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Application of modified porous glasses Al_2O_3 for hydrocarbon contamination sorption

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Tests on glass texture were made in order to establish the size of porous space in modified glasses Al_2O_3 from the system Na_2O–B_2O_3–SiO_2 after extraction of dissolved boron phase during chemical treatment. A difference was observed in the size and volume of mezo- and micropores in 0.6% and 0.3% Al_2O_3 glasses depending on temperature of heating. Accounting for the difference of glass structure attempts were made to use them for the selective sorption of hydrocarbons dissolved in water. It follows from the obtained results that differences in hydrocarbon removal are as much as tens of percent. The efficiency of removal is conditioned by the type of glass and grain size of glass applied for sorption.

Keywords: porous glass, hydrocarbons, adsorption, phase separation.

1. Introduction

Leakages of oil and its products accompany exploitation and processing equipment failures and also fuel distribution. In a majority of cases in break-down situations only part of oil-products can be collected without specialist equipment. Most of them gets to the soil infiltrating groundwaters to finally get to the surface water. Hydrocarbons are environmentally noxious. They are toxic both for flora and fauna. Even small quantities of hydrocarbons may introduce organoleptic changes making water undrinkable [1].

Known purification methods are both costly and inefficient. In industrial practice mechanical sorption of hydrocarbons chemical methods and filtration processes are most frequently applied. Presently intensive researches are carried out on new cheaper technologies to increase the efficiency of the cleaning processes.

One of the most efficient methods is based on adsorption processes, where the oil products are removed with, *e.g.*, active carbon natural zeolites and diatomites. The efficiency of the process depends among others on the qualities of the used adsorbent, its specific surface shape and volume and distribution of pores.

A very interesting material that can be used for efficient removal of hydrocarbons from water is porous silica glass, where the specific surface is 50–350 m^2/g. Very positive results were obtained during tests, especially for cleaning water from fuels.

2. Experimental

2.1. Physical properties of porous glasses

During laboratory experiments sodium borosilicate glasses were used for removing hydrocarbon contaminations from water. They were used through phase separation methods and their porous structure was obtained through thermal and chemical treatment. The chemical composition of glasses used in the experiments was the following (mol%): glass XVI, SiO_2 – 57.00%, B_2O_3 – 32.40%, Na_2O – 10.00%, Al_2O_3 – 0.60%, glass XIII, SiO_2 – 58.00%, B_2O_3 – 31.70%, Na_2O – 10.00%, Al_2O_3 – 0.30%. In the course of thermal treatment glass underwent liquation processes during which two homogeneous glass phases were obtained: silica and boron-sodium sodium borate. In the course of hot chemical processing the dissolved boron phase was extracted from the HCl solution and a porous material was produced. Porous glass had a spongy skeleton of SiO_2 (96%) and the system of pores additionally developed its specific surface [2].

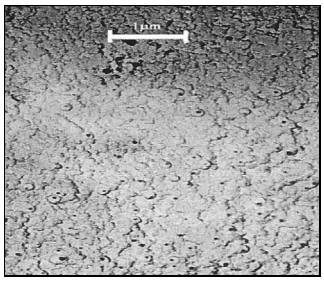

Fig. 1. TEM of Al_2O_3 (0.3%) modified glass after thermal processing (700°C/24 h), carbon replica, magn. 1000×.

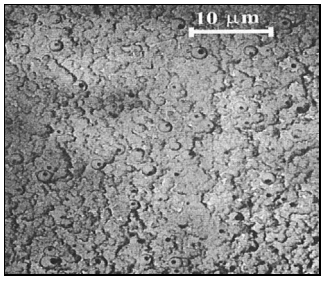

Fig. 2. TEM of Al_2O_3 (0.6%) modified glass after thermal processing (575°C/24 h), carbon replica, magn. 1000×.

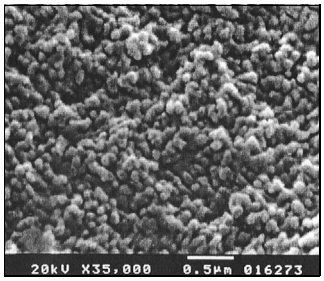

Fig. 3. SEM of Al_2O_3 (0.6%) modified glass after thermal (700°C/24 h) and chemical processing (1 mol/1 HCl/6 h).

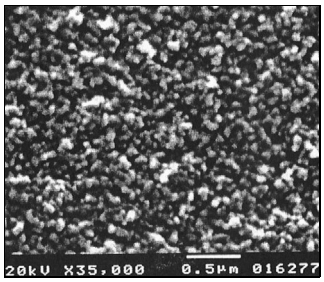

Fig. 4. SEM of Al_2O_3 (0.6%) modified glass after thermal (575°C/24 h) and chemical processing (1 mol/1 HCl/6 h).

The character, shape and location of non-homogeneities, making up canals and porous spaces in glasses subjected to phase decomposition, were determined with TEM method. Figures 1 and 2 show the observed spherical particles of dispersed phase on the background of smaller non-homogeneous areas, with no visible matrix either in XVI or XIII glasses.

The results obtained with TEM method were confirmed by observations carried out with SEM method, performed for glasses after chemical extraction of borate phase (Figs. 3 and 4).

In Al_2O_3-modified glass two types of phase decomposition were observed:

– binoidal in the case of which isolated spherical particles of scattered phase of various size and location in the visible matrix were observed;

– spinoidal in the case of which the non-spherical particles of scattered phase of high degree of bonding and regular size distribution were observed. Non-homogeneities appearing in glass were of droplet character and their size ranges from 0.1 to 5 μm forming continuous chains [2–4].

To determine the specific surface and porosity of glass, some measurements were made with the physical adsorption method at the 77 K temperature of liquid nitrogen. Basing on the obtained isotherms, the parameters of glass texture were determined. Table 1 gives specific surfaces S_{BET} calculated for relative pressure changes p/p_0 ranges 0.06 to 0.20; surfaces and volume of the mezopores calculated from the adsorption branch ($S_{mezo\text{-}ads}$ and $V_{mezo\text{-}ads}$) and from the desorption branch ($S_{mezo\text{-}des}$ and $V_{mezo\text{-}des}$) with the BJH equation [5]; surfaces and volumes of micropores (S_{micro} and V_{micro}) calculated from *t* plots on the basis of the equation of thickness of an adsorbed layer after HARKINS and JURA [6].

T a b l e 1. Selected physical properties of porous glass (thermal treatment – 24 h, chemical treatment – 4 h).

Parameter	Glass No./ Temperature of thermal treatment			
	XIII/575	XIII/700	XVI/575	XVI/700
S_{BET} [m^2/g]	49.29	58.41	346.2	191
$S_{mezo\text{-}ads}$ [m^2/g]	43.48	62.84	396.5	210
$S_{mezo\text{-}des}$ [m^2/g]	52.61	71.51	427.7	226
S_{micro} [m^2/g]	3.78	0.00	24.20	13.65
V_{singl} [cm^3/g]	0.281	0.171	0.325	0.271
$V_{mezo\text{-}ads}$ [cm^3/g]	0.278	0.181	0.358	0.298
$V_{mezo\text{-}des}$ [cm^3/g]	0.284	0.190	0.355	0.302
V_{micro} [cm^3/g]	0.001	0.000	0.008	0.004
Diameter_{des} [nm]	21.59	10.63	3.61	5.68
Diameter_{ads} [nm]	25.59	11.50	3.32	5.35

Samples had an irregular shape of grains of about 1.5–3 mm diameters. Considerable differences in the size of the pores, their distribution and total volume were observed in the analysed glasses modified with 0.3 and 0.6% Al_2O_3 (denoted as XIII and XVI, respectively), depending on the composition of the input glass and temperature of thermal processing. The analysed parameters for glass XVI processed at the temperature of 575°C were several times higher than for glass XIII.

2.2. Description of experiments

The efficiency of the hydrocarbon contamination adsorption from water was tested on porous glasses modified with 0.3 and 0.6% Al_2O_3 varying in the S_{BET} value [7]. Water was contaminated with gasoline – a hardly removable mixture of aliphatic and aromatic hydrocarbons. The water solubility of gasoline itself ranged from 131 to 185 mg/dm^3 [8] but it must be remembered that its respective values for its components were diversified. The highest solubility could be observed for such aromatics as benzene (1780 mg/dm^3), toluene (537 mg/dm^3), xylene (162 mg/dm^3) and ethylbenzene (167 mg/dm^3).

In each series of experiments 30 dm^3 water samples contaminated with Pb-free gasoline were used. They were analysed for oil-products content before the purification process, using the IR spectrophotometry and gas chromatography method. The spectrophotometry measurements were made in a Thermo Nicolet "Avator" apparatus. Water samples were prepared according to the Polish standard PN-82/C-0456501 [9]. Tests on aromatic hydrocarbons were made with the use of a Varian Star 3400CX gas chromatography with a Saturn 2000GC/MF mass detector. Hydrocarbons were extracted from the above water samples with the use of 5 ml *n*-pentane.

Each time glasses modified with 0.3% Al_2O_3 (glass XIII) and 0.6% Al_2O_3 (glass XVI) and thermally modified at 575 and 700°C were used for cleaning water samples from hydrocarbons.

T a b l e 2. Non-polar aliphatic hydrocarbon content determined by IR spectrophotometry methods.

Hydrocarbon content in the analysed water samples [mg/dm^3]				
Input sample	XIII/575*	XIII/700*	XVI/575*	XVI/700*
24.14	20.28	19.79	14.96	16.89
20.47	17.19	16.78	12.68	14.32
16.29	13.84	13.35	10.26	11.56
9.32	8.57	8.38	6.15	6.80

*Content after adsorption on porous glass.

Porous glass (1 g) was added to a water sample (100 cm^3), the bottle was closed tightly and shaken for 1 h. Then water was decanted from glass and oil-products content was determined similar to the model tests. A series of results for non-polar aliphatic hydrocarbons determined by the spectrophotometry method after sorption on porous glasses is given in Tab. 2 (average values from three results for each sample).

3. Results and discussion

Investigation of the phenomena of phase separation in glasses were conducted using the basic Na_2O–B_2O_3–SiO_2 glass system and also its modifications by small amounts of aluminium (0.3–2.5 mol%), titanium (0.5–2.5 mol%) and zirconium (0.5–2.5 mol%) oxides. It can be stated from the analysis of obtained results from basic glass system and its modifications by TiO_2, ZrO_2 that the diameter of their pores was too big and also specific surface was too small to use this glass system to remove hydrocarbons from water [2]. The total reduction of hydrocarbons was about a few percent for this system of glass. The best results for efficient removal of hydrocarbons from water show porous silica glass Al_2O_3 modified with content of Al_2O_3 – 0.3–0.6 mol%, where the specific surface is 50–350 m^2/g.

It can be stated from the analysis of the obtained results that hydrocarbon contaminations were sorbed after using both glasses XIII and XVI. The highest degree of hydrocarbon removal (average 37%) was obtained for glass XVI/575°C which has the most developed specific surface among the analysed glasses. The degree of oil-products reduction for the same parts of waters admixed with glass XVI/700°C was 29%. Glasses XIII/575°C and XIII/700°C produced similar results, except for reduction which was ca. 15–18%. The specific surface of glass XIII was 4 to 7 times smaller than that of glass XVI but hydrocarbon sorption was only half the value of that for glass XVI.

Tests were also made on aromatics content in waters before the glass-cleaning process and after 1 h of adsorption in the presence of 1 g of glass. Table 3 presents the results of a series of measurements for glasses XIII and XVI.

The obtained results reveal that aromatic hydrocarbons can be removed from waters with the use of modified glass Al_2O_3. In the case of aromatic hydrocarbons

T a b l e 3. Hydrocarbon content in water samples analysed with the gas chromatography method.

Identified substance	Hydrocarbon content [μg/dm^3]				
	Input sample	XIII/575*	XIII/700*	XVI/575*	XVI/700*
Benzene	952.962	901.205	894.027	623.124	812.436
Toluene	12418.504	10929.784	10842.374	7338.052	9936.914
Etylobenzene	1326.213	1021.317	981.215	702.038	861.584
p-xylene	6862.048	5177.883	5092.631	4171.603	4806.203
o-xylene	3421.220	2743.320	2708.833	1631.784	2394.736

*Hydrocarbon content after adsorption in the presence of porous glasses.

the highest amount of removed contaminations from water environment was obtained for ortho-xylene and ethylobenzene (to 45%), as compared to the amounts before the adsorption process. A considerable part of toluene was reduced. Its content in water before adsorption was the highest (50%) and after the experiment of sorption it was reduced to ca. 40% for glass XVI/575°C, 20% for glass XVI/700°C, 12% for glasses XIII/575°C and XIII/700°C. For glass XVI/575°C the total reduction of aromatic hydrocarbons was 43%, as compared with the state before the cleaning process. Similar to the case where non-polar aliphatic hydrocarbons were determined, a weaker hydrocarbon adsorption effect was observed for glasses XIII/575°C and XIII/700°C, where about 17–18% of contaminations were removed.

4. Conclusions

Sorption methods are very efficient for hydrocarbon contamination removal from waters. Attempts were made to employ modified porous glasses Al_2O_3 with well-developed specific surface and great diameter of pores for hydrocarbons removal.

The experiments showed that the analysed glasses considerably adsorbed hydrocarbon contaminations from model water samples. The best cleaning qualities were observed for glass XVI/575°C. After 1 h of adsorption in the presence of 1 g of glass XVI the contamination was reduced by 34–38%, depending on the amount of hydrocarbons in water before sorption process. Analogous values for glass XIII were smaller (8–18%).

The majority of contaminations adsorbed on glasses were aromatic hydrocarbons. The best results were obtained for ortho-xylene and ethylobenzene. It can be concluded from the obtained results that in the presence of the above mentioned glasses, the contaminations in the water samples were considerably reduced. Better results were obtained for XVI than for XIII glass.

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