

# Removal of BTEX, MTBE and TAME from aqueous solutions by adsorption onto raw and thermally treated lignite

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## ABSTRACT

The removal of BTEX (benzene, toluene, ethyl-benzene and m-, p-, o-xylenes), MTBE (methyl tertiary butyl ether) and TAME (tertiary amyl methyl ether) from aqueous solutions by raw ( $L_{raw}$ ) and thermally treated lignite at 250 °C, 550 °C and 750 °C ( $L_{250}$ ,  $L_{550}$  and  $L_{750}$ , respectively) was studied, through batch experiments. Selected physical characteristics of both raw and treated lignite such as surface area and pore volume distribution were determined. Competitive adsorption effects were also explored. It was proved that the examined lignite samples were quite effective in removing BTEX, MTBE and TAME from aqueous solutions, with sample treated at 750 °C being the most effective. Among the contaminants, BTEX appeared to have the strongest affinity, based on mass uptake by lignite samples. BTEX presence was found to significantly prevent MTBE and TAME adsorption on lignite (up to ~55%). In all cases, equilibrium was achieved within 3 h. The kinetics data proved a closer fit to the pseudo second order model, while the isotherm experimental data were a better fit to the Freundlich model, producing in some cases values of the isotherm constant  $1/n$  less than one, indicating favorable adsorption. Respective batch experiments using commercial activated carbon (AC) were also conducted for comparison.

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## 1. Introduction

Water pollution phenomena have rapidly become more and more frequent and acute in recent decades. BTEX (benzene–toluene–ethyl-benzene and xylenes), MTBE (methyl tertiary butyl ether) and TAME (tert-amyl methyl ether) represent some of the most typical groundwater petroleum contaminants which have toxic and/or carcinogenic properties. Their frequent use in many industrial applications (e.g. printing and leather industries, rubber manufacture, etc.), as well as their occurrence in petroleum fuels (e.g. gasoline), has led to their extensive discharge into the aqueous environment, either through wastewater mismanagement or accidents. The most common sources of BTEX, but also MTBE and TAME, pollution in the environment appear to be leakages from underground gasoline storage tanks into groundwater and discharge from refineries [1].

The removal of these common petroleum contaminants from groundwater has been widely studied and several processes have been successfully applied, including bioremediation/natural attenuation, volatilization (air stripping/air sparging), chemical oxidation, as well as adsorption. However, in practice, the utilization of these removal processes on a large scale presents certain

advantages and disadvantages as far as applicability, site dependence, efficiency and cost parameters are concerned.

Adsorption is a process that can be applied both in situ (with permeable reactive barriers) and ex situ, it is relatively simple (compared to others), and can achieve satisfactory removal efficiencies. Activated carbon is perhaps the most widely used adsorbent for organic compounds, due to its high adsorption capacity. Yet, activated carbon is a relatively expensive material that also has a high regeneration/reactivation cost. Generally, in order to evaluate and select an adsorbent, other parameters have to be determined and taken into account (apart from its adsorption capacity), such as the resources needed for its production and regeneration, its availability and environmental compatibility. Therefore, recent research has focused on finding new, preferably natural, abundant and cheap materials for replacing activated carbon as an organic compound adsorbent. BTEX removal from water by adsorption on resins [2], surfactant modified zeolites [3], organo-clays [4], carbon nanotubes [5] and diatomite [6] have already given an interesting perspective. Moreover, porous polymeric adsorbents [7], silicalite, mordenite, zeolite- $\beta$  [8], as well as polymer [9], synthetic [10], carbonaceous [11] and solvent impregnated [12] resins and high silica [13], granular [14] and silicate-1/fly ash cenosphere (S/FAC) [15] zeolites have also been successfully tested for the removal of MTBE from water. For TAME adsorption, so far only bituminous-coal activated carbon [16] and commercial activated carbon [17] have been used.

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### Nomenclature

$q_e$	moles of adsorbate adsorbed at equilibrium per mass of adsorbent [ $\text{mmol g}^{-1}$ ]
$q_t$	moles of adsorbate adsorbed at time $t$ per mass of adsorbent [ $\text{mmol g}^{-1}$ ]
$C_t$	concentration of adsorbate in the aqueous phase at equilibrium [ $\text{mmol L}^{-1}$ ]
$t$	adsorption time [h]
$k_1$	pseudo-first order rate constant [ $\text{h}^{-1}$ ]
$k_2$	pseudo-second order rate constant [ $\text{g mmol}^{-1} \text{h}^{-1}$ ]
$k_p$	diffusion rate constant [ $\text{mmol g}^{-1} \text{h}^{-0.5}$ ]
$x_i$	intraparticle diffusion model constant [ $\text{mmol g}^{-1}$ ]
$k_H$	Henry isotherm constant [ $\text{L g}^{-1}$ ]
$k_F$	Freundlich isotherm constant (related to the maximum adsorption capacity) [ $\text{mmol g}^{-1} (\text{L mmol}^{-1})^{1/n}$ ]
$1/n$	Freundlich isotherm constant that provides an indication of how favorable the adsorption process is [dimensionless]
$k_L$	Langmuir isotherm constant (related to the affinity of the adsorbent and the adsorbate) [ $\text{L mmol}^{-1}$ ]
$Q_0$	Langmuir isotherm constant that indicates the maximum adsorbate quantity needed to fully cover the surface of the adsorbent with one layer [ $\text{mmol g}^{-1}$ ]

In this study, raw and thermally modified lignite have been tested for their adsorption potential for BTEX, MTBE and TAME from aqueous solutions.

Lignite constitutes the youngest type of coal [18] and is abundant in Greece with proven national reserves estimated at almost 5 billion tonnes, scattered across the entire Greek region, of which 3.2 billion tonnes are considered exploitable reserves suitable for electricity generation [19].

Lignite quality varies widely both within and across mines [19], depending on the age and the nature of the lignite, the deposition environment, as well as the geological setting [20]. Generally, lignite possesses a high oxygen content, which is fixed in the carboxyl and hydroxyl groups [21], making it suitable for the adsorption of metal and aromatic compounds (e.g. phenol) from aqueous solutions and wastewater [22].

Worldwide, lignite has already been tested for the adsorption of different elements and substances from water and wastewaters, either in its natural form (raw) or activated (thermally and/or chemically) (Table 1), presenting very positive results, even through different adsorption mechanisms. Also, the fact that lignite is plentiful and inexpensive makes it an even more attractive and cost-effective adsorbent. Therefore, in this paper, its potential to adsorb common petroleum contaminants, such as BTEX, MTBE and TAME, under specific conditions, has been explored and compared to that of activated carbon.

## 2. Materials and methods

### 2.1. Adsorbent

The lignite used in this study was obtained from a lignite field of the Hellenic Public Power Corporation S.A. at Achlada area of Florina in Northern Greece. That lignite deposit consists of repeated earthen and xylitic lignite, with interfering layers of clay and silt.

The lignite sample obtained was grated and sieved in order to obtain particles of diameter smaller than  $120 \mu\text{m}$ . This material was dried in an oven at  $105^\circ\text{C}$  for 24 h and finally stored in closed plas-

tic containers for further use. Its natural moisture was determined according to the standard ASTM D2216-05.

The lignite was analyzed for its chemical, as well as mineralogical, composition using X-ray fluorescence (XRF) spectroscopy and X-ray diffraction (XRD), respectively. Its calorific value was calculated using a LECO AC-350 calorimeter, while elemental analysis was also carried out using an A3000 EuroVector Elemental Analyzer for C, H, N, S, O determination. The ash content of the lignite was determined according to the standard ASTM D3174-04 method.

Finally, the  $\text{pH}_{\text{solution}}$  value of the raw lignite sample was determined according to the standard ASTM D4972-01 method.

During the experimental procedure, four different lignite samples were created and tested: (1) raw lignite ( $L_{\text{raw}}$ ), (2) lignite thermally modified at  $250^\circ\text{C}$  for 2 h ( $L_{250}$ ), (3) lignite thermally modified at  $550^\circ\text{C}$  for 2 h ( $L_{550}$ ) and (4) lignite thermally modified at  $750^\circ\text{C}$  for 2 h ( $L_{750}$ ). Thermal treatment was carried out in ambient air.

Small quantities ( $\sim 1\text{--}2\text{g}$ ) of these samples were used to determine their surface area, mean pore size and pore volume distribution using the Nitrogen Gas Adsorption Method and a Nova 2200 Quanta Chrome analyzer.

The commercial activated carbon used for comparison was Norit Row 0.8 Supra. According to the manufacturer, its surface area is  $1300 \text{m}^2/\text{g}$ , its apparent density is  $400 \text{kg}/\text{m}^3$  and has an alkaline pH. Its surface area, mean pore size and pore volume distribution were calculated in this study using the Nitrogen Gas Adsorption Method and a Nova 2200 Quanta Chrome analyzer.

### 2.2. Adsorbate solutions

The chemicals tested in this study were benzene (Riedel-de Haen, purity: 99.7%), toluene (Riedel-de Haen, purity: 99.7%), ethyl benzene (Fluka, purity: 99%), m-xylene (Fluka, purity 99%), p-xylene (Fluka, purity 99%), o-xylene (Fluka, purity 99%), methyl tertiary butyl ether (Riedel-de Haen, purity: 99%) and tert-amyl methyl ether (Supelco, purity: 99%).

A stock solution in methanol (Sigma-Aldrich, puriss p.a. >99.8% GC) was prepared in 25 mL glass volumetric flasks containing 2000 ppm from each of the above-mentioned contaminants, using glass gastight microliter syringes. The stock solution was transferred in a 22 mL glass vial, with a plastic screw cap and PTFE/silicone septum, sealed with Parafilm, without headspace, stored at  $4^\circ\text{C}$  in the dark and used within a one-month period for the daily creation of water solutions containing 5 ppm from each of the contaminants. These solutions were used for both the kinetics and isotherm determination batch experiments, in order to explore the adsorbent's capacity and efficiency. For the study of potential competitive effects within the water solution, three separate solutions containing BTEX, MTBE and TAME were also created and used in kinetics batch experiments.

Ultrapure water was used from a Barnstead EASYpure II RF/UV water purification system.

### 2.3. Kinetics batch experiments

Kinetics experiments were carried out in 40 mL glass vials with gas-tight caps, non permeable by organic vapors. Each vial contained 1.00 or 0.05 g of adsorbent, depending on the sample. Head space within each vial was minimized (to exclude any contaminant volatilization phenomena), while agitation was applied. First, three different adsorption temperatures were tested:  $15^\circ\text{C}$ ,  $20^\circ\text{C}$  and  $25^\circ\text{C}$ . The optimum temperature was then chosen and applied during all of the following experiments. In each of the test vials of the lignite samples, the contact time of the adsorbate and the adsorbent varied, with a maximum duration of 11 h. For

**Table 1**  
Recent studies on the use of lignite as an adsorbent of specific chemical elements and substances from water and wastewaters.

Study no.	Adsorbent (lignite)		Origin	Surface area (m <sup>2</sup> /g)	Adsorbate	Reference
	Raw	Treated				
1	●		Greece	3.62–13.99	Pb <sup>2</sup> , Cd <sup>2</sup> , Zn <sup>2</sup> , Cu <sup>2</sup>	[23]
2	●		Turkey	–	Pb <sup>2</sup>	[24]
3	■	■	USA (HD4000)	607–1031	EDC, PPCP	[25]
4		■	Bulgaria	171–293	NH <sub>4</sub> <sup>+</sup>	[26]
5	●		Czech Republic	–	Pb <sup>2</sup> , Cd <sup>2</sup> , Zn <sup>2</sup> , Cu <sup>2</sup>	[18]
6		■	Czech Republic	–	Pb <sup>2</sup> , Cd <sup>2</sup> , Zn <sup>2</sup> , Co <sup>2</sup> , Pb <sup>2</sup> , Ni <sup>2</sup> , Fe <sup>2</sup>	[27]
7	●		Turkey	2.06–2.96	Cd <sup>2</sup> , Zn <sup>2</sup>	[28]
8	●		Turkey	2.06–2.96	Cu <sup>2</sup> , Pb <sup>2</sup> , Ni <sup>2</sup>	[29]
9	●		Turkey	2.06–2.96	Cr <sup>6</sup>	[30]
10	●		USA	–	Ca <sup>2</sup> , Mn <sup>2</sup> , Zn <sup>2</sup> , Fe <sup>2</sup> , Fe <sup>3</sup>	[21]
11	●		Turkey	4.79	Phenol	[22]
12		■	Czech Republic	–	<sup>134</sup> Cs, <sup>60</sup> Co, <sup>152</sup> Eu	[31]
13	■	■	Turkey	8.71–507.20	Cr <sup>6</sup>	[32]
14	●		Turkey	–	Cu <sup>2</sup> , Zn <sup>2</sup> , Pb <sup>2</sup> , Cd <sup>2</sup>	[33]
15	●		Turkey	–	Cr <sup>3</sup>	[34]
16	●		India	–	Dyes	[35]
17		■	Turkey	1000	Malachite green	[36]
18	●		Germany	1.78	TCE, c-DCE, VC, benzene, Toluene, p-xylene	[37]
19	●		Turkey	2.56	Cu <sup>2</sup> , Zn <sup>2</sup>	[38]
20	●		Turkey	3.2	Hg <sup>2</sup> , Cd <sup>2</sup> , Pb <sup>2</sup>	[39]
21	●		Turkey	9.16–14.23	Non ionic dispersant	[40]
22	●		Czech Republic	7.6	Ag <sup>+</sup> , Cd <sup>2</sup> , Cu <sup>2</sup>	[41]
23	●		UK	–	Dyes, Cd <sup>2</sup> , Cu <sup>2</sup>	[42]
24	●	■	Greece	86–255	Phenols, COD	[43]
25	●	■	Turkey	0.00–7.60	Methylene blue	[44]
26	●		USA	–	Cr <sup>3</sup> , Cr <sup>6</sup>	[45]
27	●		China	–	Palladium	[46]
28		■	Greece	–	Mercury	[47]
29		■	France	300	Fluoranthene, hexachlorobenzene	[48]
30	●	■	China	2.79–432	Cr <sup>6</sup>	[49]

■ Lignite type used in the study.

activated carbon the maximum contact time tested was 90 min. The solution samples were then filtered (0.45 μm pore filter) and analyzed. Each experiment was carried out at least twice and included a blank sample, in order to determine and take into account any potential contaminant losses due to volatilization.

#### 2.4. Isotherm determination experiments

Isotherm determination experiments were also carried out in 40 mL glass vials with gas-tight caps, non permeable by organic vapors. Only samples  $L_{raw}$  and  $L_{750}$ , which had the highest adsorption capacity, as well as activated carbon, were used in

**Table 2**  
Chemical analysis results for raw lignite and comparison to other lignite samples.

Main chemicals	Content (%) on dry basis				
	$L_{raw}$	$L_{Florina, Greece}$ [20]	$L_{Megalopolis, Greece}$ [20]	$L_{Canada}$ [50]	$L_{Soma, Turkey}$ [22]
SiO <sub>2</sub>	55.58	26.0–48.2	51.8–57.5	39.1	33.4
Al <sub>2</sub> O <sub>3</sub>	13.47	12.5–26.1	20.8–23.4	17.9	16.1
Fe <sub>2</sub> O <sub>3</sub>	12.06	10.0–11.1	7.2–10.8	7.1	6.0
CaO	5.10	6.9–32.6	5.5–8.5	16.5	33.8
K <sub>2</sub> O	4.46	0.3–0.6	2.0–2.5	0.5	0.7
MgO	3.24	2.8–3.2	2.0–2.4	3.5	6.1
SO <sub>3</sub>	2.55	2.9–12.9	0.7–3.4	n.r.	2.8
Na <sub>2</sub> O	1.52	<0.1–0.1	0.2–0.4	5.8	1.1
TiO <sub>2</sub>	1.42	0.6–1.1	Traces	0.9	n.r.
P <sub>2</sub> O <sub>5</sub>	0.18	0.3–0.6	0.2–0.4	n.r.	n.r.

n.r.: Not reported.

**Table 3**C, H, N, S, O and ash content, calorific value,  $\text{pH}_{\text{solution}}$  and specific surface of raw lignite—comparison to typical values for Greek lignites.

Property	Units	Value (on dry basis)	Typical values for Greek lignites (on dry basis) [20,23]
C	%	32.39	14.1–40.2
H	%	3.03	1.1–3.2
N	%	0.58	0.2–1.0
S	%	1.26	0.1–4.3
O	%	14.32	6.5–14.7
Ash	%	40.11	9.8–59.34
Calorific value	cal/g	3220.4	930–3580
Specific surface (BET)	$\text{m}^2/\text{g}$	11.40	–
$\text{pH}_{\text{solution}}$		5.39	–

**Table 4**

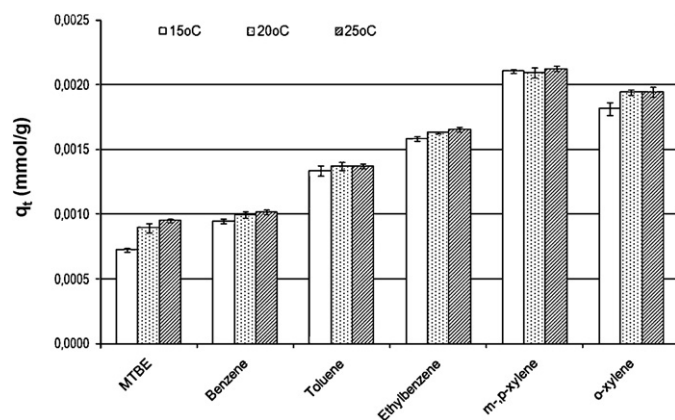
Specific surface, mean pore size and pore volume distribution of the four lignite and the activated carbon samples.

Sample	Micropore volume ( $\text{cm}^3/\text{g}$ )	Mesopore volume ( $\text{cm}^3/\text{g}$ )	Micropore area ( $\text{m}^2/\text{g}$ )	Mesopore area (external surface area) ( $\text{m}^2/\text{g}$ )	Surface area ( $S_{\text{BET}}$ ) ( $\text{m}^2/\text{g}$ )	Total pore volume ( $\text{cm}^3/\text{g}$ )	Average pore radius ( $\text{\AA}$ )
$L_{\text{raw}}$	0.0009	0.0147	2.3780	9.0220	11.40	0.0156	54.780
$L_{250}$	0.0086	0.0396	19.029	18.511	37.54	0.0482	50.928
$L_{550}$	0.0171	35.297	0.0490	24.487	59.78	0.0661	44.237
$L_{750}$	0.0321	64.461	0.0586	30.734	95.19	0.0908	38.139
Activated carbon	0.5612	1,168.0	0.1993	203.15	1,371	0.7606	22.188

these experiments. Each vial contained the adsorbent in different amounts: 0.001, 0.005, 0.01, 0.025, 0.05, 0.1 and 0.5 g for lignite and 0.01, 0.025, 0.05, 0.075 and 0.1 g for activated carbon. Head space within each beaker was minimized, while agitation, contact time (3 h for lignite and 60 min for activated carbon) and temperature were maintained constant throughout. The solution samples were then filtered (0.45  $\mu\text{m}$  pore filter) and analyzed. Each experiment was carried out at least twice and included a blank sample, in order to determine and take into account any potential contaminant losses due to volatilization.

### 2.5. Chemical analysis method

The chemical analysis of the solution samples was performed on a GC-2010 Shimadzu gas chromatographer, coupled to a QP-2010 Plus mass spectrometer, using the Headspace Solid Phase Micro Extraction (HS-SPME) method. A 65  $\mu\text{m}$  polydimethyl siloxane/divinylbenzene (PDMS/DVB) fiber was exposed to the headspace of the sample (10 mL), placed in a 22 mL glass vial, for 20 min at 20 °C, under continuous stirring at 1400 rpm.

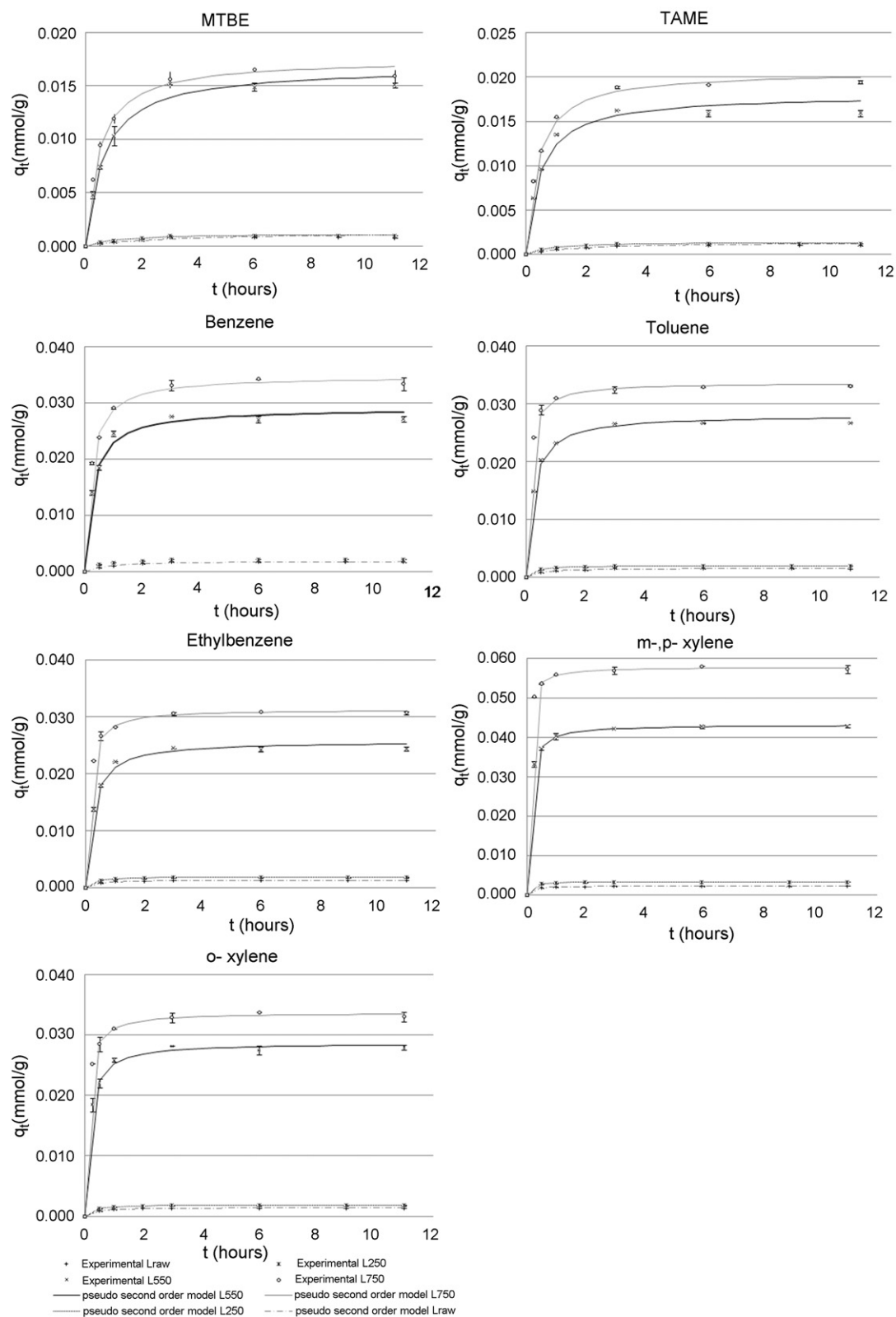


**Fig. 1.** The adsorbed moles of each contaminant per mass of the adsorbate used ( $\text{mmol g}^{-1}$ ) ( $q_e$ ) in relation to the adsorbent–adsorbate contact time ( $t$  in h), for each adsorption temperature tested using  $L_{\text{raw}}$  ( $C = 5 \text{ mg L}^{-1}$  from each contaminant,  $m_{\text{raw}} = 1 \text{ g}$ ,  $t_{\text{eq}} = 3 \text{ h}$ ).

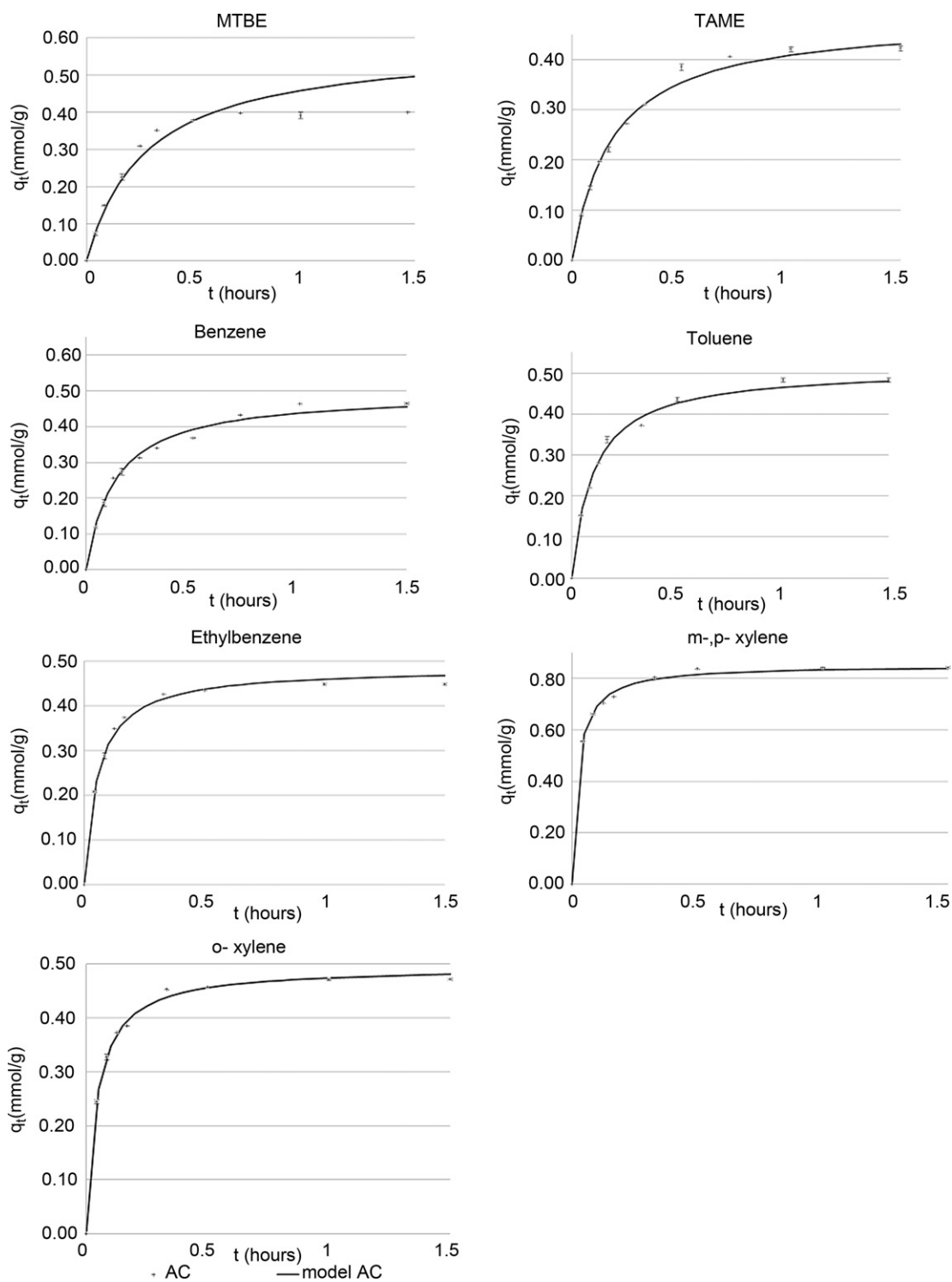
**Table 5**

Results of the pseudo second order model fits for the experimental data.

Adsorbate	Pseudo second order model		
	$k_2$ ( $\text{g mmol}^{-1} \text{h}^{-1}$ )	$q_e$ ( $\text{mmol g}^{-1}$ )	$R^2$
$L_{\text{raw}}$			
Benzene	$6.9 \pm 0.9 \text{ E}+02$	$1.8 \pm 0.1 \text{ E}-03$	0.9910
Toluene	$1.3 \pm 0.1 \text{ E}+03$	$1.6 \pm 0.0 \text{ E}-03$	0.9930
Ethyl-benzene	$2.4 \pm 0.2 \text{ E}+03$	$1.3 \pm 0.0 \text{ E}-03$	0.9877
m-,p-xylene	$2.8 \pm 0.3 \text{ E}+03$	$2.3 \pm 0.0 \text{ E}-03$	0.9798
o-xylene	$2.5 \pm 0.3 \text{ E}+03$	$1.4 \pm 0.0 \text{ E}-03$	0.9816
MTBE	$2.5 \pm 0.8 \text{ E}+02$	$1.4 \pm 0.2 \text{ E}-03$	0.9905
TAME	$4.0 \pm 0.8 \text{ E}+02$	$1.4 \pm 0.1 \text{ E}-03$	0.9920
$L_{250}$			
Benzene	$1.0 \pm 0.1 \text{ E}+03$	$2.3 \pm 0.0 \text{ E}-03$	0.9815
Toluene	$1.9 \pm 0.2 \text{ E}+03$	$2.0 \pm 0.0 \text{ E}-03$	0.9819
Ethyl-benzene	$2.4 \pm 0.2 \text{ E}+03$	$1.8 \pm 0.0 \text{ E}-03$	0.9821
m-,p-xylene	$2.8 \pm 0.1 \text{ E}+03$	$3.3 \pm 0.0 \text{ E}-03$	0.9903
o-xylene	$2.7 \pm 0.2 \text{ E}+03$	$1.9 \pm 0.0 \text{ E}-03$	0.9839
MTBE	$7.9 \pm 1.2 \text{ E}+02$	$1.1 \pm 0.1 \text{ E}-03$	0.9876
TAME	$9.1 \pm 1.0 \text{ E}+02$	$1.4 \pm 0.0 \text{ E}-03$	0.9899
$L_{550}$			
Benzene	$1.3 \pm 0.2 \text{ E}+02$	$2.9 \pm 0.1 \text{ E}-02$	0.9849
Toluene	$1.7 \pm 0.1 \text{ E}+02$	$2.8 \pm 0.0 \text{ E}-02$	0.9910
Ethyl-benzene	$1.8 \pm 0.2 \text{ E}+02$	$2.6 \pm 0.0 \text{ E}-02$	0.9911
m-,p-xylene	$3.0 \pm 0.1 \text{ E}+02$	$4.3 \pm 0.0 \text{ E}-02$	0.9978
o-xylene	$2.5 \pm 0.2 \text{ E}+02$	$2.9 \pm 0.0 \text{ E}-02$	0.9872
MTBE	$9.7 \pm 0.9 \text{ E}+01$	$1.7 \pm 0.1 \text{ E}-02$	0.9968
TAME	$1.3 \pm 0.2 \text{ E}+02$	$1.8 \pm 0.0 \text{ E}-02$	0.9875
$L_{750}$			
Benzene	$1.4 \pm 0.1 \text{ E}+02$	$3.5 \pm 0.1 \text{ E}-02$	0.9924
Toluene	$3.2 \pm 0.2 \text{ E}+02$	$3.4 \pm 0.0 \text{ E}-02$	0.9898
Ethyl-benzene	$3.2 \pm 0.2 \text{ E}+02$	$3.1 \pm 0.0 \text{ E}-02$	0.9923
m-,p-xylene	$4.7 \pm 0.3 \text{ E}+02$	$5.8 \pm 0.0 \text{ E}-02$	0.9887
o-xylene	$3.5 \pm 0.2 \text{ E}+02$	$3.4 \pm 0.0 \text{ E}-02$	0.9927
MTBE	$1.3 \pm 0.1 \text{ E}+02$	$1.7 \pm 0.1 \text{ E}-02$	0.9967
TAME	$1.3 \pm 0.8 \text{ E}+02$	$2.1 \pm 0.0 \text{ E}-02$	0.9975
AC			
Benzene	$1.5 \pm 0.1 \text{ E}+01$	$5.0 \pm 0.1 \text{ E}-01$	0.9954
Toluene	$2.0 \pm 0.2 \text{ E}+01$	$5.1 \pm 0.2 \text{ E}-01$	0.9928
Ethyl-benzene	$3.8 \pm 0.2 \text{ E}+01$	$4.9 \pm 0.1 \text{ E}-01$	0.9943
m-,p-xylene	$5.1 \pm 0.4 \text{ E}+01$	$8.5 \pm 0.1 \text{ E}-01$	0.9866
o-xylene	$4.8 \pm 0.2 \text{ E}+01$	$4.9 \pm 0.1 \text{ E}-01$	0.9965
MTBE	$6.3 \pm 1.6 \text{ E}+00$	$5.9 \pm 0.6 \text{ E}-01$	0.9885
TAME	$1.1 \pm 0.1 \text{ E}+01$	$4.8 \pm 0.2 \text{ E}-01$	0.9967



**Fig. 2.** The adsorbed moles of each contaminant per mass of the adsorbate used ( $\text{mmol g}^{-1}$ ) ( $q_e$ ) in relation to the adsorbent-adsorbate contact time ( $t$  in h), for each of the four lignite samples examined ( $C = 5 \text{ mg L}^{-1}$  from each contaminant,  $m_{\text{raw},250} = 1 \text{ g}$  and  $m_{550,750} = 0.05 \text{ g}$ ).



**Fig. 3.** The adsorbed mass of each contaminant per mass of the adsorbate used ( $\text{mmol g}^{-1}$ ) ( $q_e$ ) in relation to the adsorbent–adsorbate contact time ( $t$  in h), for activated carbon ( $C = 50 \text{ mg L}^{-1}$  from each contaminant,  $m_{AC} = 0.05 \text{ g}$ ).

Sodium chloride (3 g) was added in the sample before its analysis. Then the fiber was introduced in the GC injector at  $230^\circ\text{C}$  for 2 min and the desorbed analytes were carried, using Helium, through a SPB<sup>TM</sup>-1 ( $15 \text{ m} \times 0.2 \text{ mm} \times 0.2 \mu\text{m}$ ) capillary column. The ion source and GC–MS interface temperatures were  $200^\circ\text{C}$  and  $280^\circ\text{C}$ , respectively. Toluene- $d_8$  was used as the internal standard.

### 3. Results and discussion

#### 3.1. Adsorbents characteristics

The natural moisture of raw lignite was determined to be 12.5%, while the results obtained from its chemical analysis are presented in Table 2. As it turned out, the obtained percentages of specific



**Table 6**  
Maximum adsorbed moles of each contaminant per mass of the adsorbate used ( $\text{mmol g}^{-1}$ ) ( $q_e$ ), using different aqueous solutions and samples  $L_{\text{raw}}$ ,  $L_{750}$  and AC, under the examined experimental conditions.

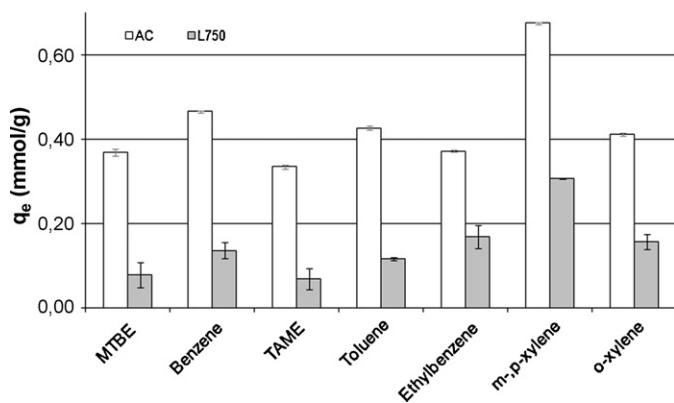
$q_e$ ( $\text{mmol g}^{-1}$ )	MTBE	Benzene	TAME	Toluene	Ethylbenzene	m-,p-Xylene	o-Xylene
Mix of all analytes							
$L_{\text{raw}}$	0.0008	0.0016	0.0010	0.0014	0.0012	0.0022	0.0013
$L_{750}$	0.0159	0.0333	0.0194	0.0331	0.0307	0.0572	0.0330
AC	0.3995	0.4648	0.4225	0.4837	0.4490	0.8419	0.4722
BTEX only							
$L_{\text{raw}}$		0.0016		0.0014	0.0013	0.0022	0.0013
$L_{750}$		0.0348		0.0343	0.0320	0.0594	0.0351
AC		0.4934		0.5129	0.4381	0.8341	0.4781
MTBE only							
$L_{\text{raw}}$	0.0015						
$L_{750}$	0.0303						
AC	0.7569						
TAME only							
$L_{\text{raw}}$			0.0017				
$L_{750}$			0.0330				
AC			0.6315				

common chemicals did not identify with those determined by other researchers for samples from the same lignite basin of Florina, as well as lignite samples from different areas of Greece and the world generally. Actually, there was quite a wide variation of values – a fact that was perhaps expected, given the different lignite formation periods and processes in the geological environment of the lignite deposits. Significantly high percentages of  $\text{SiO}_2$  could be attributed to high concentrations of quartz, clay and probably feldspars [20].

The main minerals that comprise the lignite sample of this study were found to be muscovite, kaolinite, gypsum, quartz and mullite. The remaining properties of the  $L_{\text{raw}}$  examined are summarized in Table 3.

Compared to typical values for Greek lignite samples the ash content is representative, the calorific value was close to the upper limit, whereas C, H, N, S and O content values were typical. As for the surface area, the acquired value can be considered satisfying as it is close to the higher typical values, according to the values included in Table 1 for various raw lignite samples.

Table 4 presents the results of the surface area, mean pore size and pore volume distribution analyses for all of the examined lignite samples, as well as the activated carbon sample. Thermal treatment at  $750^\circ\text{C}$  results in the maximum increase in the surface area of lignite (almost nine times), as well as a decrease in the average pore radius. This can be expected to inflict a respective increase in the adsorption capacity of sample  $D_{750}$ .



**Fig. 4.** Comparison of the adsorbed moles of each contaminant per mass of the adsorbate used ( $\text{mmol g}^{-1}$ ) ( $q_e$ ) for  $L_{750}$  and activated carbon at equilibrium (3 h and 60 min, respectively) ( $C = 50 \text{ mg L}^{-1}$  from each contaminant,  $m_{\text{adsorbent}} = 0.05 \text{ g}$ ).

The pH values of aqueous solutions of the lignite samples  $L_{250}$ ,  $L_{550}$  and  $L_{750}$  and the activated carbon sample were measured to be 6.39, 8.42 and 10.63 and 10.79, respectively. This indicates that the thermal treatment of lignite gives a more “basic character” to its aqueous solutions.

### 3.2. Adsorption kinetics

The adsorbed moles of each contaminant per mass of the adsorbate used ( $\text{mmol g}^{-1}$ ) ( $q_e$ ) in relation to the adsorbent–adsorbate contact time ( $t$  in h), for each of the 3 adsorption temperatures tested using sample  $L_{\text{raw}}$ , is presented in Fig. 1. No substantial differences were observed, especially at  $20^\circ\text{C}$  and

**Table 7**  
Results of the Freundlich fits for the experimental data.

Sample	Freundlich Isotherm		
	$k_F$ ( $\text{mmol g}^{-1} (\text{L mmol}^{-1})^{1/n}$ )	$1/n$	$R^2$
<b>Benzene</b>			
$L_{\text{raw}}$	$2.8 \pm 1.3 \text{ E}+04$	$5.0 \pm 0.2 \text{ E} 00$	0.9834
$L_{750}$	$2.2 \pm 0.1 \text{ E} -01$	$1.1 \pm 0.0 \text{ E} 00$	0.9941
AC	$1.3 \pm 1.0 \text{ E} 00$	$3.7 \pm 0.1 \text{ E} -01$	0.9946
<b>Toluene</b>			
$L_{\text{raw}}$	$1.4 \pm 0.5 \text{ E}+02$	$2.7 \pm 0.1 \text{ E} 00$	0.9804
$L_{750}$	$1.5 \pm 0.0 \text{ E} -01$	$3.1 \pm 0.1 \text{ E} -01$	0.9944
AC	$1.5 \pm 0.1 \text{ E} 00$	$3.2 \pm 0.1 \text{ E} -01$	0.9937
<b>Ethylbenzene</b>			
$L_{\text{raw}}$	$4.5 \pm 1.0 \text{ E} 00$	$1.5 \pm 0.1 \text{ E} 00$	0.9836
$L_{750}$	$3.8 \pm 0.3 \text{ E} -01$	$5.3 \pm 0.2 \text{ E} -01$	0.9870
AC	$6.4 \pm 0.2 \text{ E} -01$	$2.5 \pm 0.1 \text{ E} -01$	0.9924
<b>m-p-xylene</b>			
$L_{\text{raw}}$	$3.6 \pm 0.1 \text{ E} 00$	$1.6 \pm 0.0 \text{ E} 00$	0.9903
$L_{750}$	$4.0 \pm 0.2 \text{ E} -01$	$3.8 \pm 0.1 \text{ E} -01$	0.9932
AC	$1.2 \pm 0.0 \text{ E} 00$	$2.1 \pm 0.1 \text{ E} -01$	0.9927
<b>o-xylene</b>			
$L_{\text{raw}}$	$1.9 \pm 0.5 \text{ E}+01$	$1.9 \pm 0.1 \text{ E} 00$	0.9821
$L_{750}$	$2.4 \pm 0.1 \text{ E} -01$	$3.8 \pm 0.1 \text{ E} -01$	0.9911
AC	$9.9 \pm 0.4 \text{ E} -01$	$2.0 \pm 0.1 \text{ E} -01$	0.9915
<b>MTBE</b>			
$L_{\text{raw}}$	$2.9 \pm 2.6 \text{ E}+14$	$1.4 \pm 0.1 \text{ E}+01$	0.9800
$L_{750}$	$9.0 \pm 0.3 \text{ E} -02$	$3.1 \pm 0.1 \text{ E} 00$	0.9874
AC	$9.7 \pm 0.3 \text{ E} -01$	$1.7 \pm 0.0 \text{ E} 00$	0.9971
<b>TAME</b>			
$L_{\text{raw}}$	$2.8 \pm 2.3 \text{ E}+11$	$1.0 \pm 0.0 \text{ E}+01$	0.9827
$L_{750}$	$3.1 \pm 0.3 \text{ E} -01$	$3.3 \pm 0.1 \text{ E} 00$	0.9831
AC	$1.8 \pm 0.1 \text{ E} 00$	$5.7 \pm 0.2 \text{ E} -01$	0.9837

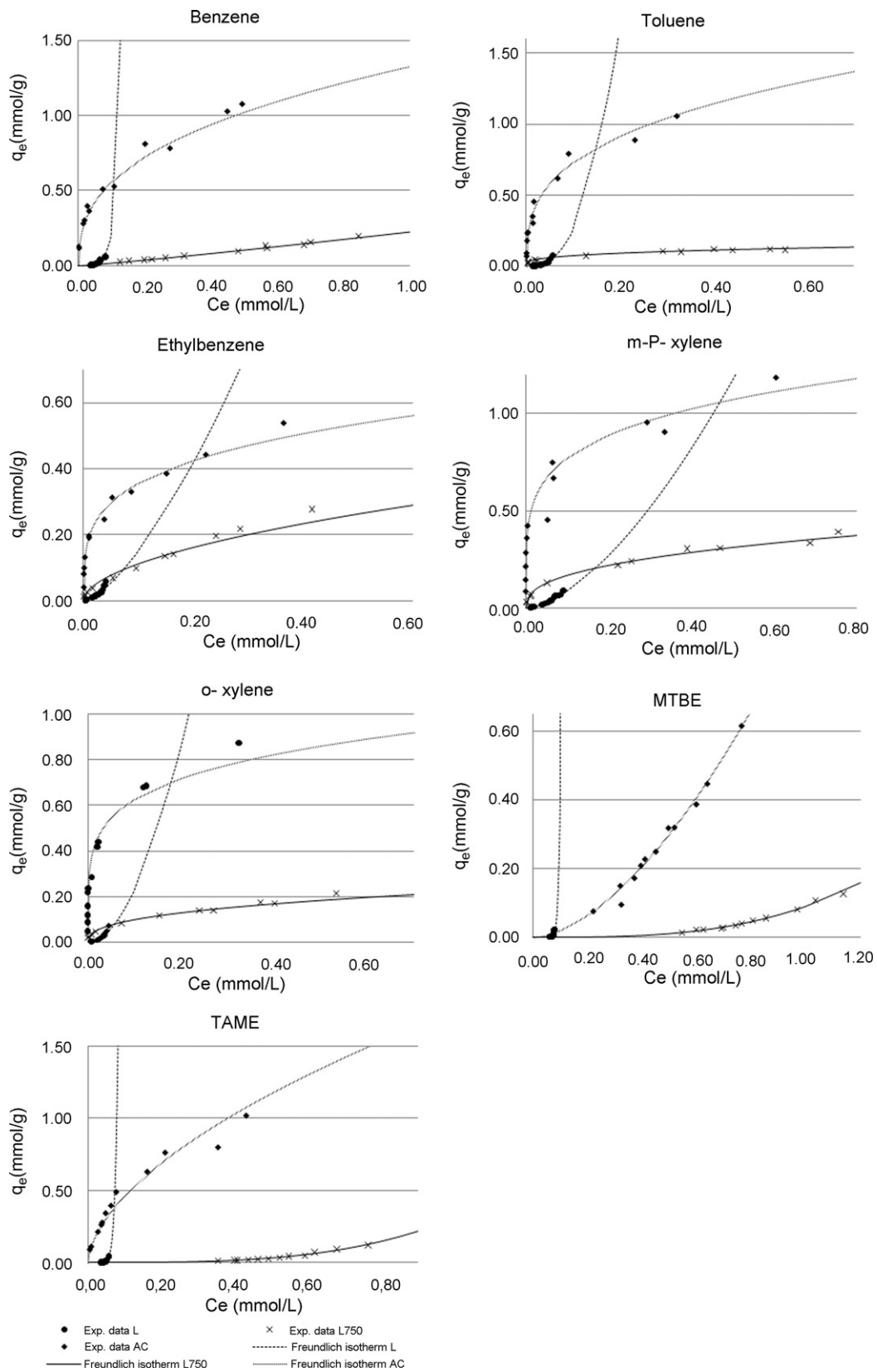


Fig. 5. Calculated Freundlich isotherms for samples  $L_{raw}$ ,  $L_{750}$  and AC.

25°C. This means that a 10°C variation at the selected range of water temperatures (which may be considered as representative for natural groundwater) does not greatly influence lignite's adsorption capacity for the specific contaminants under

the examined conditions. The value of 20°C was finally chosen for the conduction of the following experiments, as an average, realistic and representative temperature of underground waters.



The kinetics experiments using samples  $L_{\text{raw}}$ ,  $L_{250}$ ,  $L_{550}$  and  $L_{750}$  at 20 °C showed that after about 3 h of contact between the adsorbate and the adsorbent, the change of the liquid-phase concentration of the adsorbate ( $C_e$ ) became insignificant and it can therefore be assumed that equilibrium was reached. This time period needed for reaching equilibrium can be considered short, compared to others reported for the adsorption of the same contaminants by other adsorbents [6,2,4,51].

The adsorption of the selected contaminants on lignite generally increased after thermal treatment, especially at temperatures 550 °C and 750 °C. This phenomenon is clearly illustrated in Fig. 2 and can be attributed to the fact that, through thermal treatment, lignite is activated and its available surface area significantly increases.

In order to interpret the kinetic batch experimental data, three different kinetic models were used: (1) the *pseudo-first-order* kinetic model (Eq. (1)) [52], (2) the *pseudo-second-order* kinetic model (Eq. (2)) [53] and (3) the *intraparticle diffusion model* (Eq. (3)) [54].

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

$$\frac{1}{q_t} = \frac{1}{q_e^2 k_2} \cdot \frac{1}{t} + \frac{1}{q_e} \quad (2)$$

$$q_t = x_i + k_p t^{1/2} \quad (3)$$

The value of  $k_1$  was obtained by plotting  $\ln(q_e - q_t)$  against  $t$ , the value of  $k_2$  was obtained by plotting  $1/q_t$  against  $1/t$ , while the value of  $k_p$  was obtained by plotting  $q_t$  against  $t^{1/2}$ .

All the experimental data best fitted the pseudo second order kinetics model, providing correlation coefficient ( $R^2$ ) values ranging from 0.9798 up to 0.9978. The calculated values of the pseudo-second order kinetics constants  $k_2$  and  $q_e$  are presented in Table 5. Based on the  $q_e$  values, it is confirmed that thermal treatment indeed increased lignite's adsorption capacity. In the same time, thermal treatment increased the kinetics rate of the adsorption, providing higher  $k_2$  values. This is obvious, by comparing samples  $L_{\text{raw}}-L_{250}$  and  $L_{550}-L_{750}$  that were used in equal quantities in solutions of equal concentrations (1 g in solution of 5 ppm and 0.05 g in solution of 5 ppm, respectively).

As far as the adsorbent preference in the available adsorbates is concerned, it seemed (based on Fig. 2 and Table 5) to decrease in the following order: m-,p-xylene  $\rightarrow$  o-xylene  $\rightarrow$  ethylbenzene  $\rightarrow$  toluene  $\rightarrow$  benzene  $\rightarrow$  TAME  $\rightarrow$  MTBE. This order approximately corresponds to the adsorbates' descending order of hydrophobicity (based on their octanol-water coefficient log values: 3.15, 2.77, 3.15, 2.69, 2.13,  $\sim$ 1.68 and  $\sim$ 1.06, respectively), molecular weight (106, 106, 106, 92, 78, 102, 88 g mol $^{-1}$ , respectively) [52] and ascending order of water solubility (198, 175, 152, 515, 1700,  $\sim$ 5000 and  $\sim$ 47,000 mg L $^{-1}$ , respectively) [55]. Generally, it seems that the most soluble and hydrophilic substances (TAME and MTBE) have less tendency to adsorb onto the lignite samples.

Compared to activated carbon kinetic results (Fig. 3), all tested lignite samples displayed an equilibrium time 3 times longer, while even sample  $L_{750}$  presented more than 5,5 times lower adsorption capacities (Fig. 4).

The experiments conducted in order to explore potential competition phenomena that may appear in the BTEX-MTBE-TAME-lignite ( $L_{\text{raw}}$  and  $L_{750}$ ) system showed that BTEX were clearly preferred by the adsorbents used in this study, against TAME and MTBE that were the contaminants with the lowest adsorption tendency (Table 6). In fact their presence in the solution does not really influence their adsorption on lignite or activated carbon. This is attributed not only to the physicochemical properties of TAME and MTBE, but also to the presence of BTEX, that

rapidly covers the vast available surface of lignite. BTEX's lower solubility in water, as well as its higher hydrophobia, compared to that of TAME and MTBE, also promote and accelerate BTEX adsorption onto lignite and activated carbon. As a result, when TAME and MTBE are the sole adsorbates present, their adsorption is significantly higher ( $\sim$ 55%) than when BTEX are also present.

BTEX always co-exist in a contaminated site, as a result of a gasoline spill. Therefore a detailed study of the potential competitive adsorption of these contaminants onto lignite and/or activated carbon would be of little value. However, based on this study, it appears that xylenes are the components with the highest adsorption tendency onto both lignite and activated carbon and benzene the one with the lowest.

### 3.3. Adsorption isotherms

For the interpretation of the isotherm determination experimental data, three different yet very frequently applied models were used in their linear form: (1) the *Henry model* (Eq. (4)) [52]; (2) the *Freundlich model* (Eq. (5)), which has proved to be satisfactory for low concentrations and often gives an initial surface adsorption followed by a condensation effect, resulting from extremely strong solute-solute interaction; and (3) the *Langmuir model* (Eq. (6)).

$$q_e = k_H C_e \quad (4)$$

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad (5)$$

$$\frac{C_e}{q_e} = \frac{1}{k_L Q_0} + \frac{1}{Q_0} C_e \quad (6)$$

The Freundlich model best fitted the experimental data, based on its relatively high values of correlation coefficient  $R^2$  (compared to those derived from the other two models examined) that varied between 0.9800 and 0.9971. The calculated values of the Freundlich constants  $K_F$  and  $1/n$  for each of the tested adsorbates and adsorbents ( $L_{\text{raw}}$ ,  $L_{750}$ , AC) are presented in Table 7.

The Freundlich constant  $1/n$  was calculated to be higher than unity for all the adsorbates when sample  $L_{\text{raw}}$  was used, indicating that the adsorption of the selected contaminants onto the raw lignite sample is not favorable. Values of  $1/n$  lower than 1 were first observed when sample  $L_{750}$  was used, with the exception of MTBE, benzene and TAME (which however presented lower values in comparison to sample  $L_{\text{raw}}$ ), suggesting that adsorption is more favorable on this thermally treated lignite sample. Finally, when activated carbon was used, every adsorbate, with the exception of MTBE, presented  $1/n$  values lower than 1 and substantially lower than those calculated for the lignite samples.

A graphical representation of the calculated isotherms for samples  $L_{\text{raw}}$ ,  $L_{750}$  and AC is shown in Fig. 5. As it is obvious, activated carbon presents significantly higher adsorption capacity than lignite (raw and thermally treated at 750 °C) for any examined concentration, confirming its superiority as an adsorbent of organic substances. However, MTBE adsorption on activated carbon seems to fall short, at least compared to that of the rest examined contaminants, verifying activated carbon's weakness in adsorbing MTBE from aqueous solutions.

## 4. Conclusions

The goal of this paper was to explore and present lignite's capacity to adsorb certain common petroleum contaminants. Therefore, raw and thermally treated lignite was used for the adsorption of BTEX, MTBE and TAME from aqueous solutions. Lignite's adsorption performance was compared to that of activated carbon and finally the following major conclusions were drawn:

- The thermal treatment of lignite resulted in a significant increase in its surface area (up to 835% for sample  $L_{750}$ ), enhancing its adsorption capacity.
- Adsorption equilibrium was reached within 3 h; a period that is 3 times longer than that needed when activated carbon was used as the adsorbent of the examined contaminants, but it can still be considered quite short at least for in situ applications, such as permeable reactive barriers. In this case, however, the amount of the lignite needed, as well as its total cost compared with those of activated carbon, must be carefully calculated, in order to evaluate lignite's overbalance. Of course, other parameters must also be taken into account, such as environmental protection and energy saving, during the adsorbent's production.
- Based on the results acquired, the pseudo second order kinetic model could be used in any potential BTEX–MTBE–TAME–lignite system under the same conditions used in this project, in order to predict other adsorption kinetic data.
- Lignite heated at 750 °C presented the highest adsorption of the examined contaminants, ranging from 0.0159 mmol g<sup>-1</sup> for MTBE to 0.0572 mmol g<sup>-1</sup> for m-,p-xylene ( $C_0 = 5$  ppm,  $m_{L750} = 0.05$  g,  $T = 20$  °C).
- The adsorbent preference in the available adsorbates decreases in the following order: m-,p-xylene → o-xylene → ethylbenzene → toluene → benzene → TAME → MTBE. As a result, the presence of BTEX significantly reduces MTBE and TAME adsorption on lignite, due to competitive effects.
- The Freundlich model best fits the isotherm experimental data, providing lower 1/n values (more favorable adsorption) as the heating temperature of the lignite increases.

Summarizing, it is important to note that lignite, due not only to its abundance and low cost but also to its promising adsorption properties recorded in this study for BTEX, MTBE and TAME, could constitute a suitable filling material for a permeable reactive barrier, designed and installed to treat gasoline contaminated aquifers. Although its efficiency cannot reach that of the activated carbon, it may be considered as a cheap substitute under certain conditions that should be determined in a detailed technical-economical study. Moreover, the possibility that lignite may not necessarily be subject to costly regeneration or disposal requirements, but can be burned and its calorific value exploited [22], makes it even more appealing. Clearly, this area of research warrants further studies to be conducted, such as column tests, modeling and pilot-tests, and a detailed cost-benefit analysis.

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