Bulgarian Chemical Communications, Volume 46, Number 1 (pp. 157 – 164) 2014

Removal of detergents by zeolites and membranes

B. Tsyntsarski[1], B. Petrova[1], T. Budinova[1*], N. Petrov[1], A. Sarbu[2], T. Sandu[2],
M. Ferhat Yardim[3], A. Sirkecioglu[3]

[1]Institute of Organic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev str., BL.9, 1113 Sofia
[2] National Research and Development Institute for Chemistry and Petrochemistry-ICECHIM, Polymers Department, 202 Independentei Spl., Bucharest, Romania
[3] Istanbul Technical University, Department of Chemical Engineering, 34469 Maslak, Istanbul, Turkey

Received January 16, 2013; Accepted February 12, 2013

The adsorption of sulfonic and phenolic substances in detergents by natural zeolites from Turkish and Romanian deposits was investigated. The zeolites were characterized by IR spectroscopy and surface measurements. The effects of contact time and pH on the adsorption process were investigated. It was established that the specific surface area is the determining factor which influences mostly on the adsorption of detergents. The removal of detergents was also investigated by applying different membranes. They have demonstrated higher adsorption capacity values than zeolites.

Key words: zeolite; membrane; adsorption; detergent; water

INTRODUCTION

The production of different washing materials has been always accompanied by regular accumulation of substantial quantities of detergents in waste waters. Currently used detergents generally consist of surfactants, bleaching agents, additives for secondary benefits, enzymes, etc. The effective removal of these hardly degradable pollutants from waste waters is a global problem of great importance. Many research efforts on the improvement of the adsorption process and adsorbent materials for removal of organic pollutants from waste water streams have been developed in the last years. Activated carbon is the most used adsorbent; however its regeneration is difficult and expensive. Recently many researchers are investigating new, efficient and regenerable adsorbents, such as inorganic materials, e.g. zeolites and clay materials [1-8]. An important benefit of zeolites is that they are stable and inclined to regeneration. Since the thermodynamics and kinetics of gas-phase adsorption of organic molecules by zeolites have been thoroughly investigated, the studies of adsorption of organic molecules by zeolites from aqueous solutions are relatively rare [7]. The adsorption from aqueous solution depends not only on the zeolite pore structure, but also on the competition between the organic molecules and water molecules for the zeolite adsorption sites.

Advances in nano-scale science and engineering are providing unprecedented opportunities to develop low-cost and environmentally acceptable water purification processes. Besides, the adsorptive materials, membranes, membrane separation techniques are also promising as an effective alternative for water purification from various pollutants. The fundamental understanding of membrane performance is important for the suitable selection and application in industrial systems. There are many studies on the removal of organic substances from diluted solutions using membranes [9-14], but reports on separation of toxic detergents by membranes are rare in the literature. This paper gives a brief overview of the use of membranes in the purification of water, contaminated by toxic detergents.

This work aims to investigate the influence of structural and surface properties of zeolites and membranes on detergent removal (sulfonic and phenolic substances) in aqueous solution. This is a part of our efforts to develop an average scale module for purification of small factories waste waters from different pollutants, on the base of multi-layered filter containing natural zeolites and polymer membranes.

---

* To whom all correspondence should be sent:
E-mail: goriva@orgchm.bas.bg

EXPERIMENTAL

Characterization of the initial materials

In this study three zeolite samples and two membrane samples were investigated towards adsorption of sulfonic and phenolic substances. The first zeolite sample is from Romania (location: Marsid, Bocsa-Borla) and the other two zeolite samples are from Turkey (location: Bigadic and Gordes).

The membrane samples are prepared as follows:

Membrane M1 - from polymer mixture of 80 % C1 (prepared from monomer mixture of 90 % acrylonitrile (AN) and 10 % vinyl acetate (AcV) and 20 % polyvinyl alcohol (APV) , with coagulation bath composition of 70 % iso-propanol (IzOH) and 30% water.

Membrane M2 – polymer mixture of 80 % C2 (prepared from a monomer mixture of 80 % AN, 20% AcV) and 20 % APV.

Analytical methods for characterization of zeolites

The following methods were applied and equipment’s were used for characterization of the zeolites:

- X-ray diffractometer BRUKER D8 ADVANCE, equipped with DIFFRA Cplus Commender XRD (Bruker AXS), and using Bragg-Brentano diffraction method, with coupling Θ-Θ in vertical configuration.
- Surface measurements were performed by porosimeter ASAP 2020 (Micromeritics).
- The samples were also analyzed by FTIR spectroscopy, using Bruker IFS 113V spectrophotometer, with resolution of 1 cm^{-1}. The samples were mixed with potassium bromide and the mixture was pressed into pellets to be used in the analysis.

Adsorption from aqueous solutions

Adsorption experiments were carried out by using a zeolite sample Marsid with two fractions: ≤0.09 mm and 0.10-0.14 mm.

The adsorption capacity of the adsorbents for sulfonates and phenolic compounds were investigated by using Bulgarian commercial dishwashing liquid (pH 6.7). Adsorption experiments were conducted using aqueous solutions, containing different volumes of liquid detergent. Portions of adsorbents with amount of 0.1 g were used in the adsorption measurements. They were added to portions of the liquid detergent with volume of 5-30 mL and water was added in order to obtain final volume of 50 mL for each solution. Then the solutions were shaken for 5 min to 2 h. The amount of the sulfonates and phenolic compound were determined at wavelengths 220 and 269 cm^{-1} respectively, using UV spectrophotometer Pharo 300 [15, 16].

The factors affecting the sorption of the investigated detergents from aqueous solution, such as contact time, particle size distribution and effect of pH were studied.

The effect of pH of the solution on the equilibrium adsorption of sulfonate and phenolic compounds is investigated by using 0.1 g adsorbent and 50 mL solution (containing 20 mL liquid detergent) at 1 h contact time. The initial pH values of the solutions were adjusted with either HCl or NaOH.

RESULTS AND DISCUSSION.

Characterization of the natural zeolite samples

The results from XRD analysis (Fig.1) show that all the studied natural zeolites dominantly contain clinoptilolite.

Table 1 was prepared on the base of XRD results, which demonstrates the content of different minerals in the zeolite samples.

From XRD and atomic spectrophotometry results, the structural chemical phase composition of the samples were established and data are presented in Table 2.

The data in Table 2 show that the Turkish zeolites contain slightly higher amount of Al_2O_3 in comparison with zeolite sample Marsid. All the samples have high amount (>60%) of silicon dioxide, whereas Gordes zeolite has the highest. The content of aluminium oxide in all samples is in between 12-13 %. There are higher amounts of alkaline oxides in Bigadic and Gordes zeolites than Marsid zeolite. At the same time, the Bigadic zeolite contain more CaO and Fe_2O_3 than Marsid zeolite (contains half of the amount of Fe_2O_3 contained in Bigadic zeolite), and their content in Gordes zeolite (contains one-third of the amount of Fe_2O_3 contained in Bigadic zeolite) is the lowest.

Surface characterization results of Marsid, Bigadic and Gordes zeolites are presented in Table 3.

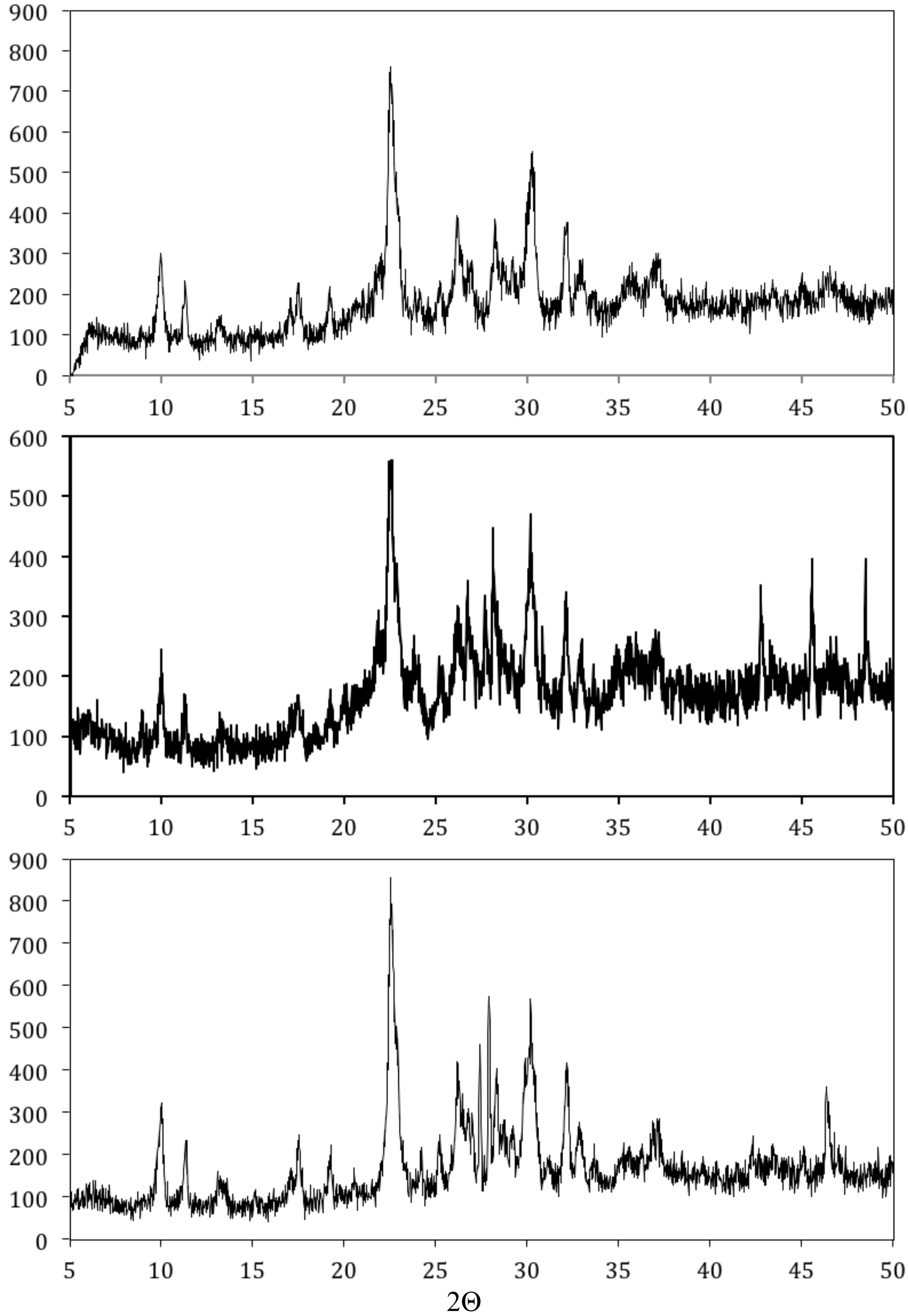


Fig 1. XRD patterns of Marsid, Gordes and Bigadic clinoptilolites

The data from Table 3 shows that the Marsid clinoptilolite has higher surface area and lower pore volume and pore radius than the other zeolites, as the average pore radius is lowest for the zeolite Marsid. Chemical character of the surface of Gordes and Marsid zeolies is probably due to the higher content of alkaline oxides.

The IR spectra of the zeolite Marsid is shown in Fig. 2. The bands are assigned to different vibration modes of the zeolite matrix were presented in Table 4 [17-19]. IR spectra (not shown) of Bigadic and Gordes zeolites are similar. IR results confirm that the investigated natural zeolites mainly contain the mineral clinoptilolite.

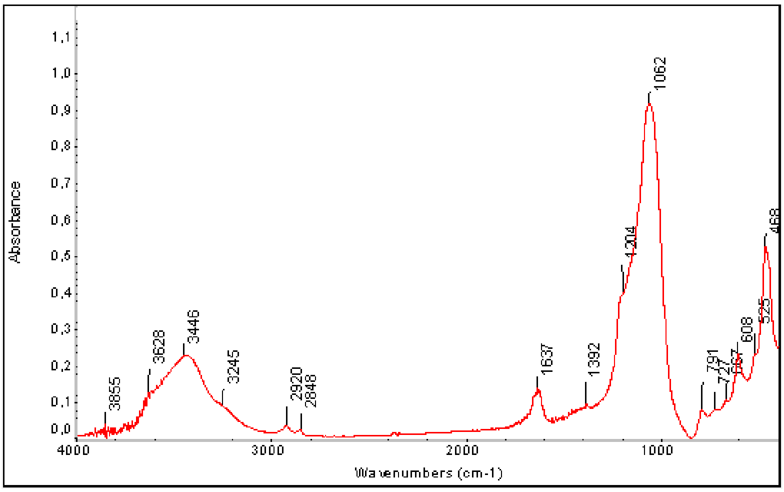


Fig. 2. IR spectra of clinoptilolite.

Table 1. Content of different minerals in zeolite samples

	Bigadic	Gordes	Marsid
Clinoptilolite content, %	95	>96	75-80
Plagioclase	+	-	+
Cristobalite	+	-	+
Quartz	+	+	+
Biotite	+	+	-
Clays	+	-	-

Table 2. Chemical composition of the clinoptilolite samples, (wt. %).

	Bigadic	Gordes	Marsid
SiO_2	64.00	71.98	66.21
Al_2O_3	13.56	12.56	12.37
Na_2O	0.45	0.96	0.39
K_2O	3.61	4.28	2.43
CaO	3.61	1.99	2.44
Fe_2O_3	1.35	0.45	0.74
MgO	-	0.42	0.86
H_2O	5.67	7.40	6.82
SiO_2/Al_2O_3	4.72	6.32	5.35

Table 3. Surface characteristics of zeolites.

Clinoptilolite	Specific Area, m^2/g	Pore Volume cm^3/g	Average Pore Diameter Å	pH
Marsid	43.4	0.061	56.36	4.8
Gordes	30	0.165	42.12	7.5
Bigadic	28	0.075	111.2	7.3

Adsorption experiments for the zeolite samples

The results of the adsorption of detergents from aqueous solutions, containing different volumes of liquid detergent, 5, 10, 15, 20 and 30 mL (for each solution water was added in order to obtain final volume of 50 mL), are shown in Fig. 3, Fig. 4 and Fig. 5 for Marsid, Gordes and Bigadic zeolites, respectively. All the isotherms are type L of Giles classification, indicating that adsorption proceeds by the formation of a monolayer in the range of concentrations used [20].

Table 4. IR bands of clinoptilolite .

Hydroxy groups of basic nature	4000-3000 cm^{-1}
CO_2 (in the air)	2300 cm^{-1}
H_2O (air+ads.)	1637 cm^{-1}
Si–O asymmetric stretching	1204 cm^{-1}
Si–O–Al asymmetrical stretching	1062 cm^{-1}
O–Si–O symmetric stretching	791 cm^{-1}
symmetric stretching of free SiO_4	727 cm^{-1}
symmetric stretching of free SiO_4	667 cm^{-1}
O–Si–O bending	608 cm^{-1}
''pore opening'' vibration of free SiO_4	525 cm^{-1}
Si–O bending	468 cm^{-1}

The experimental data were fit to the Langmuir equation in linear form [21]:

$$C_e/Q_e = 1/Q_ob + C_e/Q_o \qquad (1)$$

where C_e is the equilibrium pollutant concentration remaining in solution after adsorption (mg L^{-1}), Q_e is the amount of pollutant adsorbed on the adsorbent (mg g^{-1}), Q_o is the maximum amount of the pollutant per unit weight of adsorbent (mg g^{-1}), and b is a constant related to the affinity of adsorption sites (L mg^{-1}). The shape of the isotherms shows that the process of adsorption of detergents can be described by Langmuir theory, which states that adsorption proceeds via a monolayer formation.

Results (Fig. 3, Fig.4 and Fig. 5) show that Marsid zeolite with granulometric composition of ≤ 0.09 mm has the highest adsorption capacity. The samples with alkaline character of the surface - Bigadic and Gordes zeolites - show lower adsorption capacity towards both sulfonic and

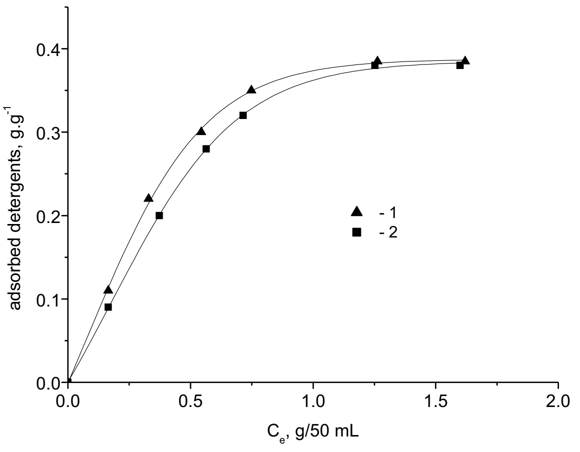


Fig. 3. Adsorption of detergents on Marsid zeolite: 1-sulfonic compounds, 2-phenolic compounds.

phenolic compounds (Fig. 4 and Fig. 5). These results indicate that the determining factors for their adsorption properties are the surface area and the pore size distribution of the samples, as well as the different chemical composition and chemical character of the surface.

Fig 6 shows the adsorption of sulfonic and phenolic compounds on the zeolite Marsid sample with particle size 0.10-0.14 mm. The enhancement of the particle size decreases the specific surface area, which causes reduction of the number of the active sites.

Comparing Fig 3 and Fig. 6 allows to understand the effect of the granulometric composition of the zeolites on the adsorption of both detergents (all zeolites show similar dependence).

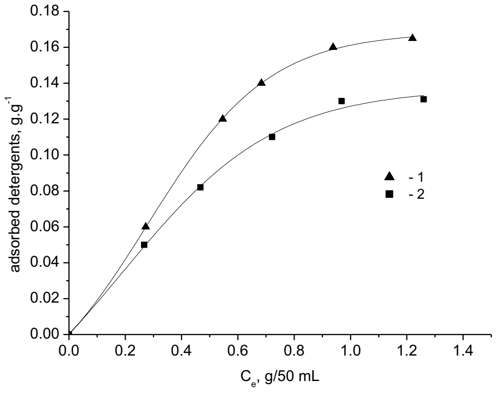


Fig. 4. Adsorption of detergents on Gordes zeolite: 1 - sulfonic compounds, 2 - phenolic compounds.

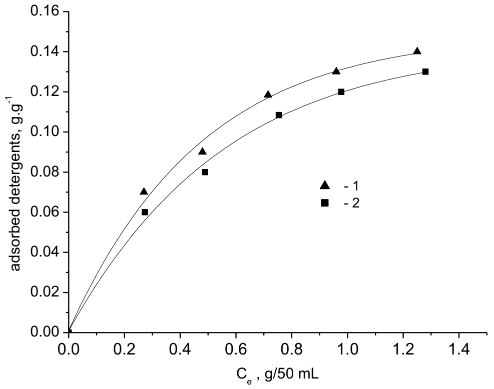


Fig. 5. Adsorption of detergents on Bigadic zeolite: 1 - sulfonic compounds, 2 - phenolic compounds.

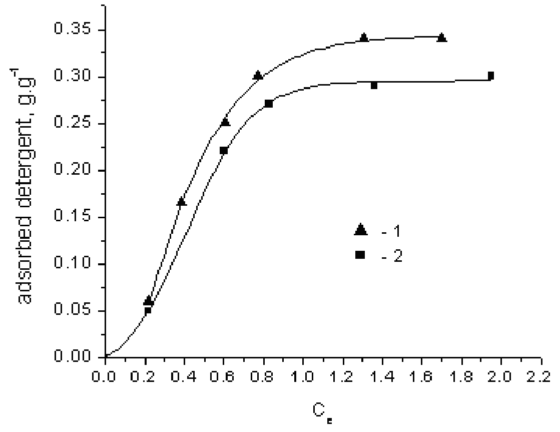


Fig. 6. Adsorption of detergents on Marsid zeolite samples with particle size 0.10-0.14 mm.

The increase of the size of the particles leads to decrease of the adsorption activity. Figure 7 shows the effect of the contact time on the removal of sulfonic compounds by Marsid zeolite. Data indicate that the removal of sulfonates increases with time and attains equilibrium in 30 minutes for all initial concentrations of the sulfonate solutions.

Sulfonate adsorption increases sharply for a short time and slows gradually when equilibrium is approaching. This behavior can be attributed to the decrease in the number of available sites on the zeolite surface during the process. The plot shows that the amount of sulfonate compounds adsorbed on the adsorbents (mg/g) vary in smooth and continuous curves, leading to saturation, which indicates the possibility for formation of monolayer coverage of sulfonates on the surface of the adsorbent. The kinetic curves (not shown) of the removal of sulfonates versus contact time for other zeolite samples show the same dependence.

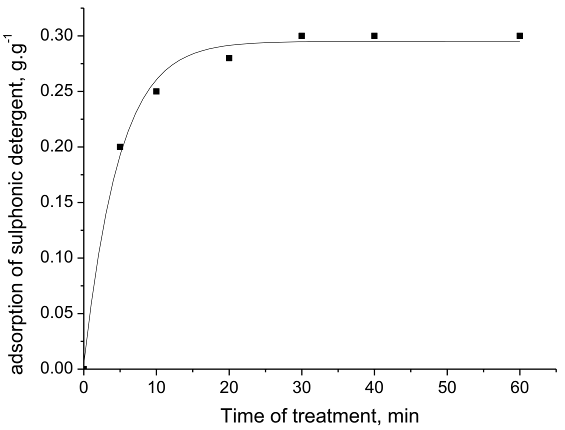


Fig. 7. Effect of contact time on adsorption at different concentrations of sulfonic compounds on zeolite Marsid.

Effect of pH on adsorption on zeolites

The pH of the aqueous solution has strong effects on the adsorption of different substances on the zeolite surface. pH is one of the key factor that control the adsorption in such processes, since it influences the electrostatic interactions between the adsorbent and the adsorbate.

The adsorption depends on the nature of the surface of the adsorbent and of the substances in the water solution. It was established that the Marsid zeolite has the lower pH value than other zeolites. Fig. 8 and Fig. 9 shows the effect of pH values on the adsorption of detergents on Gordes and Marsid zeolites. The target pH value was obtained by adding adequate amounts of NaOH or HCl diluted solutions to the initial non-buffered solution, containing sulfonic and phenolic compounds. The uptake of both compounds was found to be maximal at pH 6, independently with the fact that they have different pH values at initial conditions. As expected, these results confirm that both compounds are preferentially adsorbed from their neutral solutions. For both pollutants the amount adsorbed appeared to be much altered at neutral pH.

As the pH increases, the surface of zeolites is being negatively charged until solution pH > pH_{PZC}, where the amount of negative charges becomes predominant in the zeolite surface. At this point, the fall in the uptake is probably due to the repulsive interactions, that appear between the anionic form of the adsorbates and the charges on the clinoptilolite surface. Other reason could be the competitive adsorption between sulfonate/phenolic and chlorine ions (probably present as impurities), which hinders detergent uptake.

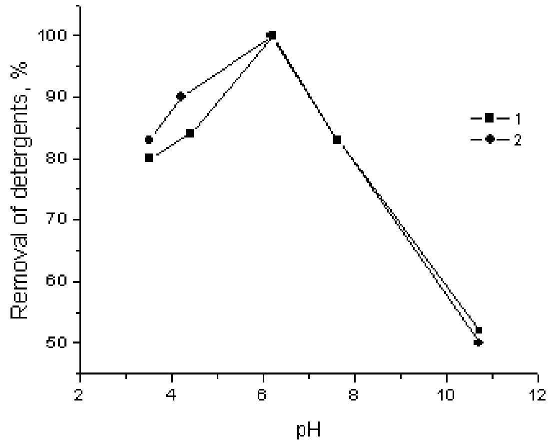


Fig. 8. Effect of pH on the retention of sulfonic and phenolic compounds on Gordes (pH 8.16) zeolite 1 - sulfonic compounds, 2 - phenolic compounds.

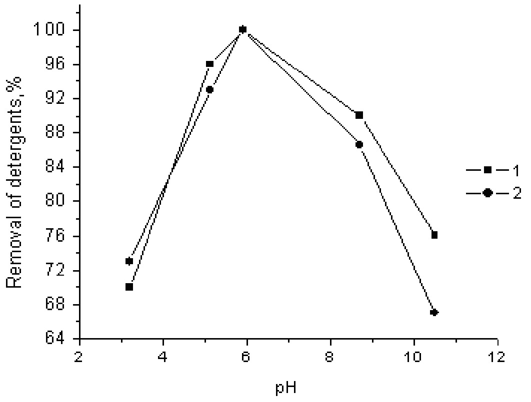


Fig. 9. Effect of pH on the retention of sulfonic and phenolic compounds on Marsid (pH 4.8) zeolite, 1 - sulfonic compounds, 2 - phenolic compounds.

Adsorption of detergents using membranes

Two types of membranes with different chemical composition are used in the experiments. The results are presented in Fig. 10 and Fig. 11.

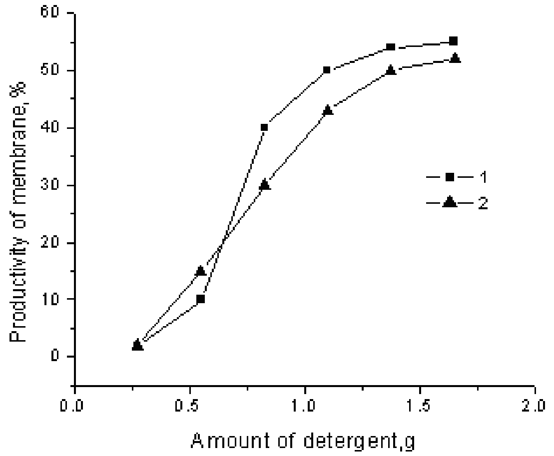


Fig. 10. Dependence of productivity of purification of detergents (1 - sulfonic; 2 -phenolic compounds) on membrane M1, at different amount of detergents in 50 mL solution.

As can be seen from Figure 10 and Figure 11, the removal of detergents from water increases sharply in the case of membrane M2 by attaining the highest value of 82 %, whereas the removal is 52 % for the membrane M1.

The differences in chemical composition of the acrylic copolymers affect the structure of the resulting membranes.

As can be seen from Fig.12, the membrane M1 is more compact (dense), with smaller pores, compared to the membrane M2, which is less compact, with more and larger pores.

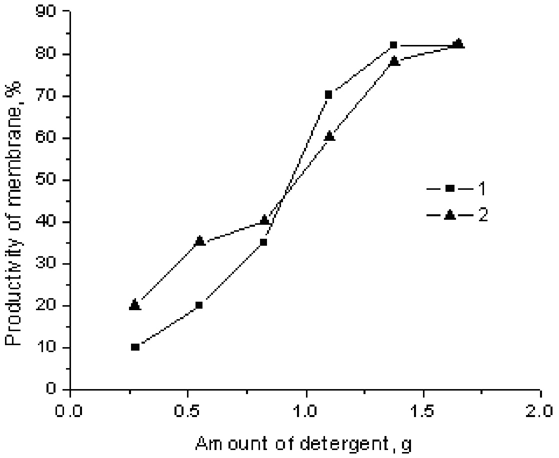


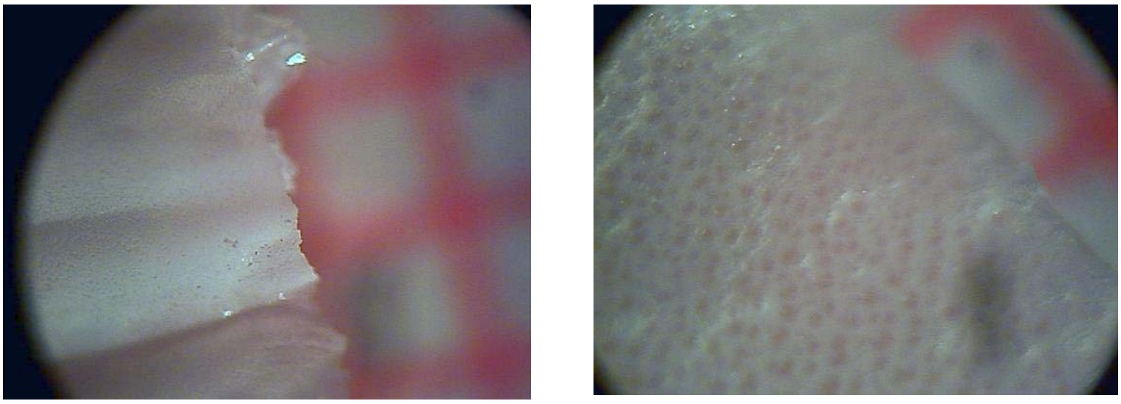
Fig. 11. Dependence of productivity of purification of detergents (1 – sulfonic; 2 -phenolic compounds) on membrane M2, at different amount of detergents in 50 mL solution.

It seems that the differences in chemical composition and the morphology of the membranes lead to their different purification efficiency towards detergents.

CONCLUSIONS

The main factors, determining the adsorption properties towards detergents, are the surface area and the pore structure of the zeolites. Increasing the particle size leads to decrease in the adsorption capacity of the samples, due to reduced surface area. The uptake of both sulfonic and phenolic compounds was found to be maximal at pH 6. These results confirm that both compounds are prefferably adsorbed from their water solutions in neutral forms.

The experiments conducted with membranes demonstrated that they have considerably higher adsorption capacities compared to zeolites. The chemical composition and morphology of the membranes is believed to be very important factor affecting the efficiency of the membrane for the removal of sulfonic and phenolic compounds from waste waters.



a b

Fig.12. Optical microscope images of membranes M1 (a) and M2 (b).The red square has area of 1 mm^2.

REFERENCES

1.G.A. Garwood, M.M. Mortland, T.J. Pinnavaia, *J. Mol. Catal.* **22**, 153 (1983).

2. T.A. Wolfe, T. Demirel, E.R. Baumann, *J. Water Pollut. Control Fed.*, **58**, 68 (1986).

3. S.A. Boyd, M.M. Mortland, *Experientia* **41**, 1564 (1985).

4. S.A. Boyd., M.M. Mortland, *J. Mol. Catal.* **34**, 1 (1986).

5. K.R. Srinivasan, H.S. Fogler, *Clays Clay Miner.*, **38**, 287 (1990).

6. R.C. Zielke, T.J. Pinnavaia, *Clays Clay Miner.*, **36**, 403 (1988).

7. H.T. Shu, D. Li, A.A. Scala, Y.H. Ma, *Sep. Purif. Technol.*, **11**, 27 (1997).

8. Y.H. Shen, *Water Res.*, **36**, 1107 (2002).

9. L. Kastelan-Kunst, K. Kosutic, V. Dananic, B.F.T. Kunst, *Water Res.*, **31**, 2878 (1997).

10. W. Reimann, *Desalination*, **109**, 51 (1997,).

11. M.J. Rosa, M.N. De Pinho, *J. Membr. Sci*., 1994, 89, 235-243.
12. F. Van Voorst Vader, *Trans. Faraday Soc.*, **56**, 1067 (1960).
13. J.-L. Rigaud, D. Levy, D. Mosser, O. Lambert, *Eur. Biophys. J.* **27**, 305 (1988).
14. S.M. El-Said, *Ass. Univ. Bull. Environ.* Res., **7,** 137 (2004).
15. Y.L. Hoffman, H.P. Angstadt, *Chromatography*, **234**, 666 (1987).
16. B. Petrova, T. Budinova, B. Tsyntarski, N. Petrov, C.O. Ania, J.-B. Parra, *Bulg. Chem. Commun.,* **42**, 141 (2010).
17. O. Korkuna, R. Leboda, J. Skubiszewska-Zieba, T. Vrublevska, V.M. Gunko, J. Ryczkowski, *Microporous&Mesoporous Materials*, **87**, 243, (2006).
18. M. Akgul, A. Karabakan, *Microporous&Mesoporous Materials*, **145**,157 (2011).
19. M. Ostrooumov, P. Cappelletti, R. DeGennaro, *App. Clay Sci.*, **55**, 27 (2012).
20. G.H. Giles, T.H. MacEwan, S.N. Nakhwa, D. Smith, *J. Chem. Soc.*, 3973 (1960).
21. I. Langmuir, *J. Am. Soc.*, **409**, 161 (1916).

ИЗВЛИЧАНЕ НА ДЕТЕРГЕНТИ ЧРЕЗ ЗЕОЛИТИ И МЕМБРАНИ

Б. Цинцарски[1], Б. Петрова[1], Т. Будинова[1*], Н. Петров[1], А. Сарбу[2], Т. Санду[2], М. Ферхат Ярдим[3], А. Серкичиоглу[3]

[1] *Институт по органична химия с Център по фитохимия, БАН, Акад. Г. Бончев, бл.9, София 1113*
[2] *Национален изследователски институт по химия и петрохимия, пл. Независимост 202, Букурещ, Румъния*
[3] *Истанбулски технически университет, Факултет по инженерна химия, 34469 Маслак, Истанбул, Турция*

Постъпила 16 януари 2013 г.; Приета за печат 12 февруари 2013 г.

(Резюме)

Изследвана бе адсорбцията на сулфонати и фенолати, съдържащи се в детергенти, с помощта на природни зеолити от Турция и Румъния. Зеолитите бяха охарактеризирани посредством ИЧ спектроскопия и изучаване на повърхностните свойства. Изследвано бе влиянието на времето на контакт и на pH върху процеса на адсорбция. Установено бе, че специфичната повърхност е определящ фактор, който влияе в най-голяма степен върху адсорбцията на детергентите. Бе изследвано и извличането на детергенти с помощта на различни мембрани, които показаха по-висок адсорбционен капацитет в сравнение с изследваните зеолити.