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BTEX and MTBE adsorption onto raw and thermally modified diatomite

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ABSTRACT

The removal of BTEX (benzene, toluene, ethyl-benzene and xylenes) and MTBE (methyl tertiary butyl ether) from aqueous solution by raw (D_R) and thermally modified diatomite at 550, 750 and 950 °C (D_{550}, D_{750} and D_{950} respectively) was studied. Physical characteristics of both raw and modified diatomite such as specific surface, pore volume distribution, porosity and $pH_{solution}$ were determined, indicating important structural changes in the modified diatomite, due to exposure to high temperatures. Both adsorption kinetic and isotherm experiments were carried out. The kinetics data proved a closer fit to the pseudo-second order model. Maximum values for the rate constant, k_2, were obtained for MTBE and benzene (48.9326 and 18.0996 g mg^{-1} h^{-1}, respectively) in sample D_{550}. The isotherm data proved to fit the Freundlich model more closely, which produced values of the isotherm constant $1/n$ higher than one, indicating unfavorable adsorption. The highest adsorption capacity, calculated through the values of the isotherm constant k_F, was obtained for MTBE (48.42 mg kg^{-1} (mg/L)^n) in sample D_{950}.

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1. Introduction

In recent decades, water pollution phenomena have become more and more frequent and acute. Petroleum hydrocarbons represent one of the most common categories of groundwater pollutants that are found at many contaminated sites, making surface water and/or groundwater unsuitable for many uses (including drinking), due to their toxic and/or carcinogenic properties.

BTEX are typical hazardous organic compounds that are present in almost any petrol or gasoline spill on the soil's surface or in the subsurface. These pollutants have been found to cause many serious health side effects to humans (e.g. skin and sensory irritation, central nervous system depression, respiratory problems, leukemia, cancer, as well as disturbance of kidney, liver and blood systems) and therefore their removal from groundwater and surface waters is essential.

MTBE is also a very persistent and hazardous water contaminant that can be found at many gasoline-contaminated sites, given that it represents a very common oxygen additive to gasoline, which has been used since the middle 1970s to increase its burning efficiency and thereby reduce emissions of carbon monoxide and other organic compounds. MTBE is highly soluble in water (~23,200–54,000 mg/L) [1–3] and can be carried far away from the contamination source very quickly. Its high mobility can be verified by the fact that MTBE has been detected in the drinking water [4], rivers [5] and snow samples [6] (with no proximate apparent contamination source) of different European cities. MTBE has been associated with several health side effects (e.g. nausea, headaches, dizziness and breathing difficulties) and has been classified by U.S. EPA as a potential/suspected carcinogenic substance.

BTEX removal from groundwater has been widely studied and several processes have been successfully applied, including bioremediation, volatilization, 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. MTBE has also been widely studied and the main mechanisms that have been proposed for its removal from water include bioremediation/natural attenuation, volatilization (air stripping/air sparging), chemical oxidation, as well as adsorption.

Adsorption is a process that can be applied either in situ (with permeable reactive barriers) or ex situ, is relatively simple (compared to others) and can achieve quite 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

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Nomenclature

q_t	mass of adsorbed contaminant per mass of adsorbent at time t (mg kg^{-1})
C_o	initial liquid-phase concentration of the adsorbate (mg/L)
C_t	liquid-phase concentration of the adsorbate at time t (mg/L)
m	mass of dry adsorbent used (g)
V	volume of aqueous solution containing the adsorbate (L)
k_1	pseudo-first order rate constant (h^{-1})
q_e	mass of adsorbate adsorbed at equilibrium per mass of adsorbent (mg g^{-1})
k_2	pseudo-second order rate constant (g mg^{-1} h^{-1})
x_i	a constant proportional to the boundary layer thickness (mg g^{-1})
k_p	the intraparticle diffusion rate constant (mg g^{-1} h$^{-1/2}$)
k_H	the Henry's law constant (L kg^{-1})
k_F	a constant correlated to the maximum adsorption capacity (mg kg^{-1} (mg/L)^n)
n	a constant that gives an indication of how favorable the adsorption process
Q_o	mass of adsorbate adsorbed per mass of adsorbent that is required to cover the adsorbent surface completely as a monolayer (mg kg^{-1})
k_L	a constant related the intensity of the adsorption process (L mg^{-1})

capacity, such as production and regeneration cost, availability, environmental compatibility and energy consumption during its production and regeneration. Therefore, research has been 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 [7], surfactant modified zeolites [8] and organo-clays [9] has already proved to be an interesting perspective. Moreover, silicalite, mordenite, zeolite-β [10], as well as polymer [11], synthetic [12] and carbonaceous [13] resins and high silica zeolites [14,15] have also been successfully tested for MTBE removal from water.

In this study, raw and thermally modified diatomite have been tested for their adsorption potential for BTEX and MTBE from aqueous solutions. Diatomite, also known as diatomaceous earth or kieselguhr, is a fine sedimentary rock of biogenetic origin, which mainly consists of amorphous silicon ($SiO_2 \cdot nH_2O$) that derives from skeletons of aquatic plants, called diatoms. Diatomite is abundant in many areas of the world and has unique physical characteristics, such as high permeability (0.1–10 mD) and porosity (35–65%) [16], small particle size, low thermal conductivity and density [17] and high surface area [18]. The properties of diatomite's surface, such as hydrophobia, solubility, charge, acidity, ion exchange and adsorption capabilities, are highly governed by the presence of water, which is partially structurally connected to the crystal mesh of the diatomite, forming active hydroxyl groups on it [19].

Diatomite has already been used for the adsorption of different elements and substances from water and wastewaters, either in its natural form (raw) or modified (chemically or thermally) (Table 1), presenting very promising and positive results. Therefore, its potential capability to adsorb common petroleum contaminants, such as BTEX and MTBE, under specific conditions, has been explored in this paper.

2. Materials and methods

2.1. Adsorbent

The diatomite used in this study was obtained from the Kozani area in Northern Greece. According to the material provider, its mineralogical composition has been found to be: 22% Quartz, 13% Plagioclase, 1% Pyroxene (augite), 2% Hematite and 62% Total Clays (Muscovite: main phase 50–60%, Vermiculite: intermediate phase 20–30% and Smectite: small phase 5–20%). Its chemical composition mainly consists of 67% SiO_2, 14.7% Al_2O_3, 5.1% Fe_2O_3, 3.3% MgO, 1.9%CaO, 1.5% K_2O and 1.04% TiO_2.

The diatomite samples obtained were grated in a sphere mill. Particles of 64–120 μm diameter were separated and further used during the experiments. These samples were washed with deionised water and dried in an oven at 105 °C for 12 h. Finally, they were stored in closed plastic containers for further use.

During the experimental procedure, four different diatomite samples were created and tested: (1) raw diatomite (D_R), (2) diatomite thermally modified at 550 °C for 2 h (D_{550}), (3) diatomite thermally modified at 750 °C for 2 h (D_{750}) and (4) diatomite thermally modified at 950 °C for 2 h (D_{950}). The above mentioned temperatures and time were selected after extensive bibliographic research, in order to obtain results that could be compared to those of other studies on thermal treatment influence on diatomite's structure, properties and adsorption characteristics. Thermal treatment was carried out in ambient air.

Small quantities (~1–2 g) of these samples were used for the determination of their specific surface, mean pore size and pore volume distribution using the Nitrogen Gas Adsorption Method and a Nova 2200 Quanta Chrome analyzer. More specifically, Brunauer–Emmet–Teller method was used for the sample's specific surface determination, Barrett, Joyner, Halenda method was used for the total pore distribution determination and Dubinin–Radushkevich, as well as *t*-Method–Halsey methods were used for microporosity measurements.

Finally, the pH values of the diatomite samples were determined according to the ASTM D4972-01 standard method, while their total porosity was measured using the Water Saturation Method (measurement of the water volume needed for complete saturation of certain amount of sample).

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%), ethylbenzene (Fluka, purity: 99%), p-xylene (Fluka, purity 99%), o-xylene (Fluka, 99%) and methyl tertiary butyl ether (Riedel-de Haen, purity: 99%). These chemicals were used for the creation of a water solution, containing all six of the above mentioned common groundwater contaminants, for both the kinetics batch and isotherm determination experiments, in order to explore the adsorbent's capacity and efficiency, under the potentially competitive prevailing conditions within the water solution.

2.3. Kinetics batch experiments

Kinetics experiments were carried out in 100 ml glass beakers with gas tight, non-permeable by organic vapors, caps. A series of seven test beakers was used for each of the four samples of diatomite. Each beaker contained adsorbate solution (~250 mg/L BTEX = 50 mg/L benzene + 50 mg/L toluene + 50 mg/L ethyl-benzene + 50 mg/L p-xylene + 50 mg/L o-xylene and ~100 mg/L MTBE) and diatomite in a ratio of 1:10. Headspace within each beaker was minimized (to exclude any contaminant volatilization phenomena), while agitation and temperature (20 ± 1 °C) were stable in all of them. In each of the seven test beakers of the four diatomite sam-

Table 1
Recent studies on the use of raw and modified diatomite as an absorbent of specific chemical elements and substances from water and wastewaters.

Study no.	Adsorbent (diatomite)					Adsorbate	Reference
	Raw	Chemically treated	Thermally treated	Origin	Surface area (m^2/g)		
1	■			Rif Mountain, Morocco	14.3 (BET)	Ag^+	[28]
2		■ (polyethyleneimene)		Shanghai	–	Phenol	[18]
3		■ ($MnCl_2$–NaOH)		Jordan	–	Dyes	[17]
4		■ (HNO_3–HC–$Na_4P_2O_7$)		Al-Azraq basin, Jordan	33 (Sears Method)–raw	Dyes	[20]
5	■			Al-Azraq basin, Jordan	27,80 (Sears Method)	Dyes	[29]
6		■ (HCl–NaCl–Na_2CO_3 → 1000 °C for 2 h) + (polyglycol, octadecimal amine, cetyltrimethyl ammonium chloride, CaO, trimethylsilyl chloride)	■ (400, 800, 950, 1150 °C)	Sheng, China ChangbaiShan, China	64.70 (BET) 19.11 (BET) 40.01 (BET)–acidified Sheng	Urokinase	[30]
7	■			Kutahya-Alayunt, Turkey	–	Benzidine 2,2′-bipyridyl 4,4′-bipyridyl	[31]
8		■ ($MnCl_2$–NaOH)		Al-Azraq basin, Jordan	–	Dyes	[32]
9		■ ($Fe_2H_2O_4$)		–	–	As	[33]
10		■ ($MnCl_2$–NaOH)		Al-Azraq basin, Jordan		Cd^{+2}, Zn^{+2}, Pb^{+2}	[34]
11	■			Kayseri, Turkey	–	Cs-137, Cs-134 Co-60	[35]
12		■ ($MnCl_2$–NaOH)		Al-Azraq basin, Jordan	33 (Sears Method)–raw 80 (Zn^{+2} adsorption method)–modified	Pb^{+2}, Cu^{+2}, Cd^{+2}	[36]
13	■	■ (H_2SO_4)	■ (900 °C, 3 h)	Al-Azraq basin, Jordan	572.9 (Shears Method)	Dyes	[21]
14	■		■ (980 °C, 4 h)	Al-Azraq basin, Jordan	54,38 (BET)–raw 0.35 (BET)–treated	Dyes	[25]
15	■			Saraykoy basin, Turkey	–	Textile dyes	[37]
16		■ (HF)		Celite 577	3.81 (BET)–raw 10 (BET)–modified	Dyes	[42]
17	■	■ ($MnCl_2$–NaOH)		Al-Azraq basin, Jordan	33 (Sears Method)–raw 80 (Zn^{+2} adsorption method)–modified	Pb^{+2}	[38]
18		■ (microemulsion)	■ (980 °C)	Ceara-Mirim, Brazil	–	Cr^{+3}	[39]
19	■	■ ($Al_2(SO_4)_3$–CaO)	■ (450 °C, 2 h)	China	–	NH_4–N, TN, TP, As, Cd^{+2}, Pb^{+2}, Cu^{+2}, Zn^{+2}	[40]
20		■ (NaOH)		Taiwan	0.29 ± 0.13 (BET)–spent[a] 96.4 ± 2.4 (BET)–modified	Herbicide	[23]
21	■			Ras-Traf, Morocco	–	Pesticides	[41]
22	■			Celite 577	3.8 (BET)	Bisphenol-A	[24]
23		■ (NaOH → 85 °C, 2 h –$FeCl_2$)		USA	24.77–raw 211.1–modified	P	[43]
24	■			Ankara-Alacaatli, Turkey	18.645–20.416	Cr^{+3}	[44]
25	■	■ (acid–base)	■ (300–900 °C)	Celite 577	4.21 (BET)–raw 0.20 (BET)–spent 0.56–1.17 (BET)–thermally modified 2.15–3.78 (BET)–acid activated 1.83–33.47 (BET)–base activated	Dye	[45]

■Diatomite type used in the study.
[a] Spent diatomaceous earth, a waste generated from the production of beer.

ples, the contact time of the adsorbate and the adsorbent varied, with a maximum duration of 21 days. The solution samples were then filtered (0.45 μm pore filter) and analyzed.

2.4. Isotherm determination experiments

Isotherm determination experiments were also carried out in 100 ml glass beakers with gas tight, non-permeable by organic vapors, caps. Two series of six test beakers was used for each sample of diatomite (apart from D_{950}, which showed low adsorption capacity during the kinetics batch experiments). Each beaker contained adsorbate solution (~250 mg/L BTEX = 50 mg/L benzene + 50 mg/L toluene + 50 mg/L ethyl-benzene + 50 mg/L p-xylene + 50 mg/L o-xylene and ~100 mg/L MTBE) and diatomite in different ratios: 1:25, 1:15, 1:10, 1:5, 1:4 and 1:3. Headspace within each beaker was minimized, while agitation, contact time (10 days) and tem-

Table 2
Specific surface, mean pore size and pore volume distribution of the four diatomite samples.

Sample	Micropore volume (cm^3/g)	Micropore area (m^2/g)	Mesopore volume (cm^3/g)	Mesopore area (external surface area) (m^2/g)	Surface area (SBET) (m^2/g)	Total pore volume (cm^3/g)	Average pore radius (Å)	Micropores content (%)	Mesopores content (%)
D_R	0.0041	10.95	0.0463	27.45	38.40	0.0504	52.523	8.13	91.87
D_{550}	0.0038	10.23	0.0563	33.07	43.30	0.0601	55.492	6.24	93.76
D_{750}	0.0000	0.64	0.0521	31.17	31.81	0.0521	65.519	0.00	100.00
D_{950}	0.0000	0.49	0.0130	7.17	7.66	0.0130	67.776	0.00	100.00

perature (20 ± 1 °C) were consistently maintained in all of them. The solution samples were then filtered (0.45 μm pore filter) and analyzed.

2.5. Chemical analysis method

The solution samples were analyzed in a PerkinElmer 8700 Gas Chromatographer equipped with a Flame Ionization Detector (FID), using the Solid Phase Micro Extraction (SPME) method. The analytical conditions used were the following:

GC/FID
- Injector temperature: 250 °C
- Split mode: splitless and then split at t = 8 min (1/20)
- Oven temperature: 35 °C for 5 min and increase 5 °C/min up to 300 °C for 10 min
- Detector temperature: 300 °C

SPME
- Fiber: 100 μm polydimethylsiloxane coating
- Sampling mode: headspace
- Sample volume: 4 ml
- Salt addition: 1 g NaCl
- Adsorption time: 10 min
- Adsorption temperature: 18 ± 1 °C
- Desorption time: 5 min

2.6. Data evaluation

The amount of the adsorbate that has been adsorbed on the adsorbent can be expressed as follows:

$$q_t = \frac{C_o - C_t}{m} \cdot V \quad (1)$$

For the interpretation of the kinetic batch experimental data three different kinetic models were used: (1) the *pseudo-first order* kinetic model (Eq. (2)) [20–22], (2) the *pseudo-second order* kinetic model (Eq. (3)) [21,23,24] and (3) the *intraparticle diffusion model* (Eq. (4)) [17,21]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

$$\frac{1}{q_t} = \frac{1}{q_e^2 k_2} \cdot \frac{1}{t} + \frac{1}{q_e} \quad (3)$$

$$q_t = x_i + k_p t^{1/2} \quad (4)$$

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

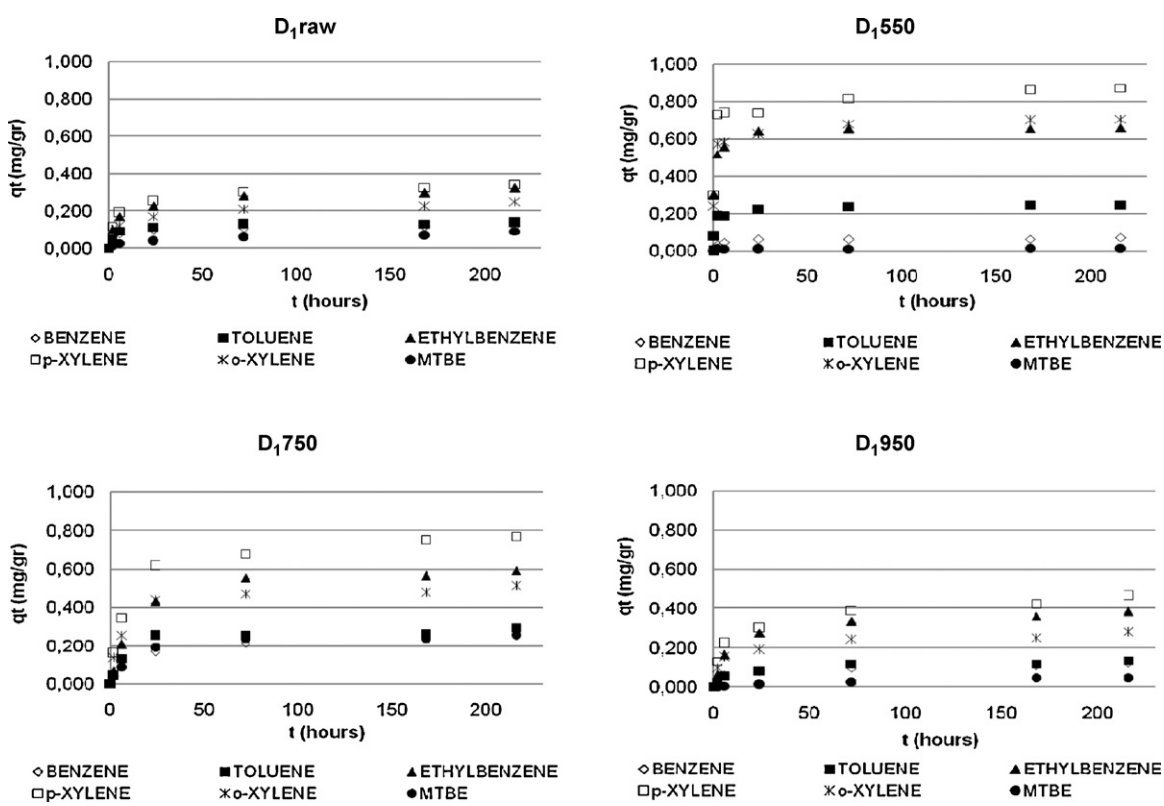

Fig. 1. The adsorbed mass of each contaminant per mass of the adsorbate used (mg g^{-1}) (q_e) in relation to the adsorbent–adsorbate contact time (t in hours), for each of the four diatomite samples examined.

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. (5)) [20,21,22], (2) the *Freundlich* model (Eq. (6)), which has proved to be satisfactory for low concentrations [24] and often represents an initial surface adsorption followed by a condensation effect, resulting from extremely strong solute–solute interaction [21] and (3) the *Langmuir* (Eq. (7)):

$$q_e = k_H C_e \tag{5}$$

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \tag{6}$$

$$\frac{1}{q_e} = \frac{1}{k_L Q_o} \cdot \frac{1}{C_e} + \frac{1}{Q_o} \tag{7}$$

3. Results and discussion

3.1. Adsorbents characteristics

The results obtained for the diatomite samples' specific surface (BET) and pore volume distribution are presented in Table 2.

As can be concluded from Table 2, thermal treatment of the diatomite causes important changes in its specific area, as well as its pore volume distribution. More specifically, thermal treatment at 550 °C caused an increase in the specific, as well as the external surface, area of the diatomite of about 12.76% and 20.47%, respectively. This is probably attributed to the removal of admixtures or adsorbed volatile compounds, through volatilization due to the high temperature of 550 °C. Thermal treatment at 750 and 950 °C seems to cause structural changes in the diatomite, since average pore radius increases, specific and external areas decrease and micropore volume tends to zero. High temperatures cause destruction of vicinal micropores' walls, which leads to a decrease in micropore and a corresponding increase in mesopore content [25]. The total pore volume of diatomite decreases at temperatures as high as 950 °C, due to structural changes caused—an observation that verifies the results of Khraisheh et al. [25].

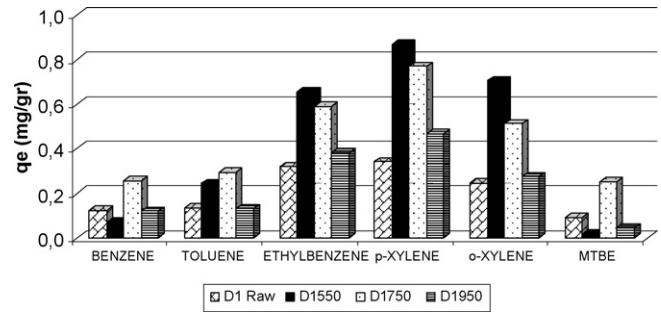

Fig. 2. The adsorbed mass of each contaminant (10 days) per mass of the adsorbate used (mg g^{-1}) (q_e) for each of the four diatomite samples examined.

The total porosity of each diatomite sample was found to be about 0.835.

The pH values of aqueous solutions of the diatomite samples D_R, D_{550}, D_{750} and D_{950} were measured to be 7.0, 7.5, 8.5 and 9.5 respectively. This indicates that the thermal treatment of diatomite gives a more "basic character" to its aqueous solutions, probably due to the fact that acidic sites in diatomite are weak and decrease when thermal treatment at temperatures between 650 and 1000 °C is applied [19].

3.2. Adsorption kinetics

The adsorbed mass of each contaminant per mass of the adsorbate used (mg g^{-1}) (q_e) in relation to the adsorbent–adsorbate contact time (t in hours), for each of the four diatomite samples examined, is presented in Fig. 1.

Table 3
Comparison of the pseudo-first order, the pseudo-second order and the intraparticle diffusion model fits for the experimental data (optimum acquired correlation coefficient values are indicated in bold).

Adsorbate	Pseudo-first order model		Pseudo-second order model		Intraparticle diffusion model	
	k_1 (h^{-1})	R^2	k_2 (g mg^{-1} h^{-1})	R^2	k_p (mg g^{-1} h$^{-1/2}$)	R^2
Diatomite sample: D_R						
Benzene	0.0153	0.8006	3.3263	**0.9916**	0.0065	0.7139
Toluene	0.0177	0.7784	1.8276	**0.9901**	0.0075	0.7025
Ethyl-benzene	0.0136	0.8298	0.9134	**0.9868**	0.0182	0.8160
p-Xylene	0.0157	0.8677	0.9214	**0.9868**	0.0193	0.7971
o-Xylene	0.0129	0.8416	0.5226	**0.9905**	0.0150	0.8445
MTBE	0.0070	0.8636	2.1956	**0.9670**	0.0055	0.9550
Diatomite sample: D_{550}						
Benzene	0.0101	0.5549	18.0996	**0.9819**	0.0037	0.7085
Toluene	0.0365	0.7363	7.2447	**0.9913**	0.0117	0.5539
Ethyl-benzene	0.0281	0.6986	4.7319	**0.9861**	0.0280	0.4699
p-Xylene	0.0210	0.7893	2.1946	**0.9877**	0.0381	0.4861
o-Xylene	0.0230	0.8064	2.6614	**0.9934**	0.0318	0.5069
MTBE	0.0099	0.7932	48.9326	**0.9898**	0.0008	0.7747
Diatomite sample: D_{750}						
Benzene	0.0140	0.8882	0.3069	**0.9994**	0.0167	0.8938
Toluene	0.0118	0.5854	0.1868	**0.9829**	0.0398	0.8382
Ethyl-benzene	0.0185	0.8167	0.0557	**0.9896**	0.0180	0.7569
p-Xylene	0.0204	0.9205	0.1581	**0.9994**	0.0481	0.8140
o-Xylene	0.0149	0.6790	0.3335	**0.9986**	0.0302	0.7506
MTBE	0.0146	0.7206	0.4441	**0.9924**	0.0162	0.8279
Diatomite sample: D_{950}						
Benzene	0.0118	0.8769	2.0324	**0.9863**	0.0071	0.8739
Toluene	0.0127	0.7716	0.7896	**0.9932**	0.0083	0.8774
Ethyl-benzene	0.0161	0.8748	0.2091	**0.9930**	0.0242	0.8440
p-Xylene	0.0124	0.8583	0.5710	**0.9815**	0.0271	0.8644
o-Xylene	0.0120	0.7796	1.2817	**0.9740**	0.0153	0.8073
MTBE	0.0222	0.9408	0.0002	**0.9904**	0.0035	0.9804

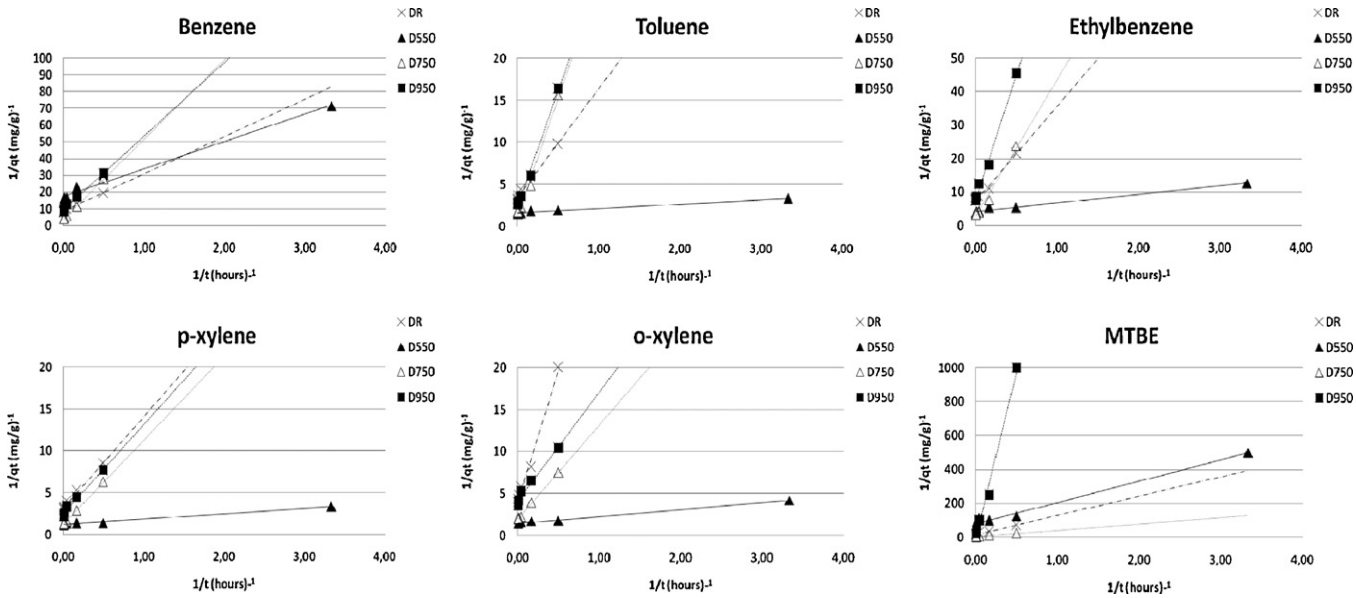

Fig. 3. Pseudo-second order kinetics for adsorption BTEX and MTBE adsorption onto raw and thermally modified diatomite.

After about 240 h (10 days) of contact between the adsorbate and the adsorbent, the change of the liquid-phase concentration of the adsorbate (C_e) becomes insignificant and it can therefore be assumed that equilibrium has been reached. This time period needed for reaching equilibrium is long, compared to others reported for BTEX adsorption [7,9], but not for MTBE adsorption as well [26].

Moreover, it is evident that the mass of the adsorbed contaminant on each of the examined diatomites generally increases after thermal treatment, especially at temperatures 550 and 750 °C. This phenomenon is clearly illustrated in both Figs. 1 and 2 and can be attributed to the fact that through thermal treatment diatomite's pores "clear", since potential impurities are removed (possibly through desorption and volatilization) and its available specific surface increases. Moreover, structural changes that thermal treatment causes to diatomite, may increase its specific surface and total pore volume (as in sample D_{550}), as well as altering its active sites and hydrophobia.

Compared to activated carbon, all tested diatomite samples present almost 160 times longer equilibrium time and 20 times lower adsorption capacities (conclusions supported by author's unpublished data). Long equilibrium time (10 days) may not be a problem in the case of contaminated aquifers with low groundwater velocities (a few centimeters per day). In this case, the time necessary for the contaminants adsorption within a potential permeable reactive barrier filled in with diatomite is available.

Table 4
Comparison of the Henry, Freundlich and Langmuir isotherm fits for the experimental data (optimum acquired correlation coefficient values are indicated in bold).

Sample	Henry isotherm		Freundlich isotherm			Langmuir isotherm		
	k_H (L mg^{-1})	R^2	k_F (mg kg^{-1} (mg/L)^n)	$1/n$	R^2	k_L (L mg^{-1})	Q_o (mg kg^{-1})	R^2
Benzene								
D_R	0.004	0.623	3.681E−05	2.473	**0.982**	−0.022	−0.080	0.979
D_{550}	0.006	0.235	1.549E−13	8.128	**0.914**	−0.030	−0.015	0.838
D_{750}	0.007	0.395	1.349E−07	4.451	**0.946**	−0.034	−0.039	0.916
Toluene								
D_R	0.005	0.620	1.919E−03	1.327	**0.681**	−0.006	−0.710	0.667
D_{550}	0.008	0.248	6.607E−12	7.287	**0.931**	−0.032	−0.024	0.849
D_{750}	0.008	0.331	9.817E−09	5.502	**0.970**	−0.040	−0.040	0.940
Ethyl-benzene								
D_R	0.009	0.469	4.436E−02	0.545	**0.485**	0.047	0.478	0.412
D_{550}	0.014	0.284	7.413E−11	6.072	**0.965**	−0.020	−0.081	0.953
D_{750}	0.015	0.453	1.954E−06	3.632	**0.985**	−0.025	−0.025	0.978
p-Xylene								
D_R	0.009	0.367	6.109E−02	0.475	**0.445**	0.064	0.460	0.372
D_{550}	0.014	0.289	2.735E−10	5.714	**0.928**	−0.020	−0.091	0.924
D_{750}	0.015	0.481	3.177E−06	3.466	**0.966**	−0.023	−0.023	0.965
o-Xylene								
D_R	0.006	0.267	4.603E−02	0.457	**0.349**	0.065	0.325	0.260
D_{550}	0.009	0.250	6.023E−13	7.246	**0.944**	−0.021	−0.042	0.877
D_{750}	0.008	0.314	1.021E−09	5.458	**0.954**	−0.023	−0.023	0.951
MTBE								
D_R	0.001	0.386	5.917E−10	4.377	**0.952**	−0.010	−0.030	0.943
D_{550}	0.001	0.366	4.365E−11	4.820	**0.913**	−0.009	−0.026	0.886
D_{750}	0.000	−1.36	4.842E+01	−1.529	**0.823**	0.020	−0.019	0.806

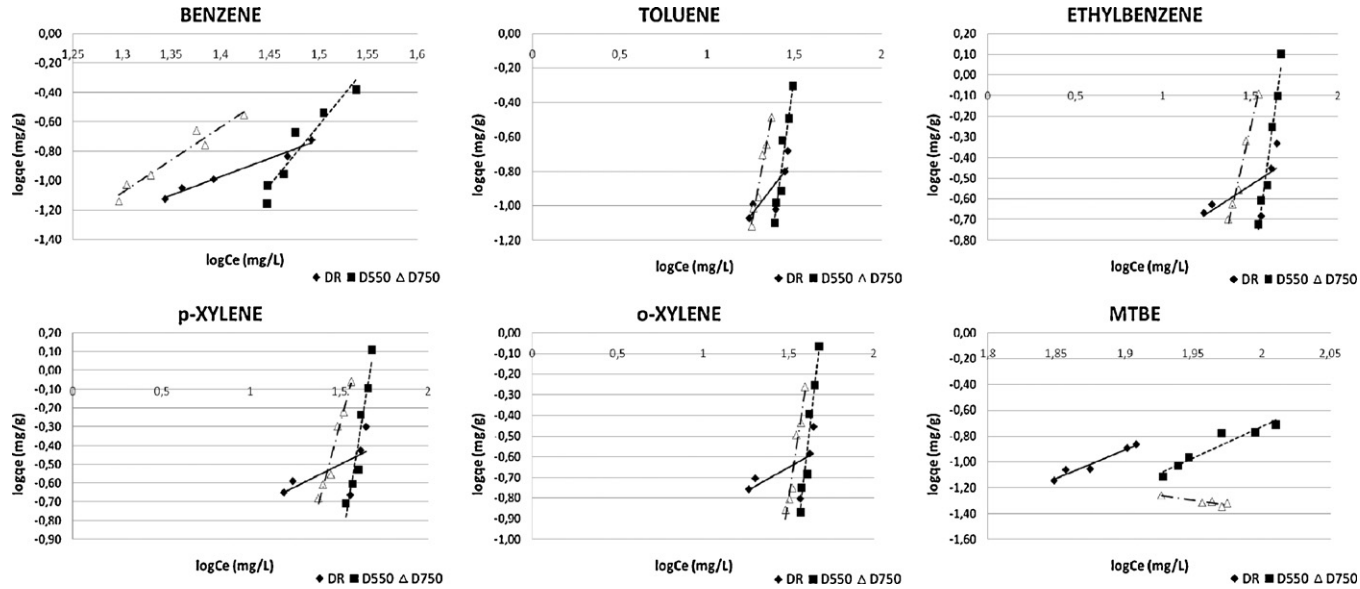

Fig. 4. Freundlich isotherm fits for the experimental adsorption data for raw and thermally modified diatomite (at 550 and 750 °C).

However, the amount of the diatomite needed, as well as its total cost compared with those of activated carbon, must be carefully calculated, in order to evaluate diatomite's overbalance. Of course, other parameters must also be taken into account, such environmental protection and energy saving, during the adsorbent production.

As far as the adsorbent preference in the available adsorbates is concerned, Fig. 2 indicates that it decreases in the following order: p-xylene → ethyl-benzene → o-xylene → toluene → benzene → MTBE. This order can be related to the adsorbates' descending order of hydrophobicity (based on their octanol–water coefficient log values: 3.15, 3.15, 2.77, 2.69, 2.13 and ~1.06, respectively), molecular weight (106, 106, 106, 92, 78, 88 g mol^{-1}, respectively) [22] and approximately ascending order of water solubility (198, 152, 175, 515, 1700 and ~47.000 mg/L, respectively) [1,27]. Generally, it seems that the most soluble and hydrophilic substances (benzene and MTBE) have less tendency to adsorb onto the diatomite samples.

The above mentioned adsorbent preference order provides important information on the potential competition phenomena, that may appear in the BTEX–MTBE–diatomite system. BTEX are clearly preferred by the adsorbent used in this study, against MTBE that is the contaminant with the lowest adsorption tendency. This is attributed not only to the physicochemical properties of MTBE, but also to the presence of BTEX, that rapidly covers the vast available surface of diatomite. BTEX's lower solubility in water, as well as higher hydrophobia, than that of MTBE, promote and accelerate BTEX adsorption onto diatomite and other adsorbents, such as activated carbon. As a result, when MTBE is the only present adsorbate, its adsorption is slightly higher (<5%) than the one determined in this study (conclusions supported by author's unpublished data).

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 diatomite would be of little value. However, based on this study, it appears that xylenes are the components with the highest adsorption tendency onto diatomite and benzene the one with the lowest.

The fit of the results of the experimental data to the pseudo-first order, pseudo-second order and intraparticle diffusion models for each of the adsorbates was carried out, according to Eqs. (2)–(4), respectively. The calculated model rate constants are provided in Table 3. As is evident in Table 3, the experimental data for each of the adsorbates examined best fit the pseudo-second order kinetics model, providing correlation coefficient (R^2) values ranging from 0.9670 (for the MTBE–diatomite sample, D_R) up to 0.9994 (for p-xylene–diatomite sample, D_{750}). The fitting of the experimental data of BTEX and MTBE adsorption onto the tested diatomite (both raw and thermally modified) on the pseudo-second order kinetics model is presented in Fig. 3.

Based on the results acquired, the pseudo-second order kinetic model can be used in any potential BTEX–MTBE–diatomite system, which is under the same conditions that were used in this project, in order to predict other adsorption kinetic data. However, before its application, probably on the design of a column test apparatus or a pilot permeable reactive barrier on a real site, its validity and/or precision should be further explored and finally determined, by calculating the mean square error, through the conduction of more experiments, using different initial concentrations of the contaminants tested.

3.3. Adsorption isotherms

The adsorption isotherms that derive from the experimental data for each of the tested adsorbates and adsorbents are presented in Table 4. Freundlich model best fits the experimental data (Fig. 4), based on its relatively high values of the correlation coefficient R^2 (compared to those derived from the other two models examined) that vary from about 0.349 to 0.985.

The Freundlich constant $1/n$ was calculated to be higher than unity for the majority of the adsorbate and adsorbent combinations, indicating that the adsorption of the selected contaminants onto the diatomite samples is not favorable. Values of $1/n$ lower than one was noticed only for o-xylene, p-xylene and ethyl-benzene in sample D_R.

Freundlich constant k_F values were very low for the majority of the adsorbate and adsorbent combinations, indicating low adsorbent capacity. Relatively high k_F values were calculated for raw diatomite (sample D_R).

4. Conclusions

The goal of this paper was to explore and present diatomite's capability to adsorb certain common petroleum contaminants. Therefore raw and thermally modified diatomite was tested for

the adsorption of BTEX and MTBE from aqueous solutions. The results showed that thermally modified diatomite at 550 °C present the highest adsorption capacity for the majority of the examined contaminants. Diatomite samples thermally modified at 750 and 950 °C presented lower adsorption capacity, which is directly connected to structural changes, such as specific area and total pore volume reduction, caused by the high temperatures applied. The highest adsorption percentages were achieved for p-xylene and ethyl-benzene and the lowest for MTBE and benzene.

The adsorption kinetics of the examined contaminants onto the diatomite samples can be well described by the pseudo-second order reaction model. Furthermore, the Freundlich model appeared to fit the experimental data better than the Henry and Langmuir models for describing the adsorption behavior of BTEX and MTBE from an aqueous solution on raw and thermally modified diatomite.

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