Adsorption of landfill leachates onto activated carbon Equilibrium and kinetics

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Abstract

The adsorption of stabilized leachates generated in a municipal landfill onto three commercial activated carbons has been investigated. Norit 0.8, Chemviron AQ40 and Picacarb 1240 have been used as adsorbents. Equilibrium experiments have been conducted to obtain the experimental isotherm profiles. Isotherms have been plotted based on the adsorption of general parameters, for instance chemical oxygen demand, total carbon, absorption at 410 nm and absorption at 254 nm. Different literature models and error functions have been used to adequately fit the experimental data. As a rule of thumb, three-parameter models do adjust experimental results better than two-parameter models. Norit 0.8 shows better adsorption characteristics than the rest of activated carbons, both in terms of contaminant level reduction of per unit mass of absorbent and in terms of the process kinetics.
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1. Introduction

Comparative studies for urban solid wastes management and disposal have reported landfilling as the most suitable technology to deal with this type of wastes [1]. However, in spite of the economical benefits of the method and easiness of implementation, generation of toxic leachates might cause serious problems to the surroundings. Leachate from landfills can be a major hazard to health if the landfill is not properly operated and taken care of. These leachates can seep into the ground, moving into the nearby underground water supplies of a community with all the negative consequences implicated in the process.

Among technologies aimed at the reduction of the leachate hazardous nature, both secondary and tertiary treatments have been studied and reported in the specialised literature. Aerobic and anaerobic biodegradation processes have been applied to effectively reduce the contaminant load of leachates generated

from young landfill sites [2,3]. Nevertheless, the main contaminant fraction of leachates from stabilized tips is composed by biologically refractory substances (i.e. humic substances), preventing, therefore, the adequate performance of secondary technologies [4]. As a consequence, tertiary treatments seem to be the alternative technologies to deal with leachates from landfills in the methanogenic phase. Thus, in order to fulfil the standards of quality for aqueous discharges or/and reutilisation of contaminated wastewaters, oxidation systems (UV, O_3, Fenton's reagent, advanced oxidation processes), membrane based technologies and adsorption processes have been investigated [5–7].

Among tertiary treatments, adsorption onto activated carbon (AC) has been reported as one of the most effective methods to remove high molecular weight compounds (present in stabilized leachates) from aqueous matrix. However, few works can be found on the use of AC to process sanitary landfill leachates, either as a single stage or in combination with other complementary technologies. Hence, Morawe et al. [7] investigated the performance of a two-column system in series as a post-treatment for a biologically treated leachate. With this system, chemical oxygen demand (COD) reductions up to 90% were observed (i.e. from roughly 900–80 ppm). Additionally,

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Nomenclature

$A(t)$	adjustable parameter in Temkin equation (g or absorbance unit g^{-1} AC)
b	adjustable parameter in Langmuir equation ((g or absorbance unit $L^{-1})^{-1}$).
B_T	adjustable parameter in Temkin equation ((g or absorbance unit $L^{-1})^{-1}$)
C	concentration in the liquid phase (g or absorbance unit L^{-1})
k_{ads}	kinetic parameter of modified Lagergren equation (h^{-1}).
K_F	adjustable parameter in Freundlich equation ((g or absorbance unit g^{-1} AC)(g or absorbance unit $L^{-1})^{n-1}$)
m_{AC}	mass of activated carbon (g)
n	adjustable parameter in Freundlich equation
Q	concentration in the solid phase (g or absorbance unit g^{-1} AC)
Q_m	adjustable parameter in Langmuir equation (g or absorbance unit g^{-1} AC)
t_0	kinetic parameter of modified Lagergren equation (h)
V	liquid phase volume (L)

Greek letters

α_R	adjustable parameter in Redlich–Peterson equation (g or absorbance unit g^{-1} AC)
β_R	adjustable parameter in Redlich–Peterson equation ((g or absorbance unit $L^{-1})^{-1}$)
γ	adjustable parameter in Redlich–Peterson equation
δ_T	adjustable parameter in Toth equation ((g or absorbance unit g^{-1} AC)(g or absorbance unit $L^{-1})^{\lambda-1}$)
ξ	adjustable parameter in Sips equation
λ	adjustable parameter in Toth equation
σ	adjustable parameter in Toth equation (g or absorbance unit L^{-1})
Φ_D	adjustable parameter in Dubinin–Radushkevich equation (g or absorbance unit g^{-1} AC)
Ψ_D	adjustable parameter in Dubinin–Radushkevich equation
ω_S	adjustable parameter in Sips equation ((g or absorbance unit $L^{-1})^{-1}$)
Ω_S	adjustable parameter in Sips equation (g or absorbance unit g^{-1} AC)

Table 1
Leachate characterization from Badajoz landfill site

COD	3600
BOD$_5$	400
N-Kjeldahl	250
TC	870
IC	300
pH	8.20

Average values. Units in $mg\,L^{-1}$.

ter case, these authors reported an increase in the non-adsorbable fraction of leachates after the oxidation pre-treatment with ozone.

In addition to the lack of studies based on the usage of AC in landfill leachate remediation, equilibrium data of the system leachate-AC are rarely mentioned or studied rigorously. Isotherm data provide a fundamental tool at the time of design and scale-up of adsorbers. Similarly, kinetic results are valuable information to weigh up the suitability and effectiveness of the adsorption process. Again, few works can be found in the literature focused on the latter subject.

Consequently, in the present research, an analysis of the equilibrium adsorption of a stabilized leachate onto three commercial activated carbons is presented. Also, the kinetics of the adsorption process is investigated by using different amounts of activated carbon. Experimental data based on measurements of chemical oxygen demand (COD), colour at 410 nm (Abs$_{410}$), total carbon (TC) and absorbance at 254 nm (Abs$_{254}$) have been fitted to different models previously reported in the literature and the results discussed after the fitting process.

2. Experimental

Leachates were collected from the landfill site of Badajoz (South West of Spain). Table 1 summarizes the main characteristics of the leachates used in this study (average values are shown). From Table 1 it is observed that this effluent presents a low value of COD and BOD$_5$. The rates BOD$_5$/COD and TOC/COD situated in the range 0.1–0.3 and 0.2–0.4, respectively, and pH above 7 indicates the stabilized nature of the leachate. Among metallic species analysed, Al, Fe, Cr, Mn and Ni show the highest concentrations with other metals detected at trace levels. A periodic characterisation of these leachates can be found elsewhere [10].

Chemical oxygen demand (COD) was determined in a Dr. Lange spectrophotometer, the method based on the standard dichromate reflux method [11]. Total carbon (TC) concentrations were obtained by means of a DC-190 Dorhman analyzer. Absorbance of samples at 254 and 410 nm was determined by means of a U2000 model HITACHI spectrophotometer.

The commercial activated carbons used in this study were Norit 0.8, Picacarb 1240 and Chemviron AQ40. The main characteristics of manufactured ACs are detailed in Table 2.

The bottle point isotherm technique was employed to determine the equilibrium capacity of the commercial activated carbons investigated. Experiments were conducted at the original pH of the leachate. Accordingly, experiments were carried out in glass vials (25 cm^3 capacity) sealed by Teflon caps.

Ramírez et al. [8] utilised and compared two combined processes, for instance coagulation-flocculation-activated carbon and Fenton's oxidation-activated carbon, claiming the improvement of the adsorption process after the chemical oxidation stage due to the generation of smaller and more adsorbable molecules. Moreover, Fettig et al. [9] also utilised a pre-oxidation step before running the adsorption step onto AC. However, in the lat-

Table 2
General characteristics of activated carbons

Property	Norit 0.8	Chemviron AQ40	Picacarb 1240
Bulk density (g cm^{-3})	0.39	0.76	0.45
Moisture content (wt.%)	2	2	2
Specific surface area (m^2 g^{-1})	1150	1180	1050
Ash content (wt.%)	7		–
Shape	Pellets	Granules	Granules
Particle size (mm)	<0.6	0.4	1–1.2

Different known quantities of adsorbent mass were then added to the bottles (from 0 to 100 g L^{-1}). The samples were kept in a constant-temperature water bath (GRANT shaker, model OLS 200) and shaken continuously. Upon equilibration time, the supernatant liquid phase was characterised and the solid-phase COD, TC and absorbance (410 and 254 nm) accumulations on the activated carbons calculated via a mass balance [12].

Kinetics runs were conducted in a 1 L agitated batch reactor, thermostatized at 20 °C.

3. Results and discussion

3.1. Adsorption equilibrium

3.1.1. Isotherm models
In this work, several isotherm equations were tested to adequately correlate the experimental data.

Testing several isotherm models involves not only finding the best fit of the experimental data but the consideration of additional information derived from the estimated parameters (i.e. sorption nature, energy calculations, surface heterogeneity, etc.). Limiting the number of isotherm models also limits the aforementioned information.

Thus, the following models were adopted:

- Freundlich isotherm (FR):

$$Q_e = K_F C_e^{1/n} \tag{1}$$

- Langmuir isotherm (LG):

$$Q_e = \frac{Q_m b C_e}{1 + b C_e} \tag{2}$$

- Redlich–Peterson isotherm (RD):

$$Q_e = \frac{\alpha_R \beta_R C_e}{1 + \beta_R C_e^\gamma} \tag{3}$$

- Temkin isotherm (TM):

$$Q_e = A(T) \ln[B_T C_e] \tag{4}$$

- Dubinin–Radushkevich isotherm (DR):

$$Q_e = \Phi_D \exp\left\{ -\Psi_D \left(\ln\left[1 + \frac{1}{C_e}\right] \right)^2 \right\} \tag{5}$$

- Toth isotherm (TH):

$$Q_e = \frac{\delta_T C_e}{(\sigma + C_e)^\lambda} \tag{6}$$

- Sips isotherm (SP):

$$Q_e = \frac{\Omega_S (\omega_S C_e)^\xi}{1 + (\omega_S C_e)^\xi} \tag{7}$$

Each model differs in the thermodynamic or empirical base behind its determination and each one presents its own set of advantages and inconveniences (Ho et al. [13]). In the above expressions, Q_e and C_e stand for the values of the measured parameter (i.e. COD, TC or absorbance) in the solid per mass unit of adsorbent and the remaining concentration of the aforementioned parameters in the liquid after equilibrium conditions are attained. The rest of parameters appearing in expressions (1)–(7) are characteristics constant in each isotherm model (see nomenclature).

3.1.2. Error functions
To assess for the best fitting in each particular case, an optimisation procedure based on the work by Ho et al. [13] was performed. Thus, a non-linear regression analysis was conducted by considering different error functions leading to a different set of parameters. Choosing any specific error function can bias the fit, i.e. towards high concentration values when absolute deviations are considered [13]. The function errors considered were:

- Sum of error squares:

$$\text{Err}^2 = \sum_{i=1}^{i=N} (Q_e - \bar{Q}_e)_i^2 \tag{8}$$

- Composite fractional error function:

$$\text{CFEF} = \sum_{i=1}^{i=N} \left[\frac{(Q_e - \bar{Q}_e)^2}{Q_e} \right]_i \tag{9}$$

- Derivative Marquardt's percent standard deviation:

$$\text{DMPSD} = \sum_{i=1}^{i=N} \left[\frac{Q_e - \bar{Q}_e}{Q_e} \right]_i^2 \tag{10}$$

- Average relative error:

$$\text{ARE} = \sum_{i=1}^{i=N} \left| \frac{Q_e - \bar{Q}_e}{Q_e} \right|_i \tag{11}$$

- Sum of absolute errors:

$$\text{SAE} = \sum_{i=1}^{i=N} \left| Q_e - \bar{Q}_e \right|_i \tag{12}$$

where Q_e and $\bar{Q}_e$ represent the measured and calculated concentrations of any specific parameter in the solid phase after equilibrium conditions apply.

To ascertain the parameter set that best fit experimental results, the following procedure was carried out [13]:

1. Consider an isotherm model (i.e. Freundlich model) and an error function (i.e. SAE). Compute the adjustable parameters of the isotherm model (K_F and $1/n$) that minimize the error function. Register the value of the error function.
2. With the values of K_F and $1/n$ previously obtained, select a different error function (i.e. ARE) and calculate its value. Repeat this step for the rest of error functions and determine

the rest of values without changing K_F and $1/n$. At the end of the process five values have been computed.
3. Initialize the procedure by minimizing a different function error, which will lead to a different parameter set. Determine the rest of error function values.
4. Among the five values obtained for each function error, select the maximum and normalize the rest with respect to this maximum. Add all the normalized values.
5. Accordingly, the best parameter set fitting the experimental results is the one obtained by using the error function generating the minimum value of the normalized error sum.

The previous scheme was therefore applied in a first instance to model the adsorption isotherms in terms of COD.

3.1.3. Experimental and model data

Table 3 presents the best results for the sum of normalized errors and parameter estimation in the adsorption of leachate COD onto Norit RO 0.8 activated carbon. Additionally, Fig. 1 shows the fits obtained with the best models.

According to Table 3 and regardless of the isotherm model considered, the use of Err^2 as the function error provides in all cases the lowest values for the sum of normalized errors.

Table 3
Adsorption of leachates onto Norit RO 0.8. COD isotherms

| Function	Err^2	CFEF	DMPSD	ARE	SAE
Freundlich					
K_F	0.15	0.14	0.13	0.15	0.15
$1/n$	0.75	0.83	0.90	0.76	0.72
$\sum$(normalised error)	3.48	4.37	3.79	4.62	3.89
Langmuir					
Q_m	0.71	0.94	1.70	0.75	0.65
b	0.29	0.19	8.50×10^{-2}	0.27	0.33
$\sum$(normalised error)	3.31	4.63	4.06	4.53	3.73
Redlich–Peterson					
γ	1.55	2.60	4.57	1.41	1.20
α_R	1.40	5.18	58.6	1.13	0.87
β_R	0.13	3.10×10^{-2}	2.40×10^{-3}	0.17	0.23
$\sum$(normalised error)	3.45	4.70	4.18	4.60	3.90
Temkin					
$A(T)$	1.09E−01	9.10×10^{-2}	5.10×10^{-2}	6.40×10^{-2}	0.11
B_T	5.18	5.77	8.58	8.58	5.01
$\sum$(normalised error)	2.05	3.59	3.76	4.74	3.14
Dubinin–Radushkevich					
Φ_D	0.32	0.31	0.26	0.33	0.34
Ψ_D	1.08	1.06	1.00	1.17	1.16
$\sum$(normalised error)	2.78	4.33	4.77	4.78	3.83
Toth					
λ	2.50	2.30	1.97	2.52	2.55
δ_T	77.5	77.4	77.2	77.6	77.6
σ	10.9	14.1	24.1	10.7	10.3
$\sum$(normalised error)	3.30	4.74	4.20	4.54	3.77
Sips					
ξ	1.15	1.11	9.00E−01	7.60E−01	1.07
Ω_S	0.52	0.66	74.1	74.4	0.56
ω_S	0.50	0.33	8.60×10^{-4}	2.80×10^{-4}	0.43
$\sum$(normalised error)	3.20	4.70	4.09	4.61	3.75

COD isotherms.
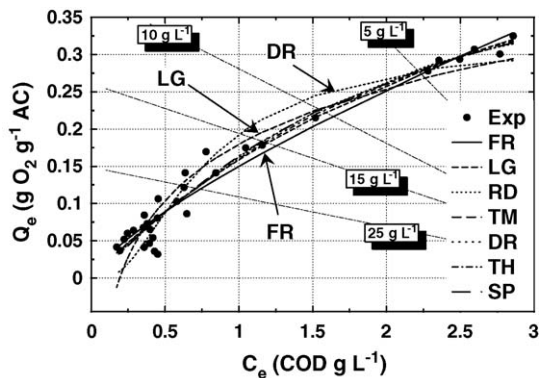
Fig. 1. Adsorption of leachates onto NORIT RO 0.8. COD isotherm curve. Symbols: experimental points. Lines: model calculations. Straight lines: operating lines of kinetic runs.
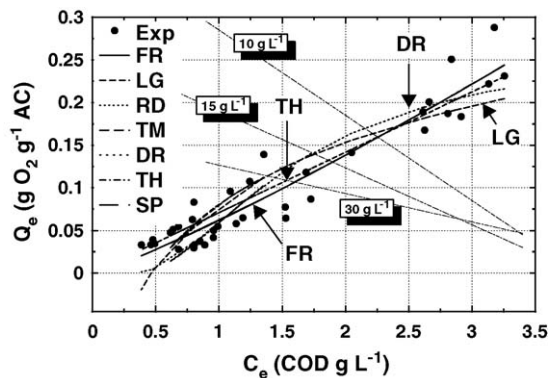

Fig. 2. Adsorption of leachates onto CHEMVIRON AQ40. COD isotherm curve. Symbols: experimental points. Lines: model calculations. Straight lines: operating lines of kinetic runs.

Additionally, among the different models tested, the best results were obtained for those models allowing for a three parameter calculation, i.e. in this order: Redlich Peterson, Sips and Toth gave the lowest values of Err^2. Among the two parameter models (results not shown), Langmuir and Freundlich isotherms achieved the best fits. From Fig. 1 it is seen how the Freundlich, Langmuir and Dubinin–Radushkevich isotherm curves show a slightly different profile than the rest, the remaining curves are almost superposed.

The values of "n" calculated by means of the Freundlich isotherm indicate the slightly favourable nature of the adsorption process. Also, it should be pointed out that Norit 0.8 is the only AC presenting this positive tendency. Values of "n" in the range 1.1–1.4 reflect the linear trend of the isotherm. Additionally, it is observed a low scattering of parameter values obtained by minimisation of the different error functions.

In the case of models accounting for a finite limit of Q_e at high values of C_e, Langmuir and Sips isotherms give values in the range 0.5–0.7 g O_2/g AC (anomalous values are neglected). Lower figures are obtained from the Dubinin–Radushkevich model (in the proximity of 0.3 g O_2/g AC) while the Redlich–Peterson isotherm results in slightly higher values (0.9–1.4 g O_2/g AC). The uncertainty in the analytical assay and, specially, the complex nature of leachates prevented the attainment of reliable data at high COD equilibrium concentrations. Some experimental points (not considered in the analysis) obtained at $C_e > 3.0$ g L^{-1} of COD estimated a L3 isotherm type (Giles classification) with a sharp increase in Q_e. However, other points measured in the same region resulted in a foreseeable finite limit for Q_e in the range 0.5–0.6 g O_2/g AC.

As stated in the introduction section, concerning landfill leachate adsorption equilibrium onto AC, scarce data are available in the literature. However, similar values have been previously reported for the removal of COD from a chemical pre-treated leachate [8] in the interval 0.11–0.44 g O_2/g AC depending on the commercial AC used.

Tables 4 and 5 present the results obtained when Chemviron AQ40 and Picacarb 1240 were used as adsorbents. Thus, from Table 4 and Fig. 2 an unfavourable isotherm shape is observed when utilising Chemviron AQ40. Again, minimization of Err^2 led to the lowest values of the normalized error sum.

The isotherm models of Freundlich, Redlich Peterson and Sips fitted the experimental data better than the rest of models. In this case, however, and given the experimental trend observed, models accounting for a finite Q_e led to abnormal results, i.e. extremely large monolayer capacity values. Freundlich equation allowed for the concave profile of the isotherm giving the lowest value of Err^2. The worst fits were found for the Temkin and Dubinin–Radushkevich expressions while Langmuir parameters approached this model to the simple Henry's law.

In the case of Picacarb 1240, the unfavourable adsorption profile experienced (see Fig. 3), once more resulted in a poor data correlation calculated by some of the isotherm models and non-sense parameter estimation. In this particular case, Err^2 and DMPS error functions were the expressions yielding the best fits. The isotherm models of Freundlich, Redlich–Peterson and Sips showed the lowest values of the error functions used with no appreciable differences between them.

An analogous analysis was thereafter completed by measuring other parameters (TC and absorbance) and their equilibrium concentrations when changing the nature of the adsorbent. Figs. 4–6 depict the isotherm equilibrium data based on the adsorption of total carbon, absorbance at 410 nm and absorbance at 254 nm for experiments carried out by using Norit 0.8, Chemviron AQ40 and Picacarb 1240, respectively. In these figures,
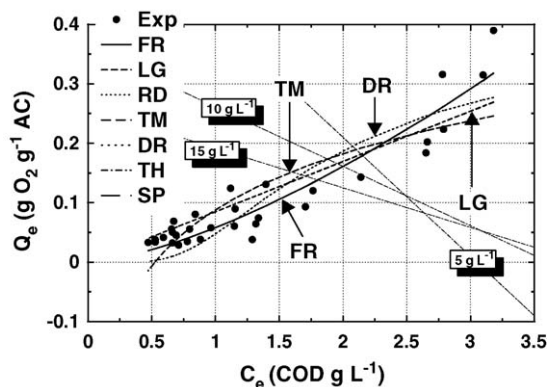

Fig. 3. Adsorption of leachates onto PICACARB 1240. COD isotherm curve. Symbols: experimental points. Lines: model calculations. Straight lines: operating lines of kinetic runs.

Table 4
Adsorption of leachates onto Chemviron AQ40

Function	Err²	CFEF	DMPSD	ARE	SAE
Freundlich					
K_F	6.20×10^{-2}	5.80×10^{-2}	5.50×10^{-2}	5.20×10^{-2}	5.55×10^{-2}
$1/n$	1.16	1.19	1.15	1.26	1.22
$\sum$(normalised error)	4.14	4.78	4.51	4.70	4.74
Langmuir					
Q_m	173	173	173	173	173
b	4.10×10^{-4}	3.70×10^{-4}	3.30×10^{-4}	3.70×10^{-4}	4.10×10^{-4}
$\sum$(normalised error)	3.19	4.49	3.93	4.82	4.09
Redlich–Peterson					
γ	−0.16	−0.19	−0.15	−0.15	−0.22
α_R	6.20×10^{-2}	5.80×10^{-2}	5.50×10^{-2}	5.50×10^{-2}	5.50×10^{-2}
β_R	6.70×10^{5}	6.70×10^{5}	6.70×10^{5}	6.70×10^{5}	6.70×10^{5}
$\sum$(normalised error)	4.25	4.78	4.47	4.73	4.80
Temkin					
$A(T)$	0.11	7.90×10^{-2}	4.70×10^{-2}	3.70×10^{-2}	9.00×10^{-2}
B_T	2.15	2.53	3.53	5.19	2.64
$\sum$(normalised error)	2.81	4.04	3.52	4.35	4.01
Dubinin–Radushkevich					
Φ_D	0.27	0.23	0.15	0.23	0.27
Ψ_D	3.18	2.74	1.83	2.96	3.25
$\sum$(normalised error)	2.54	3.93	4.56	4.67	3.68
Toth					
λ	0.39	0.40	0.41	0.40	0.39
δ_T	1.86	1.85	1.76	1.76	1.79
σ	4.55×10^{3}	4.60×10^{3}	4.60×10^{3}	4.60×10^{3}	4.60×10^{3}
$\sum$(normalised error)	3.18	4.48	3.94	4.82	4.09
Sips					
ξ	1.17	1.19	1.16	1.26	1.22
Ω_S	44.6	44.6	44.6	44.6	44.6
ω_S	3.60×10^{-3}	3.70×10^{-3}	3.00×10^{-3}	4.80×10^{-3}	4.10×10^{-3}
$\sum$(normalised error)	4.05	4.79	4.63	4.78	4.76

COD isotherms.

the best fits have also been plotted (lines). Thus, in spite of the scattering of the experimental data, Norit 0.8 seems to be the most suitable adsorbent among the ACs tested. Both, the isotherm shape and Q_e values corroborate the previous statement. From Figs. 5 and 6, it is observed how values of Q_e (either measuring TC or absorbance) obtained in the case of

Norit 0.8 practically double up those obtained with Chemviron AQ40 or Picacarb 1240, independently of the range of C_e analyzed. Analogously to COD equilibrium, it can be said that the use of Err² as the error function provides, in most of cases, the best fits for TC or absorbance regardless of the isotherm model applied.
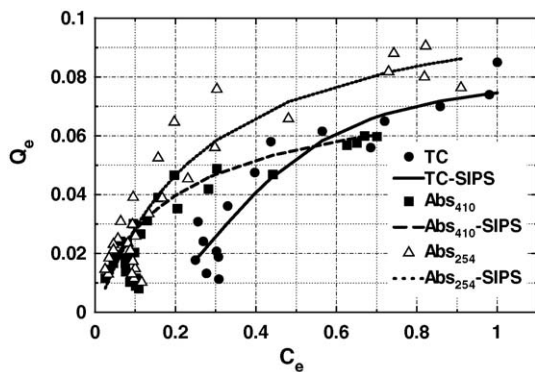

Fig. 4. Adsorption of leachates onto NORIT RO 0.8. TC, absorbance at 410 nm and absorbance at 254 nm isotherm curves. Symbols: experimental points. Lines: best fit model calculations.
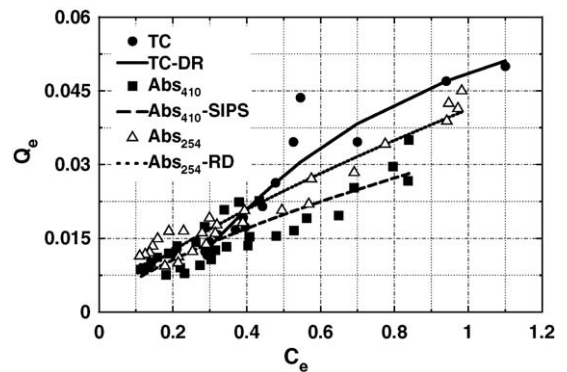

Fig. 5. Adsorption of leachates onto CHEMVIRON AQ40. TC, absorbance at 410 nm and absorbance at 254 nm isotherm curves. Symbols: experimental points. Lines: best fit model calculations.

Table 5
Adsorption of leachates onto Picacarb 1240

Function	Err^2	CFEF	DMPSD	ARE	SAE
Freundlich					
K_F	5.80×10^{-2}	5.95×10^{-2}	5.70×10^{-2}	6.40×10^{-2}	6.10×10^{-2}
$1/n$	1.47	1.35	1.15	1.09	1.27
$\sum$(normalised error)	3.34	4.28	4.47	4.61	4.49
Langmuir					
Q_m	328	218	173	173	173
b	2.58×10^{-4}	3.19×10^{-4}	3.34×10^{-4}	3.81×10^{-4}	4.41×10^{-4}
$\sum$(normalised error)	3.31	4.11	2.92	3.83	4.30
Redlich–Peterson					
γ	-0.47	-0.35	-0.15	-8.75×10^{-2}	-0.27
α_R	5.80×10^{-2}	5.95×10^{-2}	5.70×10^{-2}	6.40×10^{-2}	6.10×10^{-2}
β_R	6.70×10^5	6.70×10^5	6.70×10^5	6.70×10^5	6.70×10^5
$\sum$(normalised error)	3.34	4.28	4.47	4.61	4.49
Temkin					
$A(T)$	0.14	9.00×10^{-2}	4.00×10^{-2}	4.35×10^{-2}	0.10
B_T	1.90	2.33	3.38	4.16	2.26
$\sum$(normalised error)	3.21	4.36	2.76	3.80	4.34
Dubinin–Radushkevich					
Φ_D	0.38	0.24	0.12	0.10	0.27
Ψ_D	4.35	2.66	1.31	9.60E−01	2.83
$\sum$(normalised error)	2.83	3.85	3.36	3.84	4.19
Toth					
λ	0.37	-0.15	-0.15	-0.17	-0.18
δ_T	1.86	2.00×10^{-2}	1.70×10^{-2}	1.60×10^{-2}	1.60×10^{-2}
σ	4.55×10^3	4.55×10^3	4.55×10^3	4.55×10^3	4.55×10^3
$\sum$(normalised error)	3.32	4.11	2.92	3.83	4.30
Sips					
ξ	1.47	1.35	1.21	1.21	1.21
Ω_S	296	296	296	296	296
ω_S	3.00×10^{-3}	1.80×10^{-3}	9.00×10^{-4}	9.00×10^{-4}	9.50×10^{-4}
$\sum$(normalised error)	4.11	4.86	4.53	4.61	4.93

COD isotherms.

3.2. Adsorption kinetics

Given the global nature of analyzed parameters (COD, TC, absorbance), complexity of the effluent treated and relative uncertainty in the analytical methods used, no intricate kinetic models have been tested [14]. Consequently, the modified Lagergren equation proposed by Ho and McKay [15] has been used. This equation is of the form:

$$\frac{C}{C_0} = 1 - \frac{m_{AC}}{C_0}\{Q_e - \exp[\ln(Q_e) - k_{ads}(t + t_0)]\} \qquad (13)$$

where m_{AC}, C and C_0, k_{ads} and t_0 stand for the mass of activated carbon used, concentration in the liquid phase at time t and 0, adsorption rate constant and the characteristic time parameter of the model, respectively. The latter parameter, t_0, is incorporated to the model to enhance the range of applicability of the original first-order Lagergren equation [15].

Table 6 and Figs. 7–9 show the experimental and model results for kinetic experiments of COD adsorption onto Norit 0.8, Chemviron AQ40 and Picacarb 1240 activated carbons. The model does a good job when simulating the experimental results obtained. Moreover, values of Q_e derived from the model do agree with those obtained from the intercept of the operating line (Eq. (14) represented in Figs. 1–3) and the isotherm curve:

$$m_{AC}\frac{dQ}{dt} = -V\frac{dC}{dt} \qquad (14)$$

Values of k_{ads} and t_0 are significantly affected by COD analysis uncertainty and no general conclusions can be withdrawn.
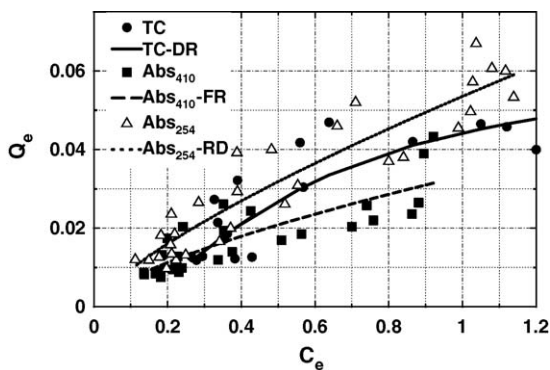

Fig. 6. Adsorption of leachates onto PICACARB 1240. TC, absorbance at 410 nm and absorbance at 254 nm isotherm curves. Symbols: experimental points. Lines: best fit model calculations.

Table 6
Kinetic parameters of the modified Lagergren equation for COD adsorption onto different commercial activated carbons

	m_{AC}	Q_e	k_{ads}	t_0
Norit 0.8	5	0.253	0.115	0.51
	10	0.200	0.080	2.62
	15	0.175	0.055	4.00
	25	0.102	0.030	8.54
AQ40	5	0.258	0.046	7.24
	10	0.168	0.023	12.98
	15	0.128	0.031	1.04
	25	0.140	0.266	0.00
	30	0.079	0.072	1.08
Picacarb	5	0.136	0.058	2.61
	10	0.148	0.027	5.97
	15	0.119	0.031	3.47

Nevertheless, broadly speaking, it can be said that t_0 is inversely proportional to k_{ads}. Thus, for the case of adsorption onto Norit 0.8, the higher the amount of AC used, the higher the initial rate of COD removal and consequently the value of t_0. As a consequence, k_{ads} diminishes when increasing the amount of activated carbon used (k_{ads} is calculated after the initial fast adsorption
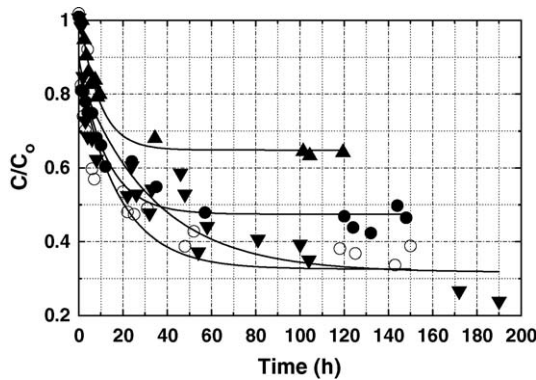

Fig. 7. Adsorption of leachates onto NORIT RO 0.8. Dimensionless COD concentration profiles. Influence of activated carbon concentration. Symbols: (▲) 5 g L^{-1}, (●) 10 g L^{-1}, (○) 15 g L^{-1}, (▼) 25 g L^{-1}. Lines: Lagergren model calculations.
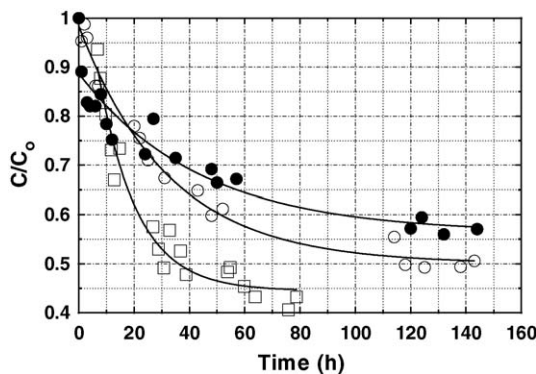

Fig. 8. Adsorption of leachates onto CHEMVIRON AQ40. Dimensionless COD concentration profiles. Influence of activated carbon concentration. Symbols: (●) 10 g L^{-1}, (○) 15 g L^{-1}, (□) 30 g L^{-1}. Lines: Lagergren model calculations.
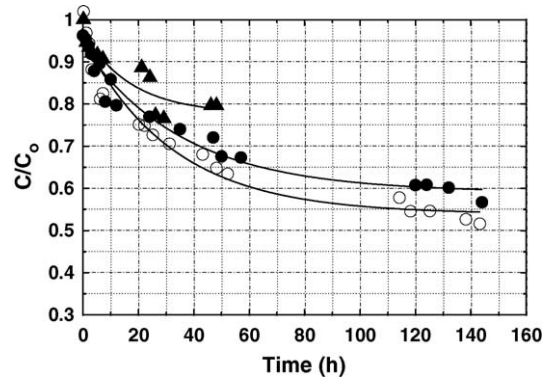

Fig. 9. Adsorption of leachates onto PICACARB 1240. Dimensionless COD concentration profiles. Influence of activated carbon concentration. Symbols: (▲) 5 g L^{-1}, (●) 10 g L^{-1}, (○) 15 g L^{-1}. Lines: Lagergren model calculations.

period). Also, as mentioned before, given the inherent experimental errors associated to COD measurements and effluent complexity, no clear trend is observed for the estimated parameters deduced from adsorption experiments on the rest of ACs.

By comparison of kinetic runs carried out under analogous operating conditions but different AC, it is observed how values of k_{ads} are slightly higher for experiments carried out by using Norit 0.8. Contrarily, t_0 values are lower for Norit 0.8 experiments than those obtained with the rest of adsorbents.

4. Conclusions

Adsorption of leachates onto three activated carbons, i.e. Norit 0.8, Chemviron AQ40 and Picacarb 1240 has been shown to be an alternative technology to deal with this type of recalcitrant effluents.

Among the adsorbents studied, Norit 0.8 presents the best results if compared to the other two activated carbons. Thus, Norit 0.8 exhibits a slightly favourable COD isotherm shape, whereas Chemviron AQ40 and Picacarb 1240 show a rather linear COD isotherm or even unfavourable isotherm (depending on the adopted model).

In general, three-parameter models fit the experimental data better than the two-parameter models. In this sense, the Redlich–Peterson and Sips isotherms gave the best results, both models including features and assumptions from the Langmuir and Freundlich equations.

The kinetics of the process indicates a minimum adsorption time in the range 60–80 h to attain equilibrium conditions. The Lagergren equation is capable of modelling the adsorption regardless of the type and amount of activated carbon used.

In spite of the positive effect of adding activated carbon to leachates, the process seems to be prohibitive from an economic point of view. However, it can be optimized (to reduce the consumption of activated carbon) by combining the adsorption stage with other treatments. Hence, separation of humic and fulvic acids prior to the adsorption might lead to an improved use of the adsorbent. Also, oxidation steps conducted before the adsorption might result in the formation of smaller and more

easily adsorbable species. Some works can be found in the literature focused on the investigation of integrated processes [16].

Acknowledgements

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