of coal tar as reported by EPRI [20]. The density is 1.3 and the average molecular weight is 200 g/mol as estimated from the concentration and molecular weight of the identified constituents. For the residue an average molecular weight of 300 g/mol was assumed [20].

Among the compounds identified and quantified, three compounds were monitored as target pollutants: phenol, naphthalene and phenanthrene. The two PAH chosen are the most abundant in the studied coal tar and have different volatilities. Phenol was taken into account because more hydrosoluble. The fraction named here “residue” was considered insoluble. The BTX

were not detected in the aqueous eluates because of their low content and volatilization during the sample’s preparation. The global dissolution of the coal tar was monitored by UV detection.

2.2. Partition equilibrium study

The study of partition equilibrium of the organic compounds between coal tar and water was carried out at controlled temperature (25 °C) in glass flasks with teflon-lined caps. Precisely known masses of the two phases (50 g of coal tar and 200 g of water) were brought into contact with vigorous shaking for 10 days. The aqueous solution separated by centrifugation was analyzed by high performance liquid chromatography (HPLC). The equilibrium time was established by a previous study: essays were performed for different durations until depletion of the dissolved amount.

2.3. Dissolution in percolation column

The study of the dissolution dynamics of the coal tar in a porous medium crossed by a water flow requires assays in percolation columns where the hydrodynamic conditions can be controlled. For these assays, a glass column of internal diameter 26 mm was packed with glass beads 2 or 4 mm in diameter to a height of 78 mm. The total volume of the packed bed was maintained constant ($V_t = 41.4 \text{ cm}^3$) as well as the total volume of the pores ($V_p = 17 \text{ cm}^3$).

Before packing the columns, the coal tar was dispersed using a fine metallic spatula in the inert macroporous medium formed by the glass beads. This porous medium was doped with different coal tar contents. Glass beads were chosen as inert non-porous matrix in order to: (1) maintain a precise granulometric distribution; (2) avoid possible adsorption of compounds dissolved in water; (3) ensure good reproducibility of assays; and (4) facilitate the repartition of coal tar in thin layers on the bead’s surface. A water upflow was used to ensure total saturation of the column (Fig. 1).

The constituents of coal tar dissolved in water were detected using a UV on-line detector at the column output. The global absorbance of the aqueous solution at 254 nm was monitored against time.

Numerous assays were carried out with various combinations of flow rates, coal tar saturation levels and glass bead diameters (Table 2, the parameters modified in the various assays are in

Table 1
Composition of the studied coal tar

Compound	Concentration c g/kg	Molar fraction y
Monocyclic aromatic		
Benzene	0.920	0.0037
Hydrocarbons		
Toluene	1.200	0.0040
Ethyl-benzene	0.047	0.000013
Xylene	1.700	0.0049
Polycyclic aromatic hydrocarbons		
Naphthalene	17.000	0.038
Acenaphthylene	4.200	0.0079
Acenaphthene	0.720	0.0013
Fluorene	4.900	0.0085
Phenanthrene	14.000	0.023
Anthracene	5.700	0.0092
Flouranthene	8.700	0.012
Pyrene	6.100	0.0086
Benzo(a)anthracene	3.600	0.0045
Chrysene	3.300	0.0041
Phenols		
Phenol	1.300	0.0040
Cresol	1.800	0.0047
2,4-Dimethylphenol	0.420	0.00099
Residue		
Not identified	924.4	

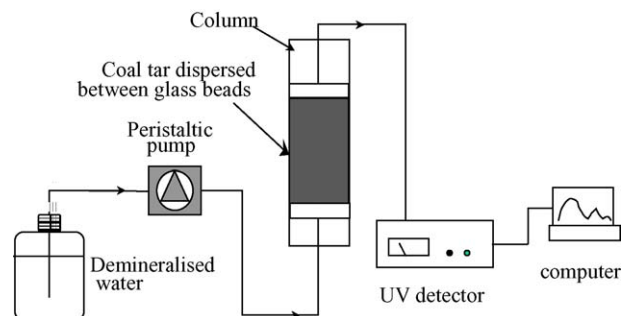


Fig. 1. Experimental set up for the column assays.

Table 2
Experimental parameters of column assays

Parameter	Assay 1	Assay 2	Assay 3	Assay 4	Assay 5	Assay 6
Diameter of glass beads, d (mm)	2	2	2	2	2	4
a_{sb} (m^{-1})	4780	4530	5380	8610	4790	4820
Coal tar volume, V_c (cm^3)	1.7	0.85	3.4	8.5	1.7	1.7
Coal tar saturation, $\tau = V_c/V_p$	0.10	0.05	0.20	0.50	0.10	0.10
Flow rate, Q (cm^3/h)	75	75	75	75	35	75
Darcy velocity, u (cm/h)	14.2	14.2	14.2	14.2	6.6	14.2
Pore volume, V_o (cm^3)	15	16	13.2	8.2	14.9	15.2
Mobil water fraction, $\varepsilon (V_o/V_t)$	0.36	0.39	0.32	0.20	0.36	0.37
Pore velocity, $v (u/\varepsilon)$ (cm/h)	39.1	36.3	44.2	70.8	18.3	38.6

bold type). Given the low solubility of coal tar in water, its mass varies only little during the assays. The saturation level established at the beginning was therefore considered as constant during the assays. For assay 1, in addition to the on-line UV absorbance, the three target compounds (phenol, naphthalene and phenanthrene) were periodically analyzed in the aqueous solution sampled at the column output.

The hydrodynamic regime in the column was studied using a non-reactive tracer. A solution of KCl at 100 mg L^{-1} was injected into the column and the response monitored by conductimetry at the column outlet.

2.4. Analytical methods

HPLC analyses of aqueous samples were carried out using a Shimadzu LP-64 chromatograph equipped with an isocratic pump, a $20 \mu\text{L}$ Rheodyne 7010 injection valve, a 3 cm Kromasil C18 guard column, a 25 cm Kromasil C18 column and a Shimadzu SPD-6A UV detector set at 254 nm. Solvent used as a mobile phase was acetonitrile/water 80/20 (v/v) (HPLC solvent grade, Prolabo) at a constant flow rate of 1.0 mL/min. The different peaks were integrated and the sum of their surface calculated in order to quantify globally all the aromatic compounds dissolved in water. The analytical error varies from 5 to 10% depending on the solution concentrations.

3. Modeling

3.1. Coal tar–water partition equilibrium

The aqueous concentration of an individual compound is a direct function of its relative abundance in the coal tar phase. A detailed discussion of this is presented by [1] and can be summarized by:

$$c_{w,i} = y_i s_{w,i} \left(\frac{f^L}{f^S} \right)_i \quad (1)$$

where $c_{w,i}$ is the equilibrium concentration of solute i in water, y_i is the equilibrium molar fraction of solute i in the coal tar, $s_{w,i}$ is the solubility in water of the pure compound i at the same conditions of temperature and pressure, f^L/f^S is the liquid–solid reference fugacity ratio for the pure compound i . This water/organic phase partition model is usually applied even if it does not take

into account the high non-ideal character of both organic and aqueous solutions [18,21,22].

The coal tar studied here contains in comparable proportions organic compounds with different physico-chemical properties such as phenols, relatively volatile polycyclic aromatic hydrocarbons (naphthalene and substituted compounds) and very slightly volatile PAH which are practically insoluble in water. It was already shown that, in this case, the Eq. (1) does not give satisfactory results [16,23] and the consideration of the aqueous solution non-ideality is necessary [16,24]. Thermodynamic theory of phase equilibria dictates the equality of fugacities for components across phases. For a given component “ i ” this equality may be written in terms of activity coefficient as:

$$x_i \gamma_{w,i} f_i^0 = y_i \gamma_{c,i} f_i^0 \quad (2)$$

where x and y are the respective molar fractions in water and in coal tar, γ are the activity coefficients in the respective phases and f^0 are the fugacities under defined standard conditions. For the usual standard conditions, i.e. pure compound ($x = 1, y = 1$) in liquid state at the same temperature and pressure as the mixture, we obtain:

$$x_i = \frac{y_i \gamma_{c,i}}{\gamma_{w,i}} = y_i K_{x,i} \quad (3)$$

the partition coefficient K_x depends on the temperature, the composition of the phases (x_j, y_j) and all the possible intermolecular interactions i – j .

Given its composition, the coal tar can be considered as a diluted solution with respect to each constituent (Table 1). The most concentrated constituent analyzed is naphthalene whose molar fraction is about 0.037. The aqueous solution in equilibrium with the coal tar is also diluted with respect to each constituent (experimental results presented in Table 3). In the case of diluted solutions, it can be shown [25] that the activity coefficients γ only depend on interactions between the solute i and the solvent (the major constituent) and do not depend on the complex composition of the solution. Consequently, for real diluted solutions, the partition coefficient $K_{x,i}$ of each solute i is a constant which depends only on the temperature and nature of the solvents. Then, $K_{x,i}$ can be determined from a water–coal tar equilibrium partition experiment.

Table 3
Equilibrium parameters and mass transfer parameters for the selected compounds

Parameters	Phenol	Naphthalene	Phenanthrene
Pure compound water solubility s_w (g/m ³) ^a	82000	31.7	1.29
f^L/f^S ^a	1	3.53	5.65
Diffusion coefficient in water D_w (m ² /s)	9.7×10^{-10}	6.6×10^{-10}	5.0×10^{-10}
Batch studies			
Equilibrium concentration in water c_w^{eq} (g/m ³)	20.7 (21.44)	11.0	0.210
Partition coefficient K (m ³ coal tar/m ³ water)	1.4×10^{-2}	5.0×10^{-4}	1.1×10^{-5}
Column study—assay 1			
Correlated mass transfer coefficient k_t (m/s)	3.8×10^{-7}	3.4×10^{-7}	3.1×10^{-7}
Effective interfacial area fraction f_s	0.70	0.65	0.63

^aFrom [15].

**Estimated [32].

For practical reasons, the equilibrium relationship (3) has been used in the form:

$$c_{w,i} = c_{c,i} K_i \quad (4)$$

where $c_{w,i}$ and $c_{c,i}$ are, respectively the molar concentrations of solute i in water (mol/m³ water) and in coal tar (mol/m³ coal tar) and K_i is the partition coefficient of solute i in m³ coal tar/m³ water, defined by:

$$K_i = K_{x,i} \frac{M_c \rho_w}{M_w \rho_c} \quad (5)$$

where M and ρ are the respective molar weights and densities of water (subscript w) and coal tar (subscript c).

3.2. Non-equilibrium dissolution in percolation column

The non-equilibrium dissolution model was established and applied for the experimental conditions presented in Section 2. The following hypotheses were adopted:

- The transport of the aqueous solution in the column is convective-dispersive with a constant flow rate Q . The one-dimensional flow regime can be modelled by a series of n identical open continuous stirred tank reactors (CSTR). The CSTR-series model is equivalent with a advection–dispersion model (many fundamental works like those of Levenspiel [26] or Villiermaux [27]). The application of a CSTR model has some advantages in the resolution of the system of equations, which becomes ODE-type. The dispersivity of the porous medium is then characterized by the number of tank reactors in the series, n , which value is determined by a tracer response study.
- The constituents diffuse in the coal tar layer towards the tar–water interface. In the experimental conditions used (thin tar layer), the internal diffusion in the tar does not constitute a significant limiting factor for mass transfer towards the aqueous phase. This hypothesis has been verified (see Section 4). In consequence, the composition in the tar layer is considered homogenous.
- The volume of the tar layer remains constant during the experiments because only a very low tar fraction is solubilized.

- The transfer towards water of tar compounds takes place across an aqueous film of thickness δ at the tar–water interface. The thermodynamic equilibrium takes place at the tar–water interface (local equilibrium assumption, generally adopted [9,16,17]) and then the water-side concentration of each constituent is calculated in function of the coal tar concentration (considered homogenous as stated above):

$$c_w|_h = c_c K \quad (6)$$

- As explained in Section 3.1 the partition coefficient K is independent of the composition of the two phases, it depends only on temperature.

The diagram of the dissolution model is presented in Fig. 2 (for a reactor j of the series).

The dissolution-convection model contains the mass balance equations for each constituent of the tar. The equations below are written for the reactor j with $j = 1, \dots, n$.

- Depletion of tar is due to the flux of constituents towards the water:

$$\frac{dc_{c,j}}{dt} = -a_s k_t \frac{V_0}{V_c} (K c_{c,j} - c_{w,j}) \quad (7)$$

where V_0 is the aqueous phase volume and V_c the coal tar volume.

- In the mobile aqueous phase, the accumulation of a constituent is due to the flux from the tar and to the convective transport.

$$\frac{dc_{w,j}}{dt} = a_s k_t (K c_{c,j} - c_{w,j}) + \frac{n}{t_m} (c_{w,j-1} - c_{w,j}) \quad (8)$$

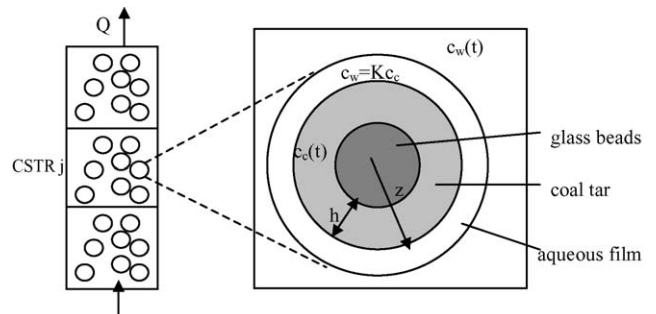


Fig. 2. Modelling principle for the dissolution process in percolation column.

in these equations, k_t is the mass transfer coefficient across the aqueous film for a given compound, a_s is the specific exchange surface between tar and water (m^2/m^3 water), and t_m is the characteristic convection time of mobile water defined by:

$$t_m = \frac{V_0}{Q} \quad (9)$$

the parameter of mass transfer across the aqueous film, k_t , is considered time independent for the duration of our experiments, 75 h. It can be determined by: (i) adjustment to the experimental data $c_{w,\text{exp}}(t)$ for each constituent and (ii) correlations of appropriate dimensionless numbers for the experimental conditions used. The use of empirical correlations in the case of tar dissolution has already been reported. Powers et al. [8] and Miller et al. [28] report the correlations for flow of water through a bed of soluble particles under different hydrodynamic conditions. Despite the development of these correlations, the determination by simulation of the behaviour of tar in a water-saturated porous medium is difficult, even impossible due to lack of knowledge concerning the interfacial area. In order to estimate the mass transfer parameter k_t , we used the correlation established by Nelson and Galloway [29] for a flow through a packed bed. The dimensionless expression of the mass transfer coefficient is the Sherwood number (Sh). It is calculated according to the hydrodynamic characteristics using the numbers of Reynolds (Re) and Schmidt (Sc):

$$Sh = 0.18 \left[\frac{1}{(1-\varepsilon)^{0.67}} - \frac{1}{(1-\varepsilon)^{0.33}} \right] Re Sc^{0.67} \quad (10)$$

with

$$Re = v\rho_w \frac{d}{\mu_w} \quad Sc = \frac{\mu_w}{(\rho_w D_w)} \quad Sh = k_t \frac{d}{D_w} \quad (11)$$

where v is the pore velocity, ρ_w the bulk density of the aqueous phase, d the particle diameter, μ_w the aqueous phase viscosity, ε the volume fraction of water, and D_w the diffusion coefficient of a given compound in water.

The maximum specific exchange surface (denoted a_{sb}) is theoretically known and given by the total surface of the beads S_b in the packed bed. Experimentally, it is difficult to achieve the theoretical maximum exchange surface due to the contact between the beads and to imperfections in the experimental protocol when putting the tar layer in position (existence of discontinuities in the tar film or presence of zones inaccessible to water due to formation of tar+beads aggregates). It is therefore necessary to introduce the effective interfacial area fraction f_s as a new parameter:

$$f_s = \frac{a_s}{a_{sb}} \quad \text{where} \quad a_{sb} = \frac{S_b}{V_0} \quad (12)$$

with these assumptions the model constituted by the balance Eqs. (7) and (8) written for each compound and for each of the 10 CSTR, has only one unknown parameter, the interfacial area fraction f_s . The model was solved to obtain the concentrations c_c and c_w in each CSTR and in function of time. An optimization method based on the minimization of the objective function

defined below was used in order to fit the model and determine the unknown parameter f_s .

$$FO = \frac{\sum_i^{\text{number_of_data}} [(c_{\text{exp},i} - c_{w,i})/c_{\text{exp},i}]^2}{\text{number_of_data}} \quad (13)$$

where $c_{\text{exp},i}$ is the experimental concentration at the data point i (at the time i) and $c_{w,i}$ the corresponding calculated concentration.

4. Results and discussion

4.1. Partition equilibrium study

The measured equilibrium concentrations in water and the solubility data of the pure compounds are presented in Table 3. The composition of the organic phase at equilibrium was estimated by mass balance calculations from the initial composition of coal tar (Table 1) and the equilibrium composition of the aqueous phase. The partition coefficients K of the three target compounds were found to differ by several orders of magnitude.

4.2. Dissolution in percolation column

Before performing simulations, an evaluation of the main dynamic processes involved in the non-equilibrium dissolution (i.e. compound diffusion in tar, interphase transfer, convective transport) may be very useful.

The characteristic diffusion time is defined [30] by the equation (14), applied for the tar thin layer:

$$t_{\text{dif}} = \frac{h^2}{D_c} \quad (14)$$

the typical values of diffusion coefficients D_c for the aromatic compounds in coal tar reported in the literature are about 2×10^{-12} to 2×10^{-11} m^2/s [30]. Considering the low thickness of the tar layers on the glass beads ($h = 0.02$ mm for a saturation level of 10% and a uniform dispersion of coal tar on the bead surface) the characteristic diffusion time does not exceed 200 s.

The characteristic external transfer time across the water interfacial film is defined [31] by:

$$t_{\text{ext}} = \frac{1}{Kk_t} \frac{V_c}{S_b} \quad (15)$$

different correlations using dimensionless numbers give values of k_t of about 10^{-7} – 10^{-6} m/s and with the experimental values for the other parameters in Eq. (14) t_{ext} takes values greater than 3000 s. Finally, the characteristic convection time of the mobile water t_m , defined by Eq. (9) is estimated to be greater than 700 s. It is observed that $t_{\text{dif}} < t_m < t_{\text{ext}}$. In a consecutive dynamic processes as the diffusion-external transfer, the slower (here the external transfer) determine the compound flux towards bulk aqueous phase. This justifies neglecting the internal diffusion in tar in the non-equilibrium dissolution model.

The hydrodynamic behaviour of the aqueous mobile phase is characterized by the number n of reactors (CSTR). This parameter has been identified by applying the balance equation for the

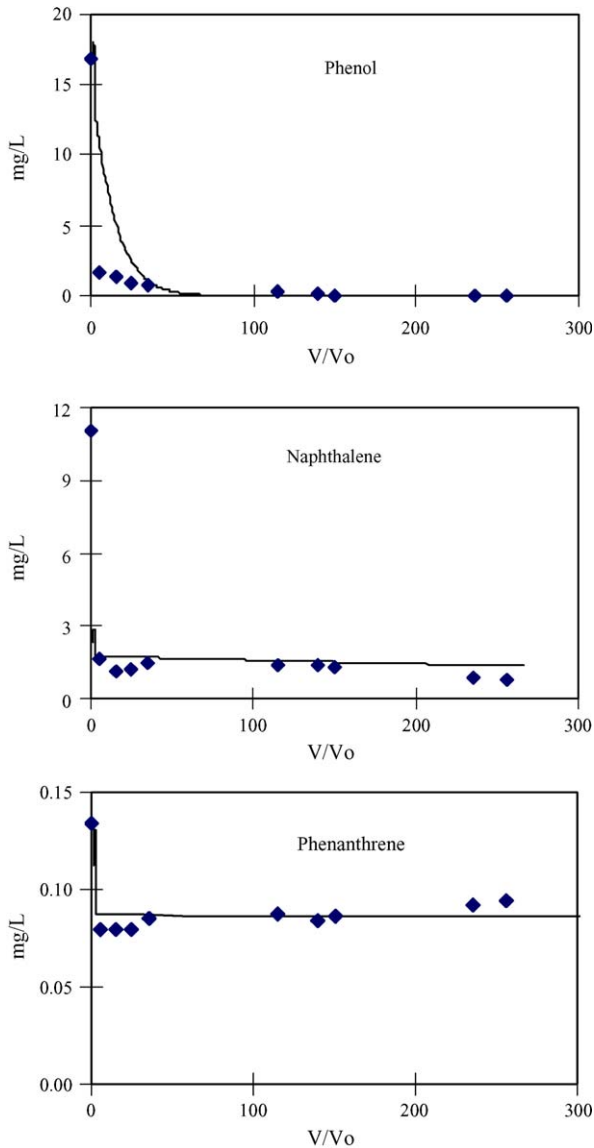


Fig. 3. Column assay 1: concentration of the target compounds at the column outlet.

transfer of the tracer. For the j CSTR in the series the balance equation is:

$$\frac{dc_{\text{tracer}, j}}{dt} = \frac{n}{t_m}(c_{\text{tracer}, j-1} - c_{\text{tracer}, j}) \quad (16)$$

a value of $n=10$ has been calculated by fitting this model with the experimental tracer concentrations at the output of the column ($j=n$). The tracer method for the hydrodynamic regime assessment is detailed in [26,27].

The experimental results for the three target compounds, i.e. phenol, naphthalene and phenanthrene, are presented in Fig. 3. It can be observed that depletion of phenol is rapid, its aqueous concentration being no longer detectable after $150 V_o$. However, phenanthrene concentration remains practically constant and equal to a third of the saturation value. Naphthalene has an intermediate behaviour with a regularly decreasing concentration. The experimental data, $c_{w,\text{exp}}$ versus time, allow application

of the model individually for each compound and identification of the unknown parameter, the fraction of useful surface f_s (Table 3). The proposed model containing an adjusted parameter gives satisfactory results for the three compounds (Fig. 3) and for assay 1 with a mean value of $f_s = 0.66$.

4.3. Global dissolution of tar in a column

In the present study the UV absorbance measurements at 254 nm of the aqueous effluent at the column output was used as a common method for monitoring tar dissolution. The signal obtained is proportional to the concentration of benzene rings in the solution. The experimental results obtained for six different assays are presented in Figs. 4–6. The ordinate axis A/A_0 corresponds to the ratio of the absorbance at 254 nm measured at the column output (A) over the absorbance of the saturated solution at equilibrium with the tar (A_0). The abscissa axis corresponds to the number of pore volume (V/V_o). The curves obtained reveal three stages in tar dissolution process: (1) at the beginning (first ten pore volumes) a rapidly decreasing peak in concentration;

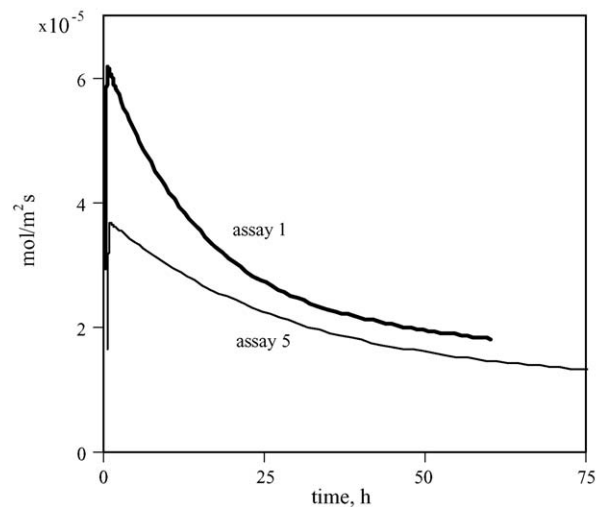
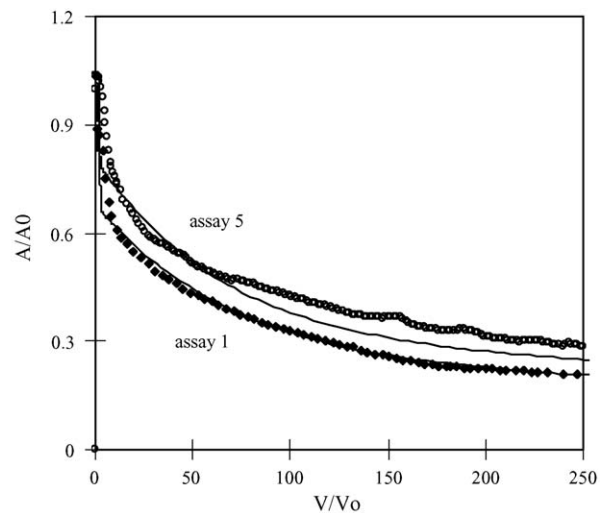


Fig. 4. Column assays 1 and 5: coal tar dissolution using two water flow rates. Relative UV absorbance (left) and released flux (right). points = experimental data; lines = simulations.

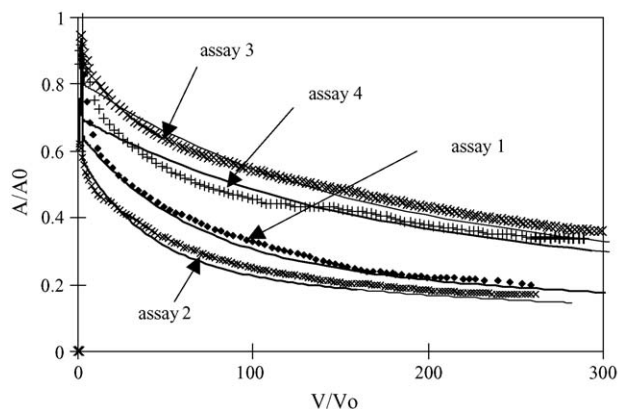


Fig. 5. Coal tar dissolution for different saturation levels: $\tau = 10\%$ assay 1; $\tau = 5\%$ assay 2; $\tau = 20\%$ assay 3; $\tau = 50\%$ assay 4. points = experimental data; lines = simulations.

(2) the concentration continues decreasing but more slowly; and (3) the dissolution rate becomes practically constant after 200 pore volumes.

Given the differences in behaviour of the various constituents reported above, coal tar cannot be assimilated to a single compound. The experimental results show that the more soluble compounds are depleted at the beginning of the dissolution process and the only slightly soluble compounds are released over a long period at low concentrations. This observation agrees with the modelling results obtained by [16]. The parameter, which differentiates tar constituents the most is their hydro-solubility or partition between tar and water. The transfer parameters vary little and their values remain in the same order of magnitude whereas the solubility in water is very different from one compound to another. In the series of PAH for example, solubility varies by several orders of magnitude: naphthalene $8.7 \times 10^{-4} \text{ mol L}^{-1}$, phenanthrene 7.2×10^{-6} , chrysene $8.8 \times 10^{-9} \text{ mol L}^{-1}$, etc. However, taking into account all of the constituents in a model is very difficult and requires a large amount of experimental data. For these reasons, tar has been considered as a mixture of four equivalent constituents according to the volatility and solubility of the major compounds detectable by UV spectroscopy. As the coal tar used did not contain the

most volatile compounds (monocyclic aromatic hydrocarbons), the four categories considered are:

- (1) The “phenol equivalent compounds”: Phenol, cresols, dimethylphenol.
- (2) The “naphthalene equivalent compounds”: Naphthalene, acenaphthylene, acenaphthene.
- (3) The “phenanthrene equivalent compounds”: Phenanthrene, anthracene, fluorene, fluoranthene.
- (4) The “heavy PAH fraction”: Pyrene, benzoanthracene, chrysene.

The PAH fractionations used above are the same as those recommended by [19] while the phenols included here are not present in previous studies reported in the literature. In the model, the equivalent compounds are characterized by: (1) their initial concentration in the tar which is the sum of the molar concentrations of the various compounds analysed; (2) the global mass transfer coefficient; and (3) the partition coefficient. The latter two were assimilated to the respective parameters of the first compound in the category. The model has been applied for the mixture of the four equivalent constituents. The concentrations in water obtained by simulation for each equivalent constituent, $c_{x,k}$, have then been used for calculating the relative absorbance A/A_0 :

$$\frac{A}{A_0} = \sum_{k=1}^4 \frac{A_k c_w}{A_0} \quad (17)$$

where A_k denotes the specific absorbance of each equivalent constituent. A_k values have been estimated from the absorbance of the compounds studied individually, determined by UV spectroscopy.

The model was firstly applied to assay 1 where the individual behaviour of the major constituents (phenol, naphthalene and phenanthrene) has been studied. It was not possible to determine experimentally the parameter K of the “heavy PAH equivalent constituent” because of very low aqueous concentrations of this compounds. This parameter, by the way the only unknown, was adjusted by fitting the model to the experimental results (expressed as A/A_0) of assay 1 (Table 4). The model was then applied to assays 2–6 maintaining the partition coefficient values K of the four categories of compounds. The mass

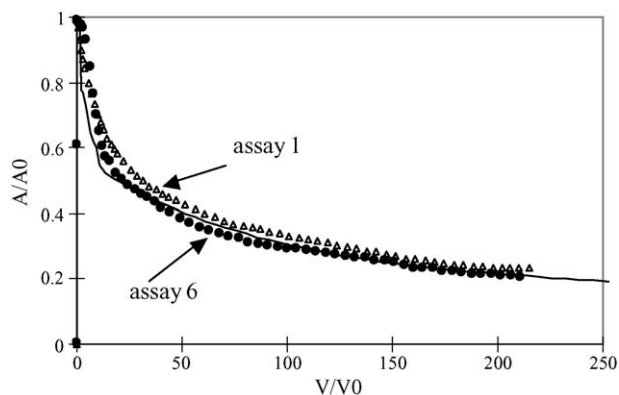


Fig. 6. Influence of the glass beads diameter on the coal tar dissolution: $d = 2 \text{ mm}$ assay 1; $d = 4 \text{ mm}$ assay 6. points = experimental data; lines = simulations.

Table 4
Model parameters for column assays 1–6

Partition coefficient K in assays 1–6	
Phenol equivalent	1.4×10^{-2}
Naphthalene equivalent	4.9×10^{-4}
Phenanthrene equivalent	1.1×10^{-5}
Heavy HAP	1.0×10^{-6}
Effective interfacial area fraction, f_s	
Assay 1	0.66
Assay 2	0.50
Assay 3	1.0
Assay 4	0.85
Assay 5	0.79
Assay 6	1.0

transfer coefficients k_t were estimated using correlation (11) for the hydrodynamic conditions of each assay. As was explained in Section 3.2, the effective interfacial area fraction f_s is an experimental unknown parameter which has to be adjusted for each assay (results presented in Table 4).

Firstly, the influence of operating conditions on the dissolution behaviour and the model capability will be discussed. The water-flow rates influence may be assessed by comparing the experimental results of assays 1 and 5 (Fig. 4). It can be seen that the compound concentrations were higher for a lower flow rate. In fact, a more adequate parameter for comparison is the flux released by the tar. The right hand side graph of Fig. 6 shows that the flux released for higher flow rates is greater. This dependence can be explained by the variation of the transfer coefficient k_t , which increases with the increasing flow rate in the column. The result obtained confirms the fact that mass transfer across the interfacial film is the limiting factor of tar dissolution in porous medium. Fig. 5 shows the experimental and simulated curves of global dissolution for four different saturation levels of tar. It can be observed that for saturation levels τ going from 5 to 20%, dissolution of tar into water is increased with the tar content. However, for a level of 50%, dissolution is less pronounced than for $\tau=20\%$. The first observation is logical as a higher coal tar content leads to a reduced pore volume and therefore higher flow rates with accentuated dissolution. Furthermore, a high saturation level implies a greater exchange surface due to the spatial distribution of tar in the column. In fact, the value of the effective interfacial area fraction f_s increases with τ (Table 2). This interpretation is not suitable for the assay with $\tau=50\%$ where it is likely that part of the tar is not accessible to the flowing water (formation of aggregates with the beads). The simulation in the case of assay 4 was successful assuming that only 25% of the tar volume was accessible to water during the time of the experiment (short-term).

Comparing assays 1 and 6 we cannot observe significant differences between assays performed with different bead's diameters. Two factors are involved here:

- The flow regime in the porosity and its influence on the transfer coefficient: as predicted by correlation (10), the diameter of the beads does not influence the value of k_t as the parameter plays the same role in Re and Sh .
- The specific exchange surface: the maximum exchange surface a_{sb} is higher for assay 1 (smaller bead diameter) but the effective interfacial area fraction seems to be lower (0.66 against 1). The experimental results in fact demonstrate a slightly accentuated dissolution for assay 1. This result is due to the more uniform dispersion of tar on the surface of beads with diameter of 4 mm.

The proposed model represents well the evolution of the dissolution process, the simulation results are even quantitative when an adjusted parameter is used (the effective interphase surface).

Finally, the proposed model was compared with two models based on the following hypotheses:

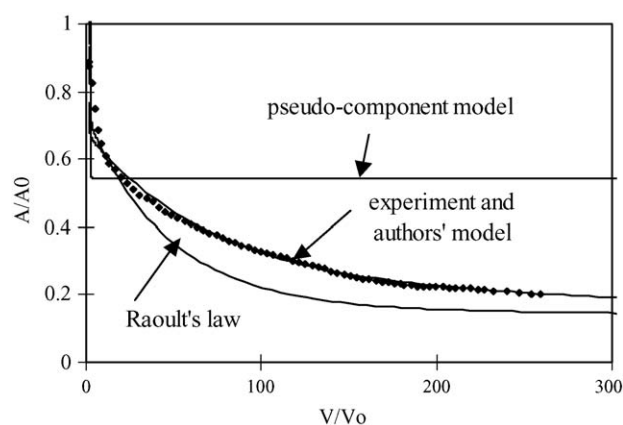


Fig. 7. Comparison of three models for the coal tar dissolution in porous medium.

- (1) The tar is considered as a pseudo unique compound. Its solubility in water, equal to the global concentration of dissolved compounds, remains constant during dissolution (as those of a pure compound). The external transfer parameter k_t has an average value. Fig. 7 shows that modelling of coal tar as a single compound is not appropriate. The simulated concentration remains constant and becomes nil when the tar is totally dissolved. Furthermore, the total dissolution of tar is an event, which does not occur in reality or takes place in the very long-term due to the presence of practically insoluble constituents.
- (2) In the model the tar–water partition model was replaced with the Raoult's law expressed by Eq. (1) to calculate the equilibrium concentration for each of the four fractions; the other parameters are unchanged. The use of Eq. (1) gives rise to an overestimation or underestimation of the concentration in water. The behaviour of tar is described only in a qualitative manner. The thermodynamic approach applied in this study allows enhancement of the non-equilibrium dissolution model and a better estimation of the tar behaviour.

5. Conclusions

A simple experimental procedure coupled with a fraction approach modelling is presented in order to assess the non-equilibrium and multi-compound dissolution behaviour of a coal tar. The main conclusions are summarized below:

- (1) In the case presented here, i.e. multi-compound equilibrium between two non-ideal phases, it can be shown that the partition of each constituent can be treated independently and characterized by a constant partition coefficient. However, this partition coefficient depends on the activities of the constituent in the aqueous phase and the tar and cannot be estimated only from the solubility of the pure compound in water.
- (2) A simple non-equilibrium dissolution model was used and validated for three target compounds (phenol, naphthalene and phenanthrene). Only one parameter was adjusted, the effective interfacial area, which is characteristic of the

experimental set-up and independent of the chemical composition or other tar's properties.

- (3) A fraction approach was used for a real coal tar containing PAHs and phenols. The compounds were grouped following their solubilities and volatilities in four fractions, each of them being modelled by an equivalent constituent. The model requires two parameters for each equivalent constituent, i.e. the partition coefficient, which may be experimentally determined and the transfer coefficient, which may be calculated using available correlations. The model was applied for different operating conditions giving reasonable good results.
- (4) A simple monitoring method (UV detection) can be used to measure the dissolution amount and a fraction-based model can be used to assess at least semi-quantitatively the non-equilibrium dissolution behaviour.

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