"Gheorghe Asachi" Technical University of Iasi, Romania

STUDY ON DEALUMINATED ZEOLITIC TUFF
FOR HYDROCARBON REMOVAL FROM WATER

Al-Jammal Noor[1*], JuzsakovaTatjána[1], Halmágyi Timea[2], Cretescu Igor[3*],
Sebestyén Viktor[1], Balázs Zsirka[1], Domokos Endre[1], Fazakas József[2], Rédey Ákos[1]

[1]Institute of Environmental Engineering, Faculty of Engineering, University of Pannonia, Veszprém, Hungary
[2]Department of Chemical Engineering, Faculty of Chemistry and Chemical Engineering,
Babes-Bólyai University, Cluj-Napoca, Romania
[3]Faculty of Chemical Engineering and Environmental Protection, "Gheorghe Asachi" Technical University of Iasi, Iasi, Romania

Abstract

This study aims to develop a new adsorbent from Jordanian raw zeolitic tuff (RZT) for oil depollution control of surface waters. Therefore the properties of chemically treated Jordanian dealuminated zeolitic tuff were investigated. Zeolitic tuff (i.e., phillipsite-rich tuffs) was modified via (i) dealumination by single acidic treatment (TZT) and (ii) further treatment of the dealuminated zeolitic tuff by microemulsion technique (MeTZT). Series of adsorbents were prepared by impregnation method and characterized by using different techniques such as: X-ray Diffraction (XRD), Fourier Transform Infrared Spectrometry (FT-IR), Brunauer–Emmett–Teller (BET) method, Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray (EDX) to obtain information about the structural, chemical and surface properties of zeolite materials. The performance of the adsorbents was followed by adsorption capacity measurements expressed as the ratio of the mass of adsorbed hydrocarbon to the weight of the used sorbent. The adsorption capacities of the dealuminated zeolitic tuff were studied under different experimental conditions for model hydrocarbon pollutants, using a Total Organic Carbon (TOC) analyzer. The obtained results revealed that the adsorption capacity of the modified zeolitic tuff improved by increasing the hydrophobic properties. A comparative account of the adsorption capacities of all adsorbents was compared to activated carbon type AquaCarb. The sorption capacity increased from 34% (for RZT) to 107% for (TZT) using kerosene as model hydrocarbon mixture, and from 85% to 162% for octane model compound, while the sorption capacity enhanced from 116% to166 % for dodecane model compound, when the sorption capacities were tested by using RZT and TZT. However, when the microemulsified treated zeolitic tuff was tested even higher hydrocarbon sorption capacities were measured than in case of the deauliminated zeolitic tuff, which supports the notion that the surface modification of the zeolitic tuff was successful.

Key words: adsorption, adsorption capacity, dealumination, oil spills, zeolitic tuff

Received: July, 2018; Revised final: February, 2019; Accepted: May, 2019; Published in final edited form: August, 2019

1. Introduction

As a consequence of the massive oil spill of about 210 million gallons in the Gulf of Mexico on 22nd April 2010 caused by the explosion at the Deepwater Horizon oil rig, both the accidental and deliberate releases of oil during production, transportation and storage became a worldwide concern. The harmful impacts on ecosystems and the long-term influence of environmental pollution by spillages and other releases alert for an immediate solution to improve the technologies for oil pollution cleanup. The new technologies for removal of oil from oil-impacted areas should take into consideration the efficiency of any remediation method that varies with oil type, time and location of the spill addition to weather conditions of the spill's place. Oil spills have remained a challenge to environmental scientists, as those can harm living organisms due to the toxic chemical impacts. Thus, the removal of oils from the

---
* Author to whom all correspondence should be addressed: e-mail: aljammal86@gmail.com; icre@tuiasi.ro

surface of the water is an urgent issue to prevent further contamination of water and to minimize overall impacts on ecological communities (Amro, 2004).

Different types of oils and petroleum fractions exhibit different properties; therefore, the environment and ecosystems are influenced in several ways (Liu and Kujawinski, 2015). The light oils and light petroleum fractions present major hazards as those can ignite or explode. Moreover, many light petroleum fractions, such as gasoline, kerosene and diesel, are considered to have toxic potential, as well. The light petroleum fractions can kill animals or plants after contact, and they are dangerous to human beings who breathe their vapors. Thus the type of spilled oil along with propagation speed of the oil on the water surface influenced by water temperature, and weathering processes such as; atmospheric temperature, wind and flow directions are very significant aspects of guiding the companies and authorities to decide on the pre-eminent remediation techniques.

The spilled oil triggers a series of physical, chemical and biological changes in the ecosystem. The spreading of the oil over large water surface area creates an oil film with about 1 mm thickness (Amro, 2004). These oil layers can be very persistent, toxic and endanger the ecosystem. Various methods are published for the removal of petroleum derivatives from water surface, e.g., precipitation, coagulation, flocculation, floating barriers, burning, bio-augmentation, reverse osmosis, bio-sorption and photo-catalysis (Ali and Gupta, 2006; Bandura et al., 2017; Blais et al., 2008; Fingas, 1995). Each method has its drawbacks, which provoke the researchers' interest in developing, finding and optimizing new adsorption methods. For example, if the oil spill is fresh, burning could be a suitable and fast solution, but the emissions of toxic combustion products will create additional serious environmental problems (Fritt-Rasmussen et al., 2011).

Adsorption is an essential pillar of the modern remediation techniques for the oil spill clean-up, and it is a widely used technique. Several sorbents such as activated carbon, polymeric resins, agricultural wastes, fly ash and zeolites have been used for water clean-up (Breck, 1974; Cretescu et al., 2015; Harja et al., 2011; Visa et al., 2014). However, the efficiency of each oil removal technique is subject to several parameters, e.g., the properties and the quantity of spilled oil, type of adsorbents, surface coverage, location and weathering conditions. Studies highlighted the adsorption as a promising and simple process as well as an economical method to eliminate this type of pollution and to mitigate the detrimental impacts of the oil spills (Behnood et al., 2013; Kemnetz and Cody, 1998). Therefore, the synthesis of adsorbents with superior oil sorption performance remains a great challenge.

Several factors influence the selection of appropriate adsorbents such as availability, cost, safe use and regeneration of the adsorbent materials. Many other parameters governed by the structure of the adsorbents play a vital role in the cleaning process such as hydrophobicity (oleophilic properties), porosity, suitable pore size and surface area. Adsorbents with the high surface area have proved to be highly efficient and versatile materials for oil removal from the water surface. Nonetheless, a small number of materials meet all these requirements for selectivity, adsorption capacity, adsorption rate and recycling.

Over the years, research is progressively concentrating on hydrophobic pure-silica or high silica-containing zeolites as a feasible alternative for activated charcoal for sorption of organic pollutants (such as volatile organic compounds). The pollutants are usually removed by sorption over activated carbon (Adebajo et al., 2003; Alsbaiee, et al., 2016; Ruhl, 1993). Recently and over the past decades, there has been a surge of interest in zeolite materials as adsorbents. Recent studies have been reported, in which zeolite and zeolitic materials were used for hydrocarbon removal from water surfaces (Bandura et al., 2015; Muir and Bajda 2016; Sakthivel et al., 2013). Due to their framework topology, sieving properties pore size, cage diameter, super cage size and distribution of framework aluminum atoms in zeolites, high adsorption capacity, hydrophobic properties, thermal stability and resistance to different chemical impacts (Li et al., 2017; Shaw et al., 2017; Weitkamp et al., 1989) the zeolites became the subject of studies. Natural zeolite minerals (for example, phillipsite, chabazite) have been assessed as appropriate agents for environmental clean-ups (Querol et al., 2006; Tsitsishvili et al., 1992). Silicon to the aluminium ratio (Si/Al) in zeolites plays a key role in determining the hydrophobic properties of the zeolites. High silica zeolites have a unified structure with a defined pore size of 0.2-0.9 nm and a high specific surface area (Kuntzel et al., 1999). The zeolites are thermally and hydrothermally stable up to 1300°C (Berk et al., 1974). Zeolites with high silica content are generally synthesized via direct synthesis or by thermochemical framework modification of zeolites using dealumination process (Jansen, 2001; Maesen and Marcurs, 2001). This type of adsorbents represents a privileged class of adsorbents for the removal of organic pollutants from water surfaces (Jiang et al., 2018).

The term "dealumination" refers to the removal of aluminum from zeolite frameworks by chemical reactions resulting in lattice deficiencies. However, in its general use, it relates to a more complex process comprising the incorporation of other elements, especially of silicon into the transient framework vacancies left temporarily by the release of aluminum (Beyer et al., 2002). Dealumination of zeolites could result in creating defects within the framework. Hence, the micro pore volume and the surface area of the delaminated zeolites will show significant variation (Yonli et al., 2012). Several dealumination processes have been developed over the years, such as (i) silylation process (Campbell et al., 1996); (ii)

modification with silicon hexafluoride (Ferey and Acad, 1998; Skeels and Breck 1984; Weitkamp, 1989); (iii) chelating agents (Kerr, 1968); (iv) treatment with mineral or organic acids (Barrer and Makki, 1964; Briscoe et al., 1989; Jones et al., 2001); and (v) by steaming (Ajot et al., 1991).

These modifications appear to be promising in case of clay minerals and zeolites (Harja et al., 2012; Kotova et al., 2017). Organo-clays and organo-zeolites display higher sorption performance to organic compounds in water media than the raw materials (Popovici et al., 2002; Rotaru et al., 2014).

Chen and coworker postulated the importance of the hydrophobic/organophilic character of high silica content zeolites (Chen, 1976), as the hydrophobicity of zeolites is directly dependent on their aluminum content. Chen was the first researcher who suggested the utilization of hydrophobic molecular sieves to remove hydrocarbons from the water surface (Chen, 1973; 1976). The increase in the hydrophobic properties stems from decreasing aluminum content in the zeolite; thus, the ionic charge of zeolite lattice will decrease. Consequently, the less ionic charge will lead to less polarity and so less hydrophilicity/more hydrophobicity feature. The low aluminum content in the zeolite crystal structure will shift the adsorption properties away from polar molecules (water) towards nonpolar substances (organic molecules) since the organophilic character increases. Silicates are not oleophilic but less hydrophilic than a charged material like zeolites (Al-Othman, 2002; Lami et al., 1993). In our previous paper (Al-Jammal and Juzsakova, 2017) it was concluded that upon acidic treatment of RZT the structure changed from crystalline to amorphous as the XRD records indicated the collapse of the crystalline structure because of the removal of elements (Al, K, Na, Ca, Mg, Fe) from the bulk phase. Changes in zeolites tuff composition were confirmed by SEM-EDX analysis as well during the preliminary studies.

In this research, the modification of the zoolitic tuff material into non-polar adsorbent by delamination process was implemented by acidic treatment (Salvestrini et al., 2015; Silaghi et al., 2016). Acid treatment leads to the extraction of extra-framework aluminum, which permits better accessibility of the micro pores and removal of possibly non-shape-selective sites. Moreover, this treatment eliminates impurities (Roberge et al., 2002).

The non-polar groups on the surface of the dealuminated zeolite tuff can interact strongly with the non-polar hydrocarbon molecules from the hydrocarbon-water mixture. Therefore, the adsorbents can easily adsorb the hydrocarbon molecules. Dealuminated zeolites have several preferences over active carbon adsorbents. It can be regenerated by calcination (Otten et al., 1992) or with steam treatment (Ruthven et al., 1988), The dealuminated zoolitic materials rarely adsorb water, only when the relative humidity is higher than 70 % compared with 50 % for activated carbon.

Sun and coworkers reported the ability of hydrophobic zeolites to remove volatile organic compounds (Sun et al., 2002). Several workers highlighted the efficiency of zeolites for oil-adsorption from oil-water mixtures. Li and coworkers reported the usage of surfactant-modified zeolite (SMZ) for removal of organic compounds from oil-fields (Li and Bowman, 1998). It was concluded that the detailed mechanistic investigations of oil spill removal by using zeolites are a fertile area for further research (Muir and Bajda, 2016). In the present study, the dealumination procedure has been carried out for the zeolitic tuff by a single acid treatment.

Further treatment for dealuminated zeolitic tuff was implemented via the microemulsion technique. The objectives of this study can be summarized as follows:

i. To produce and characterize treated zeolitic tuff as oil adsorbent with increased hydrophobic properties.

ii. To quantify the extent of the hydrocarbon adsorption over the zeolitic tuff by increasing the silicon to aluminium ratio.

2. Materials and methods

2.1. Zeolitic tuff and pretreatment

In this study, Jordanian zeolitic tuff was selected as an affordable adsorbent based on available zeolitic tuff deposits, as indicated in Fig.1.

Fig. 1. Location of zeolitic tuff deposits in Jordan

Jordanian zeolite tuffs are located at Jabal Aritayn (30 km North-East of Azraq), Tlul Al-shahba (20 km East of Al-Safawi), Tal-Rimah (35 km North-East of Al-Mafraq) and other small deposits can be found in the South Jordan (Tell Burma, Tell Juhaira and Wadi El-Hisa) and in Central Jordan (Makawer, Al-Zara, Wadi Heidan and Wadi Al-Walah).

Zeolites tuff for the experiments was obtained from the deposits of Tall Hassasn, Jabal-Arityan, and southern part of Jordan. Usually, this kind of zeolitic

tuff contains mainly Phillipsite-K mineral [(K,Na)$_2$ Al$_8$Si$_8$O$_{16}$.4H$_2$O], forsterite, chabazite-K, quartz, hematite, and sanidine. Table 1 illustrates the properties of Tell Hassan RZT (Jordanian Natural Resources Authority).

Table 1. Properties of Tell Hassan RZT

Parameters of Tell Hassan RZT	
Water absorption	8.53-10.8 %
Colors	grey, grey to brown
Unit weight	1010 kg/m^3
Specific gravity	1.56-1.80 g/cm^3
Void ratio	17.54
Pulse Velocity	3333-3564 (m/sec)
Surface abrasion	27-28
T.D.S	1250-1500 (mg/L)
Elongation	11.09
Flakiness	22.59

Hydrochloric acid of analytical grade (37%) was used for the pretreatment of raw zeolitic tuff. RZT, with a SiO$_2$/Al$_2$O$_3$ ratio of 2.5,was chosen as raw material. According to the procedure described by Al-Jammal (Al-Jammal et al., 2016), the raw zeolite tuff (RZT) was crushed, ground and sieved. The particle size selected to carry out the acidic treatment was on average of 26 μm.

These particles were washed several times with distilled water in order to remove all soluble salts and dried in an oven at 105 °C for 4 h. Then, the dried RZT was treated with diluted hydrochloric acid (16%), and the mixture was stirred with a magnetic stirrer at room temperature for at least 24 h. The treated material was then filtered by using 0.41 μm filter paper (Whatman 41) to remove the aqueous yellowish acidic solution formed during the reaction of the dilute hydrochloric acid and associated minerals. The method used in this work for treating RZT allows the separation of approximately 25% to 30% of other volcanic constituents (iron, aluminium, magnesium, calcium, and sodium oxides) from the zeolite. This result was evidenced by EDX results and reported by Salem and coworkers (Salem et al., 2010).

Micro emulsion procedure was used on the treated zeolites tuff samples according to the process described by De Castro Dantas et al., (2001). It was achieved by mixing of 10 %wt. Surfactants (saponified coconut oil; mostly lauric acid, CH$_3$(CH$_2$)$_{10}$COOH, with some myristic acid, CH$_3$(CH$_2$)$_{12}$COOH) and 25 %wt. The aqueous phase (deionized water).

Coconut oil was saponified by standard procedure ASTM D-5558/1995 to form CH$_3$(CH$_2$)$_{10}$COO$^-$Na$^+$. The mixture was then mixed with 40 %wt. co-surfactant (isoamyl alcohol, 99% P.A.) and 25%wt. oil phase (heavy distillate). Due to the spontaneous formation of micro emulsions, the mixture can be prepared in one-step by simply mixing the constituents. The sequence of the addition of the constituents is not considered a critical factor for the preparation of the micro emulsion, but it can influence the time required to reachequilibrium. This time will increase if the co-surfactant is added to the organic phase since its greater solubility in this phase will prevent the diffusion in the aqueous phase (Vandamme, 2002). To prepare microemulsified adsorbents (MeTZT), 10 g of adsorbents (TZT) and 20 cm^3 of microemulsion were mixed and then dried at 65°C for 48h to increase the hydrophobicity of the treated zeolitic tuff.

Commercial activated carbon adsorbents, namely AquaCarb activated carbons, were purchased from EVOQUA Water Technology Co. It has a high microporous structure of coconut shell-based carbon, and it has excellent volatile organic carbon (VOC) removal capacity, and it exhibits a higher adsorption capacity than coal-based carbon for surface water treatment.

Such adsorbents have a density varying between 460 and 470 kg/m^3 with a total surface area of 1100 m^2/g with a mean particle size of 1.2 mm and it is commonly used in industrial water and wastewater treatments (AquaCarb, 2018).

2.2. Morphological studies

The specific surface area, pore volume and pore size distribution in the micro pore (1.7–2 nm), mesopore (2–50 nm) and the macro pore (50–100 nm) diameter ranges were determined by nitrogen adsorption/desorption isotherms measured with a Micromeritics ASAP 2000 - type equipment. Samples of RZT and TZT with the weight of 1.0 g and previously out gassed in vacuum at 105°C were used for the experimental tests. Pretreatment of each sample was finished when the vacuum reached a value of less than 10 μmHg. The surface areas of the samples were determined by the BET (Brunauer-Emmett-Teller) method from the corresponding nitrogen adsorption isotherms. The pore size distribution and volume values were calculated from the nitrogen desorption isotherms using the BJH (Barret–Joyner–Halenda) model.

2.3. X-Ray Fluorescence (XRF) studies

X-ray fluorescence (XRF) is the emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by bombarding with high-energy X-rays or gamma rays. The phenomenon is widely used for elemental analysis and chemical analysis, particularly in the investigation of metals, glass and ceramics. The raw zeolitic tuff (RZT), the treated zeolitic tuff (TZT) and the micro emulsified TZT samples (MeTZT) have been characterized by X-Ray Fluorescence (XRF) technique. It was used conventionally to determine the elemental concentrations of the samples.

The samples were dried, ground to small particle size and homogenized before XRF analysis. The sample powder was put is sample cup (diameter 32 mm x depth 14 mm) sealed by polypropylene film. A hand-held XRF X-MET 5100 analyzer (Oxford Instruments, UK) was used with silicon drift detector

(SDD) for in-situ qualitative analysis of elements ranging between Mg and U, atomic number 12 and 92, respectively. Ten elements (Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe) were monitored and analyzed in samples. Each sample was scanned three times for 60 s.

2.4. Thermogravimetric and differential thermal analysis

Thermogravimetric (TG) and differential thermal analysis (DTA) measurements were carried out in a Derivatograph-C type thermos-analytical instrument (Hungarian Optical Works, Hungary). The samples were heated in an open ceramic crucible with 5 °C/min heating rate in a static air atmosphere.

2.5. Preparation of hydrocarbon-water stock solution

The hydrocarbon concentrations were measured by using a combustion type TOC analyzer (Elementar, model Vario TOC SELECT; detection range of 4 mg/L to 40 000 mg/L). Initially, all the glassware was washed with 2 % nitric acid and ethanol in order to remove all the impurities and to avoid any further adsorption of dust or particles from the air. Stock solutions were prepared in 250 mL flasks by adding a specific amount of model hydrocarbon (octane, dodecane, kerosene) and then toping up the flask to make up a 250 mL solution. The solutions were then kept closed for 30 min. Then the solutions were kept under sonification for an additional 30 min before being used for the batch tests. Three samples were taken for the initial concentration measurements and average values are reported here. For final concentration measurement, 40 mL samples were taken at each time interval for TOC measurement. At each test, the system was calibrated using an appropriate IC (inorganic carbon) and TC (total carbon) standard solutions.

For quality control, blank samples, as well as TC and IC samples, were also tested. All the experiments were performed in triplicate, and the average values are reported. The measured values were all within the range of ± 3%.

2.6. Adsorption studies

All the batch experiments were carried out at fixed hydrocarbon-water emulsion volume (100 mL) containing n-paraffin hydrocarbons (C_8, C_{12}) at concentrations varying from 475 mg C/L (C_8-water solution) to 377 mg C/L (C_{12}-water solution). Adsorbents were added at optimum dosage, whereas all experiments were conducted at room temperature. The dosage of adsorbent was also varied from 0.03 to 1 g to find the optimal value for maximum removal of hydrocarbon from water.

The samples were agitated using a mechanical shaker at a fixed agitation speed of 300 rpm. Equilibrium studies were carried out with varying time intervals to determine the equilibrium time and capacity. The effects of different variables (sorbent, contact time, regeneration) on the sorption capacity of the prepared adsorbent for hydrocarbon removal from water were studied. Total organic carbon (TOC) analyzer was used to measure the initial (C_i) and final oil concentration (C_f) for each experiment. The removal efficiency, RE, was calculated by (Eq. 1).

$$RE(\%) = \frac{(C_i - C_f)}{C_i} * 100 \qquad (1)$$

where: C_i: is the initial oil concentration (mg/L) and C_f: is the final oil concentration (mg/L)

The experiments were carried out according to the classical Westinghouse method of absorbability developed by Muir and coworker (Muir and Bajda, 2016). The adsorption test consisted of adding drops of hydrocarbon compounds to the dry zeolite sample with a known weight (1.5 g) until the point of maximum saturation was reached. The moment when the next drop of hydrocarbon compound flowed over the sorbent (i.e., the liquid was not absorbed) was considered to be the end of the experiment. It is to be noted that model hydrocarbons were used instead of oil.

By comparing the weights of the samples before and after the sorption of hydrocarbon compounds, the determination of the weight of the adsorbed material weight was carried out. The sorption (S) in %, was calculated based on the (Eq. 2).

$$S = \left(\frac{M_P}{M_O} \right) * 100\% \qquad (2)$$

where: M_p: a mass of adsorbed hydrocarbon, g; M_o: the weight of the sorbent, g

To study the effect of contact time and to determine the equilibrium time for maximum hydrocarbon uptake by RZT, TZT, MeTZT samples batch experiments were carried out at different contact times ranging from 10 to 90 min. The equilibrium set was checked after 24 h. Different samples were taken at pre-set time intervals, and the C_8 hydrocarbon concentrations were measured using a TOC analyzer.

The hydrocarbon concentration was measured by using a combustion type TOC analyzer. NDIR Elementar Vario TOC Select equipment was used with a measuring range of 0-60,000 mg C/L equipped with the CO_2 infrared detector. The acidification of the samples was done with hydrochloric acid (99.95 % purity). Before the experiments, all glassware was washed with 3 % nitric acid to remove all impurities and prevent further contaminations from the air.

3. Results and discussion

3.1 Morphological results

Brunauer (Brunauer, 1976) stated that the pore structure and pore size distribution have a significant effect on adsorption and transport phenomena within

the particle (Beerdsen et al., 2006) and thus their assessment provides information on the use of zeolites as adsorbents. The surface area, pore volume, and pore sizes were determined from the adsorption-desorption isotherms of nitrogen measured according to the standard procedure. As reported in our previous paper (Al-Jammal and Juzsakova, 2017), the applied acidic treatment significantly increased the pore volume and specific surface area of RZT (SBET increased by 3.5 times). During the acidic treatment, elements such as Al, Ca, Fe, Ca, Mg, Mn, Ti were dissolved and/or washed out from pores. The structure of TZT changed, specifically micropores disappeared, and the average pore diameter increased due to the collapse of the crystalline structure during the dealumination process

as confirmed by XRD in (Aljammal and Juzsakova, 2017). As mentioned earlier, one of the limiting properties of natural zeolite stems from its relatively small surface area compared to activated carbon and nanomaterials. Decker et al. (Decker et al., 2003) reported that the BET specific surface area of zeolitic tuff was between 7.8 and 12.3 m^2 g^{-1}. In contrast, the BET specific surface area of the dealuminated zeolite was 300–400 m^2 g^{-1}. To gain more insight into the surface, morphology cumulative pore volumes and pore volume distributions were plotted as illustrated in Figs. 2 and 3 for RZT and TZT samples.

For the raw and dealuminated zeolitic tuff, the pore volume distributions can be characterized by smooth peaks which disappear on the boundaries.
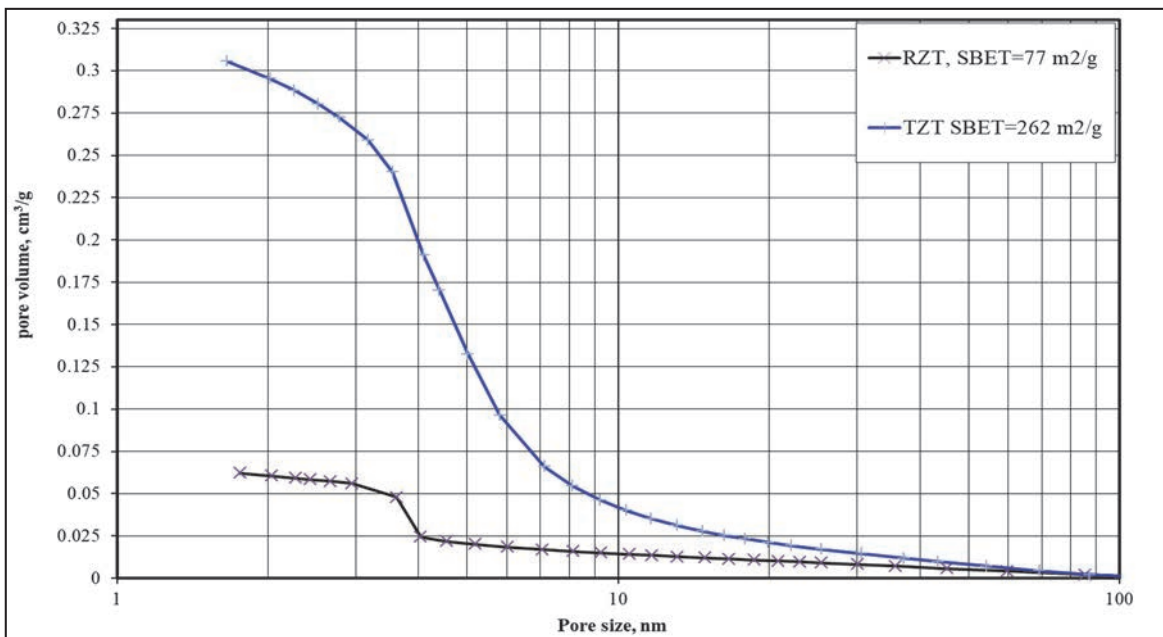

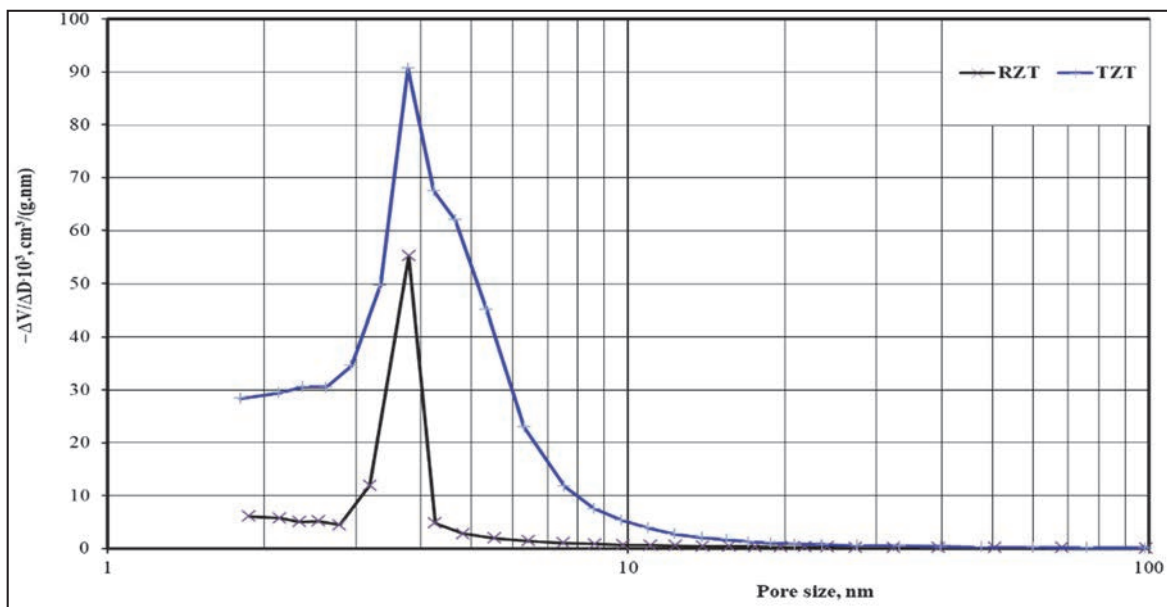**Fig. 2.** Cumulative pore volume of investigated RZT and TZT samples

Fig. 3. Pore volume distribution of RZT and TZT samples

3.2. Elemental analytical results

Table 2 shows the chemical compositions of RZT, TZT and MeTZT samples based on the XRF analyses. It has been published in the literature (Al-Jammal and Juzsakova, 2017) that the treatment of the RZT with concentrated hydrochloric acid has removed 25-30%wt. of the accompanying volcanic constituents (iron, aluminium, magnesium, calcium, and sodium oxides) (Salem et al., 2010). The average elemental concentrations (ppm) are presented in Table 2.

3.3. Thermal analytical results

Several mass loss steps can be observed in the TG-DTG curve of RZT, TZT and MeTZT samples (Fig. 4) (for detailed mass loss data, see Table 3). The first endothermic mass loss steps can be attributed to dehydration, namely the mass loss steps between 22-128°C and 128-250°C steps belong to the external and loosely bound water losses, while the exothermic step between 250-400°C could be attributed to the combustion of organic compounds. In this region, the loss of tightly bound water can also take place

(Duvarci et al., 2007; Knowlton and White, 1981; Yörükoğulları et al., 2010). The two overlapping endothermic steps between 400-613°C belong to the tightly bound water loss from the zeolite tuff structure (Duvarci et al., 2007; Knowlton and White, 1981; Yörükoğulları et al., 2010). The 3.6% w/w endothermic mass loss above 613°C (613-787°C) belongs to calcite decomposition.

After acidic treatment, the amount of externally bound water greatly increases, while the endothermic mass loss step above 613°C (calcite impurity in RZT), is completely absent due to its removal by acid treatment.

The total mass loss of sample TZT increased significantly compared to the RZT sample, mostly due to the increased external water content. The MeTZT sample shows a decreased amount of externally bound water. The thermal decomposition of adsorbed organic microemulsion compound along with the loss of remaining tightly bound water starts above 218°C in two exothermic processes and finishes around 654 °C. The total mass loss in this temperature range (220-650°C) increases slightly (0.4 w/w %) compared to the TZT sample.

Table 2. The elemental analysis of RZT, TZT and MeTZT samples using XRF technique

Element	Al	Si	P	Cl	K	Ca	Ti	Mn	Fe	S
RZT, ppm	52966	164750	3574	21668	25037	132219	31821	2407	168376	5806
TZT, ppm (↓/↑, %)*	17012 (68 ↓)	301474 (83↑)	1366 (62 ↓)	106999 (394↑)	8101 (68 ↓)	41328 (69 ↓)	26430 (17 ↓)	593 (75 ↓)	68731 (59 ↓)	1700 (71 ↓)
MeTZT, ppm (↓/↑, %)	16782 (68 ↓)	330752 (101↑)	1627 (54 ↓)	38211 (76↑)	22913 (8 ↓)	30869 (77 ↓)	29519 (7 ↓)	656 (73 ↓)	67452 (60 ↓)	1128 (81 ↓)

* ↓/ ↑, % -decrease or increase elemental concentration, %, in treated samples in comparison with RZT

Table 3. Data from thermo-analytical measurements of zeolitic tuff samples

| T_{start} (°C)	T_{max} (°C)	T_{end} (°C)	Mass loss step (%)	Step attributed to the followings	DTA
			Sample: RZT		
22	88	128	4.6	External water loss	Endothermic
128	129	250	4.6	Loosely bound water loss	Endothermic
250	311	400	2.9	Organic matter combustion/Tightly bound water loss	Exothermic
400	412/526	613	2.5	Tightly bound water loss	Endothermic
613	691	787	3.6	Calcite decomposition	Endothermic
787	818	1000	0.8	-	-
Sample mass: 52.2 mg			Total mass loss: 19.0% w/w		
			Sample: TZT		
23	88	170	13.9	External water loss	Endothermic
170	(153)	230	2.4	Loosely bound water loss	Endothermic
230	270	340	2.8	Organic matter combustion/Tightlyboundwaterloss	Exothermic
340	364	415	1.4	Tightly bound water loss	Endothermic
415	438	620	2.4	Tightly bound water loss	Endothermic
620	-	1000	1.0	-	-
Sample mass: 50.3 mg			Total mass loss: 23.9% w/w		
			Sample: MeTZT		
24	73	158	7.2	External water loss	Endothermic
158	159	218	1.6	Loosely bound water loss	Endothermic
218	266	411	4.8	Organic matter combustion/Tightly bound water loss	Exothermic
411	443	654	2.2	Organic matter combustion/Tightly bound water loss	Exothermic
654	-	1000	1.0	-	-
Sample mass: 49.8 mg			Total mass loss: 16.8% w/w		
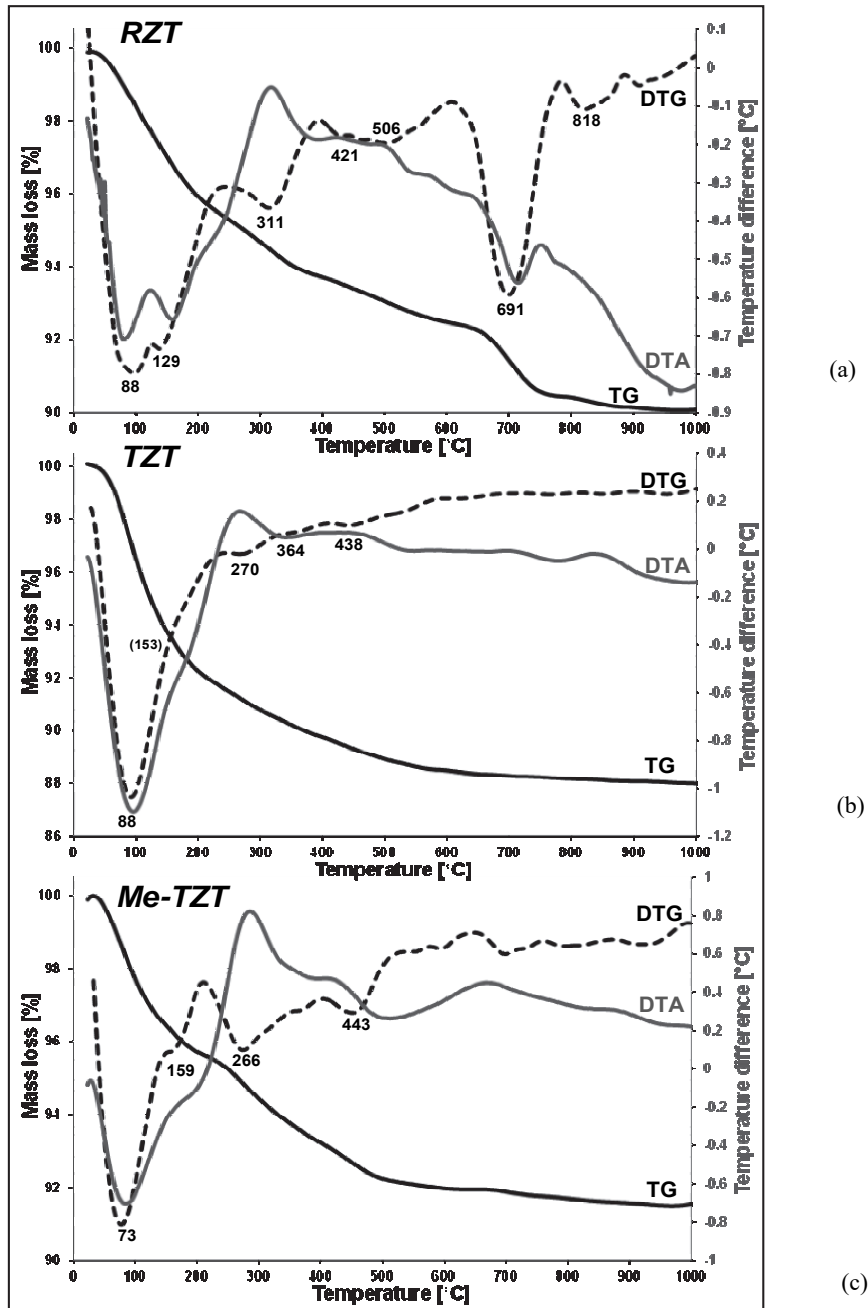
Fig. 4. TG, DTG and DTA curves for zeolitic tuff samples: (a) RZT; (b) TZT; (c) Me-TZT

However, in the MeTZT, the second mass loss step (411-654°C) has changed from endothermic to exothermic, which indicates that the majority of the water was replaced with organics after microemulsion modification. If the first exothermic mass losses step of MeTZT is corrected by the exothermic mass loss of TZT (230-340°C, 2.8% w/w), then the amount of microemulsion in MeTZT is calculated as 4.2% w/w (218-654°C). This excess indicates the amount of adsorbed organics after the microemulsion modification (42 mg in 1000 mg MeTZT).

3.4.Adsorption results

Table 4 shows the results of kerosene, n-octane and dodecane sorption using RZT, TZT and MeTZT

as adsorbents based on the classical Westinghouse method of absorbability (Muir and Bajda, 2016).In the case of all analyzed hydrocarbon compounds, it is clear that TZT and MeTZT have a much higher affinity in terms of hydrocarbons compared to the RZT. These differences can be attributed to the high surface area of TZT, and in case of MeTZT, the differences are due to the chemically attached tail groups of the surfactant, which resulted in the high hydrophobic character of the adsorbent.

For example, regarding the kerosene sample, the results showed sorption capacities of 119% and 107.4% for the MeTZT and TZT respectively and only 34% for RZT sample. Similar differences were observed in the case of n-octane and dodecane, which support the fact that the sorption properties of the TZT

samples are significantly higher than that of the RZT. These results can be explained by that fact that the pretreated and more hydrophobic zeolites such as TZT and MeTZT facilitate the inhibition of pore blockage towards the water, which in turn could result in more pores and potential surface area available for hydrocarbons diffusion and adsorption (De Ridder et al., 2012).

In addition to the standard Westinghouse experiments in order to study the effect of time on stream and to determine the maximum C_8 hydrocarbon adsorption by the zeolitic samples, batch experiments were done in the function of time. Samples were taken at different times, and the C_8 hydrocarbon concentrations were measured by TOC analyzer. All the experimental parameters such as C_8 hydrocarbon concentration; agitation speed and sample dosage were kept constant throughout the experiments. The experimental parameters used for this experiment were set at 300 rpm agitation speed, the adsorbent dosage of 0.5 g, at the initial hydrocarbon concentration of 475 mg C/L (C_8-water solution). The experiments were carried out at 27 $^\circ$C.

The dynamic sorptions of n-octane model compound over the RZT, TZT, MeTZT and AquaCarb sorbents are illustrated in Fig. 5. For the sake of comparison, the AquaCarb activated carbon sorbent was used as reference material for the sorption experiments. The results in Fig. 5 indicate that the contact time needed to reach the adsorption equilibrium for C8 hydrocarbon over RZT, TZT and MeTZT is about 20-30 min. Thus, the chosen contact time of 1.5 h is on the safe margin.

It was observed that at the beginning of the experiments, the hydrocarbon adsorbed very rapidly on the TZT, MeTZT surfaces due to the availability of large vacancies on the external surface of the TZT and MeTZT. As the outside surface of TZT and MeTZT becomes covered and saturated with C_8 hydrocarbon droplets, the rate of oil uptake started to decrease and reached equilibrium.

Regarding the microemulsified adsorbent MeTZT, it can be seen from Fig. 5 that it exhibits a high removal efficiency, which is comparable to that of the activated carbon since it reached hydrocarbon removal of 85 % after 60 min on stream. This result can be attributed to the existence of tail groups of the surfactant on the MeTZT surface. This means that the hydrophobic character of the zeolite enhanced significantly. These results are in agreement with the results reported by Ghouti and coworkers (Al-Ghouti and Al-Degs, 2011).

Table 4. The sorption of kerosene and different hydrocarbon compounds on RZT, TZT and MeTZT according to Westinghouse method

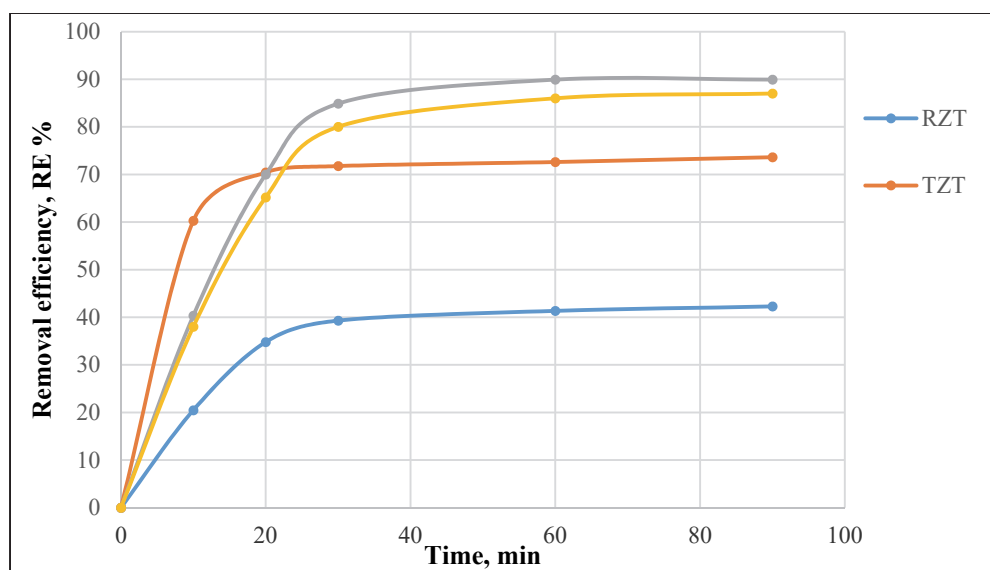| *Stock*	*Sample*	*Sample Weight, M_o (g)*	*Sample Weight + CH (g)*	*Adsorption, MP (g)*	*Sorption, S (%)*
kerosene	MeTZT	1.5022	3.2911	1.7889	119
	TZT	1.5012	3.1142	1.613	107
	RZT	1.5041	2.0127	0.5086	34
n-octane	MeTZT	1.5008	4.0981	2.5973	173
	TZT	1.5002	3.9288	2.4286	162
	RZT	1.5019	2.7785	1.2766	85
dodecane	MeTZT	1.5007	4.7451	3.2534	216
	TZT	1.5022	4.001	2.4988	166
	RZT	1.5078	3.2544	1.7466	116

Fig. 5. The change in percentage n-octane removal of over RZT, TZT, MeTZT and activated carbon (AquaCarb) in the function of contact time

It is to be noted that, the time-based results, described above, are in accord with the general theory of the oil sorption: initially the oil droplets at first have to overcome the boundary layer effect and then diffuse from the boundary layer film onto the adsorbent surface and then finally diffuse into the porous structure of the TZT and MeTZT.

The degree of hydrophobicity of zeolites, including the zeolitic tuff is directly dependent on the aluminium content of the zeolites. With the decrease of the aluminium content of the zeolite, the ionic charge of zeolite lattice is lowered. Decreasing ionic charge exhibits less polarity, and it results in lower hydrophilicity and higher hydrophobicity feature. It can be concluded that the chemical compositions of the treated zeolitic material influence the interaction between water molecules and the zeolite since the water molecules can interact with Al sites of zeolite framework and by dealumination this interaction significantly decreases (Bolis et al., 2006). The elemental composition of the acid treated and microemulsion modified zeolitic tuff as compared to raw zeolitic tuff indicates that the silicon to aluminium ratio increased from 3.1 to 17.7 and 19.7 for TZT and MeTZT respectively (Table 2). The increase of Si content in TZT and MeTZT influences its hydrophobic properties. The obtained results are in accord with the results obtained by several researchers (Grieco et al., 2013; Yonli et al., 2012).

The obtained results show that the modified/acid treated and microemulsified zeolitic tuff have improved the adsorption capacity for hydrocarbon removal from the hydrocarbon-water mixture as evidenced by the runs carried out with n-paraffin as a model hydrocarbon. The hydrocarbon removal efficiency was significantly higher over the acid treated zeolitic tuff surface as compared to the raw zeolitic tuff by the Westinghouse procedure. In the case of kerosene, the adsorption was 107% over TZT, while the untreated zeolitic tuff (with higher aluminium content) resulted in only 34 % adsorption. Similar tendencies were observed with n-octane and dodecane over TZT and RZT samples. The MeTZT exhibited even higher hydrophobicity than the acid treated zeolitic tuff. These results are in full harmony with the outcome of the previous work of the authors (Al-Jammal and Juzsakova, 2017) in which the adsorption capacities of the RZT and TZT zeolites were investigated over hydrocarbon model compounds via gas-chromatographic technique. The results show that the acidic treatment is very effective in removing framework aluminium as the Si/Al ratio increases from 2.58 to 15.06 (Al-Jammal and Juzsakova, 2017). Thus, the acid treatment succeeded to increase the silicon content by dealumination of the extra framework aluminium. The results in this study validated that the framework Si/Al atomic ratio of zeolites is an important parameter that exerts a strong influence on hydrophobicity.

The reusability of the zeolitic tuff (TZT) was studied as well. Additional tests were performed in order to study the changes in sorption capacity and the structural properties of TZT after the first test of adsorption. For this purpose, 0.5 g of spent adsorbent was reused for 100 mL n-octane-water samples under the same conditions as above to check the stability of the hydrocarbon removal efficiency of the TZT. The spent adsorbent was regenerated by washing with ethanol and dried at 105°C. The spent adsorbents were reused under the same conditions. The removal efficiencies measured were approximately 50-55 % for three cycles at 30 min contact time. It can be concluded that the removal efficiency remained as high as in the case of the fresh TZT sample.

4. Conclusions

The main aim of this research is to investigate the use of the dealuminated Jordanian zeolitic tuff for environmental damage mitigation, namely clean-up of hydrocarbon contaminated surface waters. Unfortunately, the pollution of the surface waters, including rivers, lakes, seas and oceans is rather frequent. Therefore, the naturally occurring zeolites were in the focus of our research since this class of porous materials is widely available, relatively inexpensive with high adsorption properties. The hydrophobicity of the zeolitic tuff was enhanced by acid treatment due to dealumination and by microemulsion treatment.

The changes in the morphology and composition were correlated with the hydrocarbon adsorption capacity of the zeolitic tuff. The adsorption experiments carried out with kerosene, n-octane and dodecane over raw, treated, and microemulsified treated zeolitic tuff confirmed the expectations that the removal of framework aluminium atoms enhances the sorption capacity of the zeolitic tuff. The reusability of the zeolitic tuff was proved by time on stream-regeneration cycles.

Therefore the treated zeolitic tuff seems to be a viable alternative for surface oil (hydrocarbon) removal from waters. It is to be noted that the results of the adsorption experiments according to the Westinghouse method and the batch experiments are in harmony, which shows that the surface modification of the zeolite by dealumination and microemulsification significantly improve the hydrophobicity and hydrocarbon removal efficiency of the zeolitic tuff.

References

Adebajo M.O., Frost R.L., Kloprogge J.T., Carmody O., Kokot S., (2003), Porous materials for oil spill cleanup:

a review of synthesis and absorbing properties, *Journal of Porous Materials*,**10**, 159-170.

Ajot H., Joly J.F., Lynch J., Raatz F., Caullet P., (1991), Formation of secondary pores in zeolites during dealumination: influence of thecrystallographic structure and of the Si/Al ratio, *Studies in Surface Science and Catalysis*,**62**, 583-590.

Al-Ghouti, M., Al-Degs, Y., (2011),New adsorbents based on microemulsion-modified diatomite and activated carbon for removing organic and inorganic pollutants from waste lubricants, *Chemical Engineering Journal*, **173**, 115-128.

Ali I., Gupta V.K., (2006), Advances in water treatment by adsorption technology, *Nature Protocols*, **1**, 2661–2667.

Al-Jammal N., Al-Hamamre Z., Alnaief M. (2016), Manufacturing of zeolite based catalyst from zeolite tuft for biodiesel production from waste sunflower oil,*Renewable Energy*, **93**, 449-459.

Al-Jammal N., Juzsakova T., (2017), *Review on the Effectiveness of Adsorbent Materials in Oil Spills Clean up*, Proc.7th International Council of Environmental Engineering Education International Conference, Óbuda University, Budapest, Hungary, 131-138.

Al-Othman Z.A., (2002), A review: fundamental aspects of silicate mesoporous materials, *Materials*, **5**, 2874-2902.

Alsbaiee A., Smith B.J., Xiao L.L., Ling Y.H., Helbling D.E., Dichtel W.R., (2016). Rapid removal of organic micropollutants from water by a porous beta-cyclodextrin polymer, *Nature*, **529**, 190- 613.

Amro M., (2004), *Treatment Techniques of Oil-Contaminated Soil and Water Aquifers*, Proc. of Int. Conf.on Water Resources and Arid Environment, Saudi Arabia, 1-11.

AquaCarb, (2018), AquaCarb 207C 12x30 coconut based granular activated carbon, Chemviron Carbon, On line at:
http://www.adeptpwt.co.uk/sites/default/files/AQUAC ARB%20207C.pdf.

Bandura L., Franus, M., Józefaciuk G., Franus W., (2015), Synthetic zeolites from fly ash as effective mineral sorbents for land-based petroleum spills cleanup, *Fuel*, **147**, 100-107.

Bandura L., Woszuk A., Kołodynska D., Franus W., (2017), Application of mineral sorbents for removal of petroleum substances: a review, *Minerals*, **7**, 1-25.

Barrer R.M., Makki M.B., (1964), Molecular sieve sorbents from clinoptilolite, *Canadian Journal of Chemistry*,**42**, 1481-1487.

Beerdsen E., Dubbeldam D., Smit. B., (2006). Understanding diffusion in nanoporous materials, *Physical Review Letters*, **96**, 1-4.

Behnood R., Bagher A., Nematollah J., Haghighi F., Masoumeh F., (2013), Application of natural sorbents in crude oil adsorption, *Iranian Journal of Oil & Gas Science and Technology*, **2**, 1-11

Beyer H.K., (2002), *Dealumination Techniques for Zeolites, Molecular Sieves*, In: *Post-Synthesis Modification I. Molecular Sieves (Science and Technology)*, vol. **3**, Springer, Berlin, Heidelberg, 204-255.

Blais J.F., Djedidi Z., Cheikh R.B., Tyagi R.D., Mercier G., (2008), Metals precipitation from effluents, *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management*, **12**, 135-149.

Bolis V., Busco C., (2006), Thermodynamic study of water adsorption in high-silica zeolites, *The Journal of Physical Chemistry B*, **110**, 14849-14859.

Breck D.W., (1974), *Zeolite Molecular Sieves: Structure, Chemistry, and Use*, John Wiley, New York, USA.

Briscoe N.A., Casci J.L., Daniels J.A., Johnson D.W., Shannon M.D., Stewart A., (1989), *Some Aspects of the Synthesis, Characterization and Properties of Zeolite Nu-2*, In: *Zeolites: Facts, Figures, Future*, Jacobs P.A., van Santen R.A. (Eds.), Elsevier Science Publishers,B.V. Amsterdam, The Netherlands.

Brunauer S., (1976), Pore structure of solids, *Pure and Applied Chemistry*, **48**, 401-405.

Campbel S.M., Bibby D.M., Coddington J.M., Howe R.F., (1996), Dealumination of HZSM-5 zeolites: II. methanol to gasoline conversion, *Journal of Catalysis*, **161**, 350-338.

Chen N.Y., (1973), Selective Sorption of Less Polar Molecules with Crystalline Zeolites of High Silica/Alumina ratio, USA Patent *3732326*.

Chen N.Y., (1976), Hydrophobic properties of zeolites, *The Journal of Physical Chemistry A*, **80**, 60-64.

Cretescu I., Soreanu G., Harja M., (2015), A low-cost sorbent for removal of copper ions from wastewaters based on sawdust/fly ash mixture, *International Journal of Environmental Science and Technology*, **12**, 1799-1810.

De Castro Dantas T.N., DantasNeto A.A., De A., Moura M.C.P., (2001), Removal of chromium from aqueous solutions by diatomite treated with microemulsion, *Water Research*, **35**, 2219-2224.

De Ridder D.J., Verberk J.Q.J.C., Heijman S.G.J., Amy G.L., Van Dijk J.C., (2012), Zeolites for nitrosamine and pharmaceutical removal from demineralized and surface water: mechanisms and efficacy, *Separation and Purification Technology*, **89**, 71-77.

Decker D.L., Papelis C., Hershey R.L., Harris R., Schmett G., (2003), Temperaturedependence of sorption behavior of lead and cesium metal ions on western pahute mesa and rainier mesa aquifer rocks, Desert Research Institute, Division of Hydrologic Sciences,Publication No. 45193, Reno, Nevada, USA.

Duvarci C.Ö., Akdeniz Y., Özmıhci F., Ülkü S., Balköse D., Ciftcioglu M., (2007), Thermal behaviour of a zeolitic tuff, *Ceramics International*, **33**, 795-801.

Ferey G., (1998), Thenew microporous compounds and their design, *ComptesRendus de l'Académie des Sciences - Series IIC - Chemistry*, **1**, 1-13.

Fingas M., (1995), Oil spills and their cleanup, *Chemistry and Industry*, **24**, 1005-1008.

Fritt-Rasmussen J., Brandvik P.J., (2011),Measuring ignitability for in situ burning of oil spills weathered under arctic conditions: from laboratory studies to large-scale field experiments, *Marine Pollution Bulletin*, **62**, 1780–1785.

Grieco S., Ramarao B., (2013), Removal of TCEP from aqueous solutions by adsorption with zeolites,*Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **434**, 329-338.

Harja M., Barbuta M., Rusu L., Munteanu C., Buema G., Doniga E., (2011), Simultaneous removal of astrazoneblue and lead onto low cost adsorbents based on power plant ash, *Environmental Engineering and Management Journal*, **10**, 341-347.

Harja M., Rusu L., Bucur D., Ciocinta R.C., (2012), Fly ash-derived zeolites as adsorbents for Ni removal from wastewater, *Revista de Chimie,* **57**, 587-597.

Jansen J.C., (2001), *The Preparation of Oxide Molecular Sieves, A. Synthesis of Zeolites*, In: *Introduction to Zeolite Science and Practice*, Jacobs P.A., Flanigen E.M., Jansen J.C., van Bekkum H. (Eds.), vol. **137**, Elsevier Science, Amsterdam, 175.

Jiang N., Shang R., Heijman S.G.J., Rietveld L.C., (2018). High-Silica zeolites for adsorption of organic micro-pollutants in water treatment: a review, *Water Research*, **144**, 145-161.

Jones C.W., Hwang S.J., Okubo T., Davis M.E., (2001), Synthesis of hydrophobic molecular sieves by hydrothermal treatment with acetic acid, *Chemistry of Materials*, **13**, 1041-1050.

Kemnetz S., Cody C.A., (1998), Composition of Matter Useful as an Oil Spill-Flocculating Agent, USA Patent *5725805*.

Knowlton G.D., White T.R., (1981), Thermal study of types of water associated with clinoptilolite, *Clays and Clay Minerals*, **29**, 403-411.

Kotova O.B., Harja M., Cretescu I., Noli F., Pelovski Y., Shushkov D.A., (2017), Zeolites in technologies of pollution prevention and remediation of aquatic systems, *Vestnik IG Komi SC UB RAS*, **5**, 49-53.

Lami E., Fajula F., Anglerotb D., CouriereT., (1993), Single step dealumination of zeolite beta precursors for the preparation of hydrophobic adsorbents, *Microporous Materials*, **1**, 237-245.

Li Z., Bowman R.S., (1998), Sorption of perchloroethylene by surfactant-modified zeolite as controlled by surfactant loading, *Environmental Science & Technology*, **32**, 2278-2282.

Li Y., Li L., Yu J., (2017), Applications of zeolites in sustainable chemistry, *Chem*, **3**, 928-949.

Liu Y., Kujawinski E.B., (2015), chemical composition and potential environmental impacts of water-soluble polar crude oil components inferred from ESI FT-ICR MS, *PLoS One*, **10**, 1-18.

Maesen T., Marcus B., (2001), *The Zeolite Scene*, In: *Introduction to Zeolite Science and Practice*, Jacobs P.A., Flanigen E.M., Jansen J.C., van Bekkum H. (Eds.), vol. 137, Elsevier Science, Amsterdam, 1-9.

Muir B., Bajda T., (2016), Organicallymodified zeolites in petroleum compounds spill cleanup — production, efficiency, utilization, *Fuel Processing Technology*, **149**, 153-162.

Otten W., Gail E., Frey T., (1992), Applications hydrophobic zeolites in the adsorptions technology, *Chemie Ingenieur Technik*, **64**, 915-925.

Popovici E., Cretescu I., Botezatu E., Soreanu G., Hanu A.M., Hristodor C., Maftei D., (2002), Evaluation of natural ion exchangers for the removal of radioactive isotopes from liquid effluents, *Environmental Engineering and Management Journal*, **1**, 577-588.

Querol X., Alastuey A., Moreno N., Alvarez-Ayuso E., Garacia-Sanchez A., Cama J., Ayora C., Simon M. (2006), Immobilization of heavy metals in polluted soils by the addition of zeolitic material synthesized from coal fly ash, *Chemosphere*, **62**, 171-180.

Roberge D., Hausmann H., Holderich F., (2002); Dealumination of zeolite beta by acid leaching: a new insight with two-dimensional multi-quantum and cross polarization[27]Al MAS NMR, *Physical Chemistry Chemical Physics*, **4**, 3128-3135.

Rotaru A., Cojocaru C., Cretescu I., Pinteala M., Timpu D., Sacarescu L., Harabagiu V., (2014), Performances of clay aerogel polymer composites for oil spill sorption-experimental design and modeling, *Separation and Purification Technology*, **133**, 260-275.

Ruhl M.J., (1993), Recover VOCs via adsorption on activated carbon, *Chemical Engineering Progress*, **89**, 37-41.

Ruthven D.M., (1988), *Principles of Adsorption and Adsorption Processes*, John Wiley& Sons, Canada.

Sakthivel T., Reid, D., Goldstein I., Hench l., Seal S., (2013), Hydrophobic high surface area zeolites derived from fly ash for oil spill remediation, *Environmental Science & Technology*, **47**, 5843-5850.

Salem N., Ahmed R., Awwad A., (2010), Chemical Modification of zeolitic tuff for removal of Hg(II) from water, *Environmental Research Journal*, **4**, 286-290.

Salvestrini S., Vanore P., Iovino P., Leon V., Capasso S., (2015), Adsorption of simazine and boscalid onto acid-activated natural clinoptilolite, *Environmental Engineering and Management Journal*, **14**, 1705-1712.

Shaw R., Sharma R., Tiwari S., Tiwari S.K., (2016), Surface engineered zeolite: an active interface for rapid adsorption and degradation of toxic contaminants in water, *ACS Applied Materials & Interfaces*, **8**, 12520-12527.

Silaghi M., Chizallet C., Sauer J., Raybaud P., (2016), Dealumination mechanisms of zeolites and extra-framework aluminum confinement, *Journal of Catalysis,* **339**, 242-255.

Skeels G.W., Breck D.W., (1984), *Synthesis of AlPO₄ Molecular Sieves*, Proc. of 6th Int. Zeolite Conference, Butterworths, Guilford, UK, 87.

Sun X.F., Sun R., Sun J.X., (2002), Acetylation of rice straw with or without catalysts and its characterization as a natural sorbent in oil spill cleanup, *Journal of Agricultural and Food Chemistry*, **50**, 6428-6433.

Tsitsishvili G. V., Andorikashvili T.G., Kirov G.N., Filizova L.D., (1992), *Natural Zeolites*, New York, Horwood.

Visa M., Chelaru A.M., (2014), Hydrothermally modified fly ash for heavy metals and dyes removal in advanced wastewater treatment, *Applied Surface Science*, **303**, 14-22.

Weitkamp J., Sakuth M., Chen C., Ernst S., (1989), Dealumination of zeolite beta using $(NH_4)_2SiF_6$ and $SiCl_4$, *Journal of the Chemical Society, Chemical Communications*, **24**, 1908-1910.

Yonli A.H., Batonneau-Gener I., Koulidiati J., (2012). Adsorptive removal of α-endosulfan from water by hydrophobic zeolites. an isothermal study,*Journal of Hazardous Materials*, **203-204**, 357-362.

Yörükoğulları E., Yılmaz G., Dikmen S., (2010), Thermal treatment of zeolitic tuff, *Journal of Thermal Analysis and Calorimetry*, **100**, 925-928.