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Efficiency of oil removal from real wastewater with different sorbent materials

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Abstract

The aim of this paper was to investigate the efficiency of different sorbent materials for oil removal from wastewater. Two types of sorbents were investigated: organic (loose natural wool fibers (NWF) and recycled wool based nonwoven material (RWNM)) and inorganic (sepiolite). Sorption was carried out in continuous tubular contractor (initial oil concentration of 1511 mg/dm^3) and batch tank (initial oil concentration of 5066 mg/dm^3). Wool-based sorbents showed higher sorption capacity (5.56 g/g for NWF and 5.48 g/g for RWNM) compared to sepiolite (0.19 g/g) in case of sorption in batch tank. The study on sorption in continuous tubular contractor suggested that volume of oily wastewater strongly affected oil removal. The results indicated that the combination of extractive-gravimetric and FTIR spectrophotometric methods can be recommended for precise determination of oil concentration, being suitable as a controlling tool for oil detection.

Keywords: Oil; Wastewater; Sorbents; Wool; Sepiolite

1. Introduction

Once oil comes in contact with water, it forms emulsion that needs to be treated before it is disposed, because of toxic and hazardous properties of its components. Current methods for treatment of oily wastewater before their disposal remain unsatisfactory. Even very low oil concentrations are toxic for microorganisms responsible for biodegradation in conventional sewage processes and therefore, removal of the oil phase is essential before effluent disposal. The oil removal process usually involves emulsion destabilization, which is not simple stage due to the presence of emulsifying agents that facilitate their stabilization [1–4]. Numerous techniques have been proposed for removal of oil so far [5–8].

In this paper, two types of unconventional, natural and environmentally friendly sorbents for oil removal from wastewater were investigated: organic sorbents based on wool (loose natural wool fibers (NWF) and recycled wool-based nonwoven material (RWNM)) and inorganic sorbent sepiolite [9–11]. The aim of this study was to analyze and compare their performance and efficiency. It is well established that some natural fibers (cotton, milkweed, kenaf, wool) have higher oil sorption capacities than most of the commercially available synthetic fibers, this being reason to choose wool-based sorbent materials for the research [7,12,13]. Excellent oil sorption properties and high biodegradability of natural fibers make them particularly attractive as a possible alternative to synthetic fibers [12,13]. On the other hand, clay minerals are considered to be very efficient and cheap sorbents due to their chemical and mechanical stability, high surface area and structural properties. Sepiolite is a natural hydrated magnesium silicate clay mineral, showing a unique fibrous morphology with anisotropic structure and pronounced narrow channels of specified width on the fiber surface [14]. It has the highest surface area of all the clay minerals [15]. High porosity and peculiar characteristics make them very efficient sorbents for different odours and vapours as well as for removal of metal ions, dyes and various organic compounds from water [14,16–19].

Previous studies on oil sorption properties of RWNM indicated that this material exhibited high sorption capacity for different types of oil (crude oil, diesel fuel, base oil SN150) and adequate reusability [10,12]. Thus, the research was extended to

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Table 1
Physico-chemical characteristics of real oily wastewater sample

Parameter	Obtained value
Ambient temperature (°C)	30.3
Turbidity (NTU)	32
Water temperature (°C)	22.6
pH-value	6.70
Conductivity (μS/cm)	765
Nitrates (N_2O_5) (mg/dm^3)	15.900
Nitrites (N_2O_3) (mg/dm^3)	0.090
COD (mg/dm^3)	4175
BOD_5 (mg/dm^3)	480
Residue (mg/dm^3)	2406
Suspended matter (mg/dm^3)	1598
Sediment (ml/dm^3)	10.5
Oil and grease (mg/dm^3)	5066
Lead (Pb) (mg/dm^3)	0.150
Cadmium (Cd) (mg/dm^3)	0.005
Chromium (Cr) (mg/dm^3)	0.020

real oily wastewater, which was supplied by wastewater station Makis (Belgrade, Serbia) where the wastewater after washing and maintenance of locomotives and wagons is collected. This specific oily wastewater was chosen as it is a potential pollutant for surrounding environment in case of accidental spillage and its proper treatment must be taken into consideration. Sorption experiments were carried out in continuous tubular contractor and batch tank.

2. Experimental

2.1. Chemicals

The following chemicals were used in experimental work: H_2SO_4 (p.a., Aldrich); CCl_4 (p.a., Aldrich); *n*-hexane (p.a., Riedel de Haen); anhydrate Na_2SO_4 (p.a., Aldrich); methyl-*tert*-butyl-ether (Merck); HCl (1:1, Merck); HNO_3 (1:1, Merck).

2.2. Real oily wastewater

Physico-chemical characteristics of real oily wastewater collected at wastewater station Makis (Belgrade, Serbia) are shown in Table 1. Oily wastewater mainly contained motor oils SAE-30 and SAE-40 (Oil refinery Belgrade, Serbia) and acidophylic phosphate-free surfactants.

2.3. Sorbents

NWF originated from domestic sheep. Wool fibers were washed with 0.2% of commercial detergent (Meril, Merima-

Table 2
Physical and mechanical properties of RWNM [12]

Weight (g/m^2)	235
Breaking strength[a] (N)	19.23
Bursting strength (N)	21.97
Thickness (mm)	1.56

[a] Machine direction.

Krusevac, Serbia) at 30 °C, for 1 h. After several iterations of rinsing with warm and cold water, fibers were dried at room temperature. Subsequently, fibers were carded. Sorption behavior of loose fibers was studied.

RWNM (78% wool/22% polyester) was produced from second-hand knitted military pullovers of the same quality and characteristics. The pullovers were torn off, washed, decolorized with reducing agent, dried and garneted in industrial conditions. Needle-punch process was chosen for the production of RWNM. Some physical and mechanical properties of the RWNM are given in Table 2 [12].

Particle granulation of sepiolite samples (Kosovo, Serbia) ranged from 0.5 to 3 mm.

2.4. Analytical methods for determination of oil concentration

Direct analytical methods used for determination of oil concentration were: extractive-gravimetric method and instrumental methods (refractive index determination and FTIR spectrophotometry). Extractive-gravimetric method and FTIR spectrophotometry were considered to be optimum methods particularly because of the concentration of oil in real oily wastewater sample that was less than 1%. In addition, both methods provide superior precision and reliability. FTIR spectrophotometry is based on the detection and indirect determination of hydrocarbon groups content (naphtenic, aliphatic or aromatic oil compounds) since oil can consist of different types of hydrocarbons. All direct methods for oil determination in water are very sensitive, with very good reproducibility [20–23]. Comparative analysis of different direct methods for determination of oil in water is shown in Table 3.

Extractive-gravimetric method was carried out with *n*-hexane as a solvent. The real oily wastewater sample was adjusted to pH 2 with HCl or H_2SO_4. The oily water samples and solvent were poured in the separating funnel and shaked for 2 min. After the separation, the solvent phase was filtered through the filter paper (blue ribbon) which contained anhydrated Na_2SO_4 (1.00 g) and it was placed in round flask (150 cm^3). Each wastewater sample was extracted twice. Oil concentration (C_{oil}, mg/dm^3) was

Table 3
Comparative analysis of direct methods used for determination of oil concentration

Method	Instrument	Detection limit (mg/dm^3)	Precision	Duration time
Extractive-gravimetric [20]	Distillation apparatus	1	±0.1	Minimum 48 h
Refractometry index detection [20]	Abbe's refractometer	0.1	±0.01	10 min
FTIR spectrophotometry [23]	FTIR spectrophotometer	0.04	±0.004	10 min

calculated according to equation:

$$C_{oil} = \frac{(m_1 - m_2) \times 10^{-3}}{V_{sample}} \quad (1)$$

where m_1 is the mass of round flask with oil (g), m_2 the mass of dry and empty round flask (g) and V_{sample} is volume of analyzed wastewater sample (dm^3).

Each oily wastewater sample (prepared standards of real oily wastewater sample) was adjusted to pH 2 for FTIR measurements. Wastewater sample was placed in separating funnel, with CCl_4 as a solvent, where it was shaked for 10 min in laboratory shaker. After the separation, solvent phase was filtered through the filter-paper (blue ribbon) that contained 1.00 g of anhydrate Na_2SO_4. IR spectra were scanned from 3200 to 2700 cm^{-1}. Oil concentration was determined from sum of the heights of absorption peaks that appeared at characteristic values typical for hydrocarbons (CH_3-groups appear at 2959 cm^{-1}, CH_2-groups appear at 2954 cm^{-1} and CH-groups appear at 3030 cm^{-1}).

Oil concentration (C_{oil}, mg/dm^3) was determined as:

$$C_{oil} = \frac{CV_{sol}}{V_{sample}}, \quad (2)$$

where C is the concentration of oil read on calibration curve (mg/dm^3), V_{sol} the volume of solvent (CCl_4) used for extraction (cm^3), and V_{sample} is the volume of oily wastewater sample (cm^3).

2.5. Experimental set-up

Oil sorption was investigated in the continuous tubular contractor and batch reactor. Sorption in continuous tubular contractor was carried out with 5.00 g of wool-based sorbents and 40.00 g of sepiolite. Three sorption columns (2 cm in diameter) were formed for experiments. After the removal of free oil by separation, the oil concentration was reduced from 5066 mg/dm^3 to 1511 mg/dm^3. Flow rate of wastewater was 2 cm^3/min and contact time between sorbent and water was 25 min. Experiments were conducted at room temperature. The oil concentration in water was determined by FTIR spectrophotometry.

Sorption in batch tank was carried out with 0.2500 g of wool-based sorbents and 10.0000 g of sepiolite. Sorbents were placed in Erlenmeyer flask (500 cm^3) with 400.0 cm^3 of oily wastewater, with oil concentration of 5066 mg/dm^3 and pH 6.70. Sample was then shaked in laboratory shaker for 24 h at 22 °C. Wool-based sorbents were taken out of flask and drained for 1 min, while sepiolite was removed after decantation. Sorbent efficiency was determined by the application of extractive-gravimetric method.Oil sorption capacity (q, g/g) for experiments in batch tank was determined according to following equation:

$$q = \frac{C_i - C_f}{m} \quad (3)$$

where C_i is the initial oil concentration (g/dm^3), C_f the final oil concentration (g/dm^3), m the mass of sorbent (g) and V_{sample} is the volume of analyzed wastewater sample (dm^3).

3. Results and discussion

3.1. Sorption of oil in batch tank

Sorption capacities of NWF, RWNM and sepiolite for real oily wastewater (C_{oil} = 5066 mg/dm^3) in batch tank were: 5.56 g/g, 5.48 g/g and 0.19 g/g, respectively. Apparently, wool-based sorbents showed higher sorption capacity compared to sepiolite. However, obtained sorption capacities for NWF and RWNM are significantly lower in comparison with literature data [7,10,12]. Lower sorption efficiency for real oily wastewater could be due to the form of oil present in water. The experiments in previous studies were conducted in the water baths with an oil, which was floated freely on the water surface [7,10,12]. On the contrary, real oily wastewater occurred mainly in the form of stable emulsion that was stabilized by surfactants used for washing of wagons and locomotives. Thus, it is likely that removal of oil was inhibited because of the complex interactions between surfactants, oil and wool fibers.

3.2. Sorption of oil in continuous tubular contractor

Keeping in mind the results obtained in batch system, the idea was to highlight the efficiency of investigated sorbents for emulsified oil in continuous tubular contractor. IR spectra of oil extracts of real oily wastewater samples after the sorption on NWF, RWNM and sepiolite in continuous tubular contractor are shown in Figs. 1–3, respectively.

The increase of oil concentration showed increase in absorbance, suggesting the linear correlation in case of wastewater treatment with NWF or sepiolite. However, no exact correlation between oil concentration and absorbance was established for RWNM.

The percentage of oil removal for all investigated sorbents in continuous tubular contractor is presented in Table 4, whereas the dependence of oil concentration on the effluent volume is shown in Fig. 4.

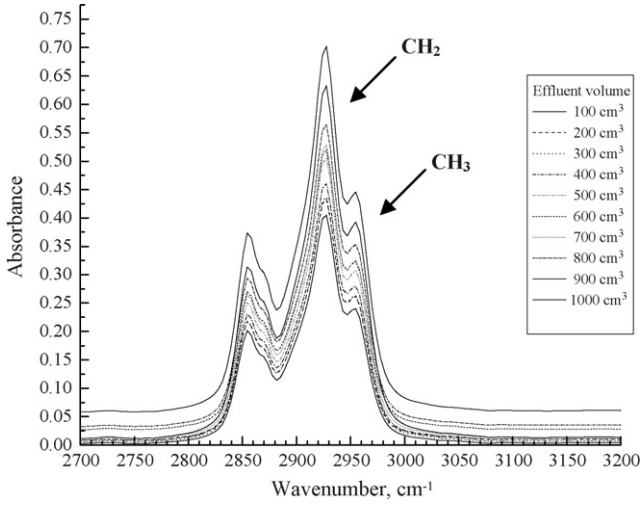

Fig. 1. IR spectra obtained for different oil concentrations after the sorption on NWF in continuous tubular contractor.

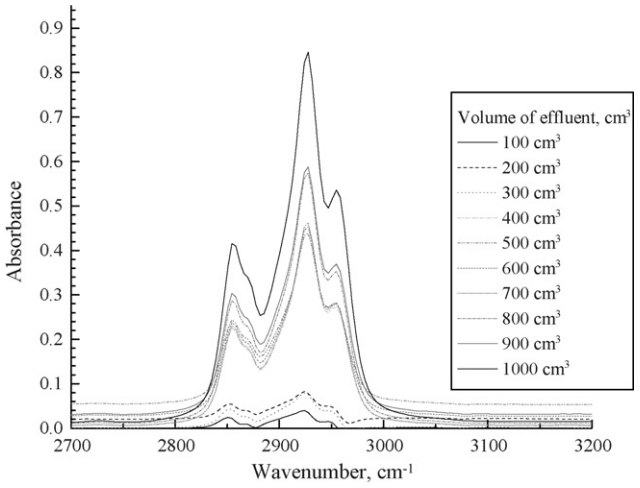

Fig. 2. IR spectra obtained for different oil concentrations after the sorption on RWNM in continuous tubular contractor.

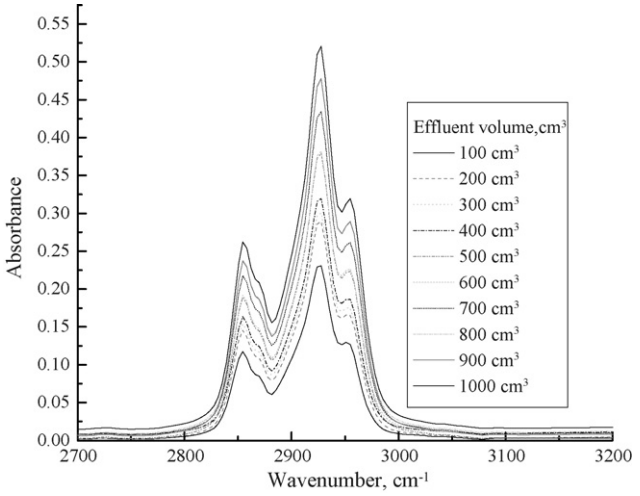

Fig. 3. IR spectra obtained for different oil concentrations after the sorption on sepiolite in continuous tubular contractor.

Table 4
The percentage of oil removal for all investigated sorbents in continuous tubular contractor

Effluent volume (cm^3)	Percentage of oil removal (%)		
	NWF	RWNM	Sepiolite
100	74	78	86
200	72	75	82
300	72	74	81
400	70	71	79
500	68	71	76
600	67	70	75
700	66	70	72
800	64	63	70
900	59	62	70
1000	55	42	67

Wastewater flow rate: 2 cm^3/min, t: 20 °C, and $\tau_{contact}$: 25 min, C_{oil} = 1511 mg/dm^3.

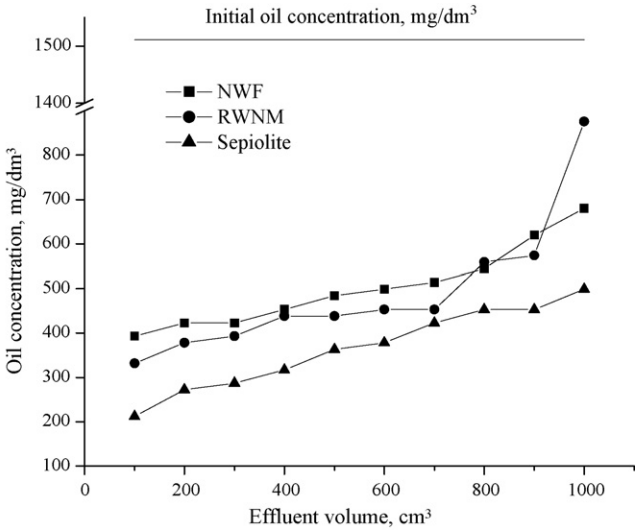

Fig. 4. The efficiency of oil removal (wastewater flow rate: 2 cm^3/min, t: 20 °C, $\tau_{contact}$: 25 min, and C_{oil} = 1511 mg/dm^3).

The results in Table 4 and Fig. 4 indicated that sorption efficiency increased in the following order: sepiolite > NWF > RWNM. The increase in effluent volume of wastewater up to 1000 cm^3, led to a decrease in sorption efficiency. The efficiency decreased for 26%, 46% and 22% in case of NWF, RWNM and sepiolite, respectively.

At the beginning of sorption process the primary sorption zone was formed in the upper part of column. As the sorption process continues the upper part of column was saturated with oil and sorption zone was moved to lower parts of column. The shift of sorption zone caused passing of oil through the column and concentration of oil in the treated water increased, as shown in Fig. 5. The break-through curve for each sorbent is presented in Fig. 5, where the relation between the inlet and the outlet concentration of oil and effluent volume is presented. Break-through point presents the moment after which oil removal does not occur any more. Break-through point was reached after the

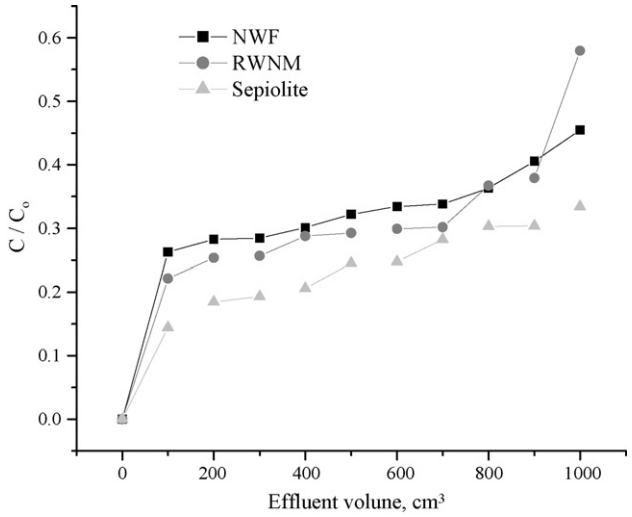

Fig. 5. Break-through curves.

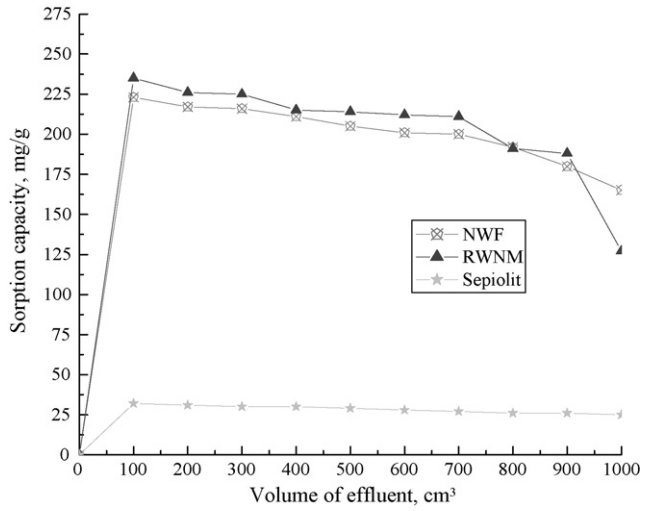

Fig. 6. The dependence of sorption capacity of NWF, RWNM and sepiolite on effluent volume in continuous tubular contractor.

fifth, the eighth and ninth pass in case of sepiolite, RWNM and NWF, respectively. As the break-through point is reached, the regeneration of sorbents is necessary.

The dependence of sorption capacity of NWF, RWNM and sepiolite on volume of effluent in continuous tubular contractor is shown in Fig. 6. Evidently, sorption capacities drastically decreased compared to results achieved in batch system. This decrease was likely due to absence of free oil in influent, which was partially present in real oily wastewater. In addition, the contact time in continuous tubular contractor was considerably shortened and the interactions between emulsified oil and sorbents were weak.

The sorption ability of sepiolite is mainly ascribed to its high surface area [24]. The numerous micropores and channels as well as elongated nature of the particles contribute to its high surface area and therefore, adsorptivity [16–19,24]. However, sepiolite showed poor sorption behavior for real oily wastewater, indicating that high surface area is only one factor influencing the sorption of oil. The hydrophobicity of sorbent must be taken into consideration and therefore, some further adequate modification of sepiolite in order to obtain hydrophobic surface should be carried out.

Better sorption behavior of NWF compared to RWNM could be attributed to oleophylic surface of raw wool fibers arising from the presence of grease (lanolin) and waxes [7,13]. However, properties of recycled wool fibers are supposed to be different from raw wool fibers as they underwent different mechanical and chemical changes. It can be assumed that recycled wool fibers do not possess (or possess in small amounts) waxes. Thus, adsorption by van der Waals forces and hydrophobic interactions between the fiber surface and oil is not expected to be the dominant mechanism of oil sorption in case of recycled wool fibers. In addition, previous studies pointed out that oil sorption on wool is most likely governed by an adsorption process due to scale-like surface of the fiber which facilitates the formation of capillary bridges of oil between neighboring fibers [10,13]. The fact that loose raw wool fibers were used in experiments should not be neglected as the loose structure provided more space between the fibers making the formation of oil bridges easier and accordingly, higher sorption capacity compared to RWNM [12].

4. Conclusion

Wool-based sorbents showed higher sorption capacity (5.56 g/g for NWF and 5.48 g/g for RWNM) compared to sepiolite (0.19 g/g) in case of batch tank. The experiments in continuous tubular contractor indicated that the oil removal was strongly affected by volume of oily wastewater. The increase in volume of effluent up to 1000 cm^3 brought about decrease in efficiency for 26%, 46% and 22% for NWF, RWNM and sepiolite, respectively. The decrease in sorption capacity of all investigated sorbents in continuous tubular contractor was likely due to absence of free oil in influent, which was partially present in real oily wastewater used for study in batch system as well as because of the much shorter contact time.

The results indicated that wool-based sorbents could be used for treatment of water and removal of oil. Combination of direct analytical methods, such as extractive-gravimetric and FTIR spectrophotometric method, are recommended for precise oil concentration determination. These analytical methods can be used as a controlling tool for oil detection.

References

[1] G. He, G. Chen, Separation of water and oil from water-in-oil emulsion by freeze/thaw method, Separat. Purif. Technol. 31 (2003) 83–89.
[2] L. Xia, S. Lu, G. Cao, Demulsification of emulsions exploited by enhanced oil recovery system, Separat. Sci. Technol. 38 (2003) 4079–4094.
[3] Á. Cambiella, E. Ortea, G. Ríos, J.M. Benito, C. Pazos, J. Coca, Treatment of oil-in-water emulsions: performance of a sawdust bed filter, J. Hazard. Mater. 131 (1–3) (2006) 195–199.
[4] V. Rajakovic, D. Skala, Separation of water-in-oil emulsions by freeze/thaw method and microwave radiation, Separat. Purif. Technol. 49 (2) (2006) 192–196.
[5] J.M. Benito, G. Ríos, C. Pazos, J. Coca, Methods for the separation of emulsified oil from water: a state-of-the-art review, Trends in Chemical Engineering, Research Trends, Trivandrum, India, vol. 4, 1998, pp. 203–231.
[6] G.N. Mathavan, T. Viraraghavan, Coalescence/filtration of an oil-in-water emulsion in a peat bed, Water Res. 26 (1992) 91–98.
[7] R.F. Johnson, T.G. Manjrekar, Removal of oil form water surfaces by sorption on unstructured fibers, Environ. Sci. Technol. 7 (1973) 439–443.
[8] T. Viraraghavan, G.N. Mathavan, Treatment of oily waters using peat, Water Pollut. Res. J. Can. 25 (1990) 73–90.
[9] C. Cooper, R. Burch, Mesoporous materials for water treatment processes, Water Res. 33 (18) (1999) 3689–3694.
[10] M. Radetic, D. Jocic, P. Jovancic, Lj. Rajakovic, Z.Lj. Petrovic, H. Thomas, The recycled-wool-based nonwoven material sorption capacity for some oils, DWI Reports, 125, 2002, pp. 463–468.
[11] A. Brown, W. Bloomfield, Methods for removing oil spills using a natural, recyclable absorbent, US Patent 5,160,629 (1992).
[12] M. Radetic, D. Jocic, P. Jovancic, Z.Lj. Petrovic, H. Thomas, Recycled wool based non-woven material as an oil sorbent, Environ. Sci. Technol. 37 (2003) 1008–1012.
[13] H.M. Choi, J.P. Moreau, Oil sorption behavior of various sorbents studied by sorption capacity measurement and environmental scanning electron microscopy, Microsc. Res. Techn. 25 (1993) 447–455.
[14] M. Dojcinovic, M. Mitrovic, M. Martic, V. Vucelic, D. Vucelic, Sorption characteristics of paper produced from sepiolite, J. Serb. Chem. Soc. 66 (2001) 385–396.

[15] R.M. Barrer, Clay minerals as selective and shape-selective sorbents, Pure Appl. Chem. 61 (1989) 1903–1912.
[16] H.M.N. Tekin, A. Dincer, O. Demirbas, M. Alkan, Adsorption of cationic polyacrylamide onto sepiolite, J. Hazard. Mater. 134 (2006) 211–219.
[17] S. Akyuz, T. Akyuz, FTIR spectroscopic investigation of adsorption of pyrimidine on sepiolite and montmorillonite from Anatolia, J. Inclus. Phen. Macrocyc. Chem. 46 (2003) 51–55.
[18] M. Radojevic, V. Jovic, D. Karaulic, D. Vitorovic, Study of sepiolite from Goles (Kosovo, Yugoslavia). I. Sorption capacity, J. Srb. Chem. Soc. 67 (2002) 499–509.
[19] N. Bekta, B. Akman, S. Kara, Kinetic and equilibrium studies in removing lead ions from aqueous solutions by natural sepiolite, J. Hazard. Mater. 112 (1–2) (2004) 115–122, 9.
[20] Standard Methods for the Examination of Water and Wastewater, 20th Ed., 1998, pp. 5–35.
[21] H. Willard, L. Merritt, J. Dean, F. Settle, Instrumental Methods of Analysis, 6th ed., Wadsworth Publ. Co., Belmont, 1981.
[22] Standard test method for oil and grease and petroleum hydrocarbons in water, ASTM (1996) 3921.
[23] JUS Standard H.Z1.151, VII, Determination of Oil in Water-Spectrophotometric Method, 1972.
[24] E. Sabah, M.S. Celik, Sepiolite: an effective bleaching adsorbent for the physical refinning of degummed rapeseed oil, JAOCS 82 (2005) 911–916.