Study of sepiolite from Goleš (Kosovo, Yugoslavia). II. Acid activation

MARINA RADOJEVIĆ[a], VIDOJKO JOVIĆ[b*], DRAGOMIR KARAULIĆ[a] and DRAGOMIR VITOROVIĆ[c#]

[a]Institute of General and Physical Chemistry, P. O. Box 551, Studentski trg 12, YU-11000 Belgrade, [b]Faculty of Mining and Geology, Djušina 7, YU-11000 Belgrade and [c]Center of Chemistry –ICTM, Njegoševa 12, YU-11000 Belgrade, Yugoslavia

The changes in the pore structure and adsorption properties of sepiolite from Goleš resulting from treatment with 4 M HCl for various periods of time were investigated. The BET method specific surface areas, pore volumes and f – plots were determined by nitrogen adsorption. The surface area progressively increased during the 70 hours of acid treatment, when a maximum was attained. The differences in the adsorption properties of the original and the acid treated sepiolite were evaluated by comparison of adsorption isotherms obtained with benzene, *n*-hexane, methanol and isooctane. The enhanced adsorption of isooctane was of great interest, since the sorption of this compound on natural sepiolites is generally very limited. The results suggest that chemical treatment of sepiolite with 4 M HCl for 70 h produces an adsorbent of optimal porosity and other adsorption properties.

Keywords: sepiolite, Goleš, acid activation, surface area, pore volume, f – plot, adsorption.

INTRODUCTION

Sepiolite is a mineral which due to its structure,[1] that is ribbons alternating with open channels along the fiber axes, has good adsorption properties. It has been shown that sepiolite has a high adsorptive capacity for many gases and vapours, especially when the dimensions of their molecules allow them to penetrate into the channels of the adsorbent.[2–10] The sorption capacity restricted to the external surface may be enhanced by chemical modification, *i.e.*, by acid treatment which is a common method of modifying clay minerals.[11–14] It is aimed at removing impurities, such as carbonates, often present in sepiolites.[15] The process generally leads to products more useful for industrial application. Thus, for example, acid activated bentonite showed considerably higher decolorizing efficiency for rape oil.[16] Del Hoyo *et al.*[17] revealed that acid activation of sepiolite affected the sorption of *N*-methyl 8-hydroxy quinoline methyl sulphate – a drug used for protection from sunburn.

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*   Author to whom correspondence should be addressed. E-mail: jvidojko@eunet.yu.

Serbian Chemical Society active member.

In essence, modification of clay minerals by acids results in the elimination of cations from the mineral structure.[18] In the case of sepiolite, the acid dissolves the brucite layer, generating two new, very reactive surfaces, containing silanol groups susceptible to condensation reactions which lead to the formation of siloxane groups.[19–22]

This study was aimed at investigating the effects of acid treatments on the sorption properties of sepiolite from Goleš.[23–25] Of particular interest was the study of the sorption of compounds whose access to the micropores of the sepiolite was generally limited.

EXPERIMENTAL

The sample of sepiolite originated from the Goleš Mine, Yugoslavia. The original sample was composed of 53.72 % SiO_2, 0.05 % Fe_2O_3, 0.13 % CaO, 25.26 % MgO, 0.03 % NiO and 0.24 % Na_2O. Its ignition loss was 21.03 %. The XRD pattern of the sample showed the presence of diffraction peaks corresponding to sepiolite only.[25]

The acid treatment was carried out at 20 ºC in a 250 cm^3 reaction flask containing 50 cm^3 4 M HCl and 5 g of the sepiolite sample. The reaction mixture was stirred for 1, 2, 4, 7, 24, 70 and 170 h. The original sample was designated S-0, and the acid activated samples: S-1, S-2, S-4, S-7, S-24, S-70 and S-170, respectively. Following the acid treatment, the magnesium dissolved in the supernatant (obtained by centrifugation) was determined by complexometric titration using a standard EDTA solution with Eriochrome T as the indicator. The solid residue was dried at 105 ºC for six hours.

Nitrogen adsorption isotherms were determined at –197 ºC, using an Autosorb 6-Quantachrome. Prior to the measurements, the samples were outgased under vacuum ($p = 1 \times 10^{-4}$ mm Hg) at 100 ºC.

The sorption of condensable vapors at 20 ºC was evaluated by using a McBain spring balance. Pretreatment of the samples consisted also of outgasing under vacuum ($p = 1 \times 10^{-4}$ mm Hg) at 100 ºC.

RESULTS AND DISCUSSION

Chemical changes

The percentage of Mg removed from the sepiolite by acid treatment for various periods of time is shown in Table I. Elimination of Mg from its octahedral position was much slower compared with data found in the literature.[18,19] This was probably due to the fiber length of this sepiolite which influenced the diffusion of the acid. The percentage of dissolved Mg gradually increased with the treatment time. The higher reaction rate at the beginning can be explained by the better accessibility of the atoms located on the most exposed positions of the fibers.

TABLE I. Magnesium extracted from the Goleš sepiolite by acid treatment

Reaction time/h	1	2	4	7	24	70	170
Mg/% extracted	14.9	29.9	36.0	44.0	47.9	73.4	91.8

Changes of adsorption properties

Nitrogen adsorption isotherms of the original and the acid treated samples are shown in Fig. 1. Data resulting from the adsorption isotherms, concerning the textural characteristics, are given in Table II. The specific surface areas were calculated using the BET method,[26] assuming a value of 0.162 nm^2 for the cross-section of a N_2 molecule. The external area of the

microsorbent was determined by the t – plot method.[27] The micropore volume was calculated from the intercept on $V = f(t)$. The micropore area was obtained from the difference between the BET surface area and the external surface area. The ratio between the inner and outer surface areas depends on the thickness of the sepiolite crystal. According to the method of Hibbino *et al.*,[9] the average fiber thickness at the sepiolite from Goleš is 15 nm. The micropore volume was obtained from the $V-t$ curve.[27] The total pore volume was calculated from the amount of nitrogen adsorbed at relative pressures near 1 (0.98–0.99), expressed in the liquid form, taking the value of 34.7 cm^3/mol for the molar volume.
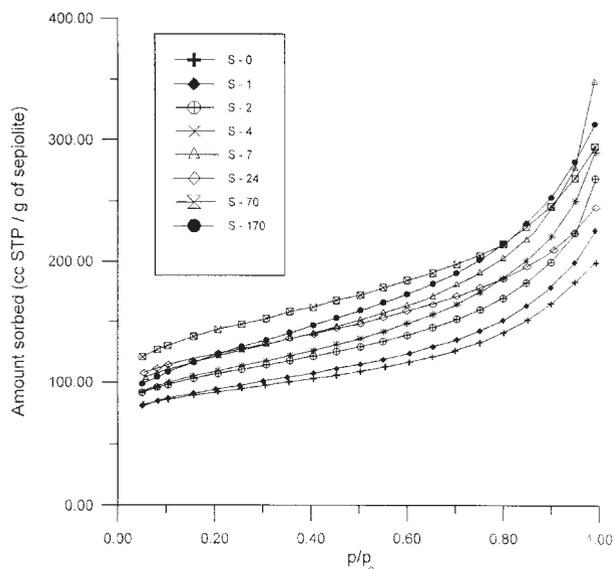

Fig. 1. Adsorption isotherms of nitrogen on the original and acid treated samples of Goleš sepiolite.

TABLE II. Data obtained from nitrogen adsorption isotherms

Sample	Specific surface area m^2/g	Specific surface area of micropores m^2/g	Specific surface area of mesopores m^2/g	Micropore volume cm^3/g	Total pore volume cm^3/g
S-0	334	207	128	0.09	0.31
S-1	341	186	154	0.08	0.35
S-2	386	215	171	0.09	0.41
S-4	396	192	204	0.08	0.45
S-7	439	219	220	0.09	0.54
S-24	447	272	175	0.11	0.38
S-70	517	309	207	0.13	0.46
S-170	441	182	259	0.07	0.49

From Table II it can be seen that the external surface area increase gradually up to a reaction time of 7 h, probably due to a thinning of the fibers, as a consequence of the exfoliation phenomenon.[20,28] Fractures in the silica sheets may occur at the points of inversion of the silica tetrahedra, the weakest point in the structure, producing at the same time a de-

crease in the micropore volume, which is compensated by an increase due to the elimination of magnesium. Therefore, up to 7 h treatment, the surface area of the micropores and their volume do not changed regularly, and no great differences were observed. Sample S-24 had a much greater surface area and volume of the micropores compared to the previous one (S-7). A maximum was reached with sample S-70, due to the dissolution of the brucite layer. A significant decrease was observed with sample S-170. The external surface area and total pore volume reached minimal values with sample S-24 and on prolonging the reaction time they commenced to increase.

Hernández *et al.*[19] proposed a possible two-step reaction mechanism for the process of acid treatment of sepiolite. In the first step, the brucite layer is eliminated by dissolution in the acid, leading to the formation of two new surfaces. The second step involves condensation of the silanol groups, resulting in a closure of the pores, *i.e.,* in a collapse of the pore structure.

We presume that these two reactions run parallel, *i.e.*, they occur at the same time. The first changes appear at the most exposed positions of the fibers, causing the external surface area to increase due a thinning of the fibers. The formation of external surface silanol groups may also lead to condensation, a fact which explains the decrease of the external surface area of sample S-24. With the next sample (S-70), the external surface area continued to increase. The decrease of the micropore area and volume with sample S-170 can be explained not only by condensation, but also by a splitting of the fibers, causing the conversion of micropores into an external surface.

The changes in the sepiolite morphology and the appearance of new pores in the acid treated samples were examined by f– plots (Fig. 2), which represent the ratio of the N_2 adsorbed on the acid treated sample *vs.* the N_2 adsorbed on the original sample at a constant p/p_0 value. The f– plots showed that the acid treated samples, excluding sample S-1, had a greater adsorption capacity compared to the untreated sample over the entire range of N_2
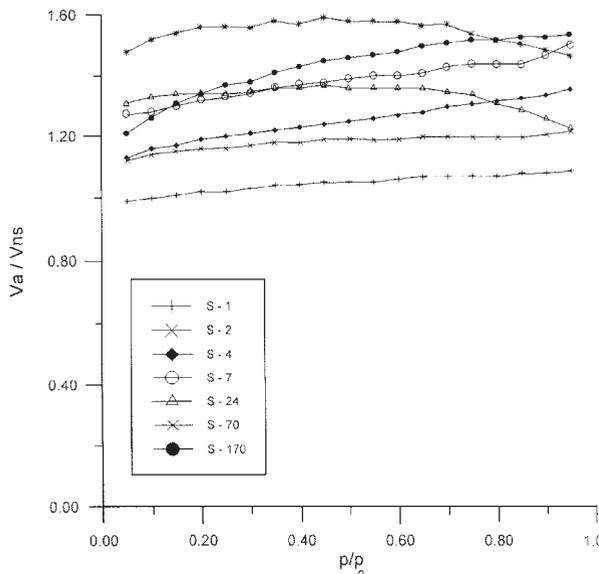

Fig. 2. f – Plots of ratios of N_2 adsorbed on acid treated sample *vs.* N_2 adsorbed on the original sample of Goleš sepiolite.

pressures (p/p_0). The f – plots were almost parallel to the x-axis, suggesting that these samples had a morphology similar to that of the original sepiolite.

During 7 h of acid treatment, the external surface increased. The adsorption isotherms of sample S-7 show that the natural and acid treated samples had the same capacity for the sorption of benzene (Fig. 3) and n-hexane (Fig. 4). The sorption capacity was greater at higher relative pressures in both cases. This is due to the increase of the external surface area and pore volume.
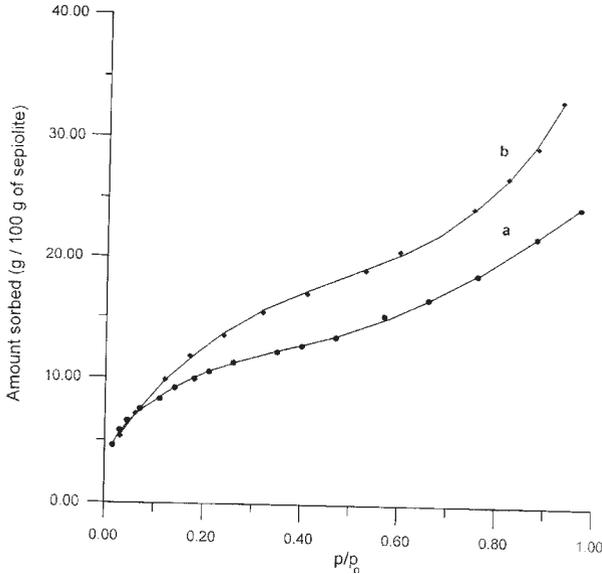

Fig. 3. Adsorption isotherms of benzene on the samples: a) S-0, and b) S-7.
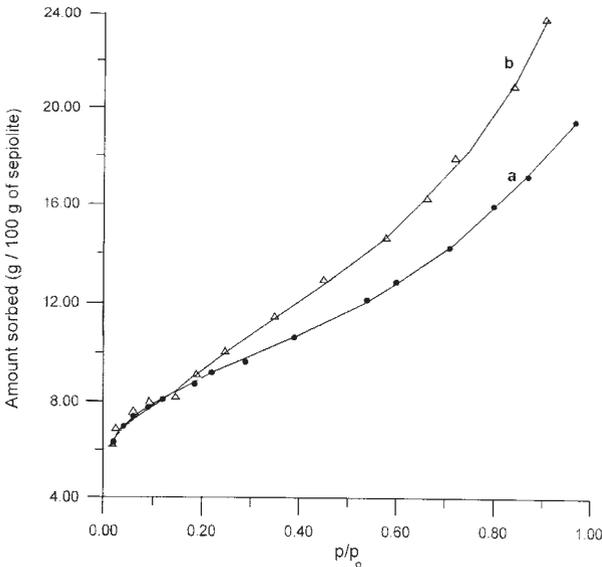

Fig. 4. Adsorption isotherms of n-hexane on the samples: a) S-0, and b) S-7.

However, the sorption of methanol (Fig. 5) was greater on the acid treated sample than on the original sample over the entire range of relative pressures (p/p_0). This observa-

tion may be explained by the theory of replacement. For the acid treated, the values of the obtained adsorption capacities were unreal. The reason why the sorption of methanol differs from the sorption of benzene and *n*-hexane may lie in the probability of methanol molecules condensing in the mesopores formed during the treatment.
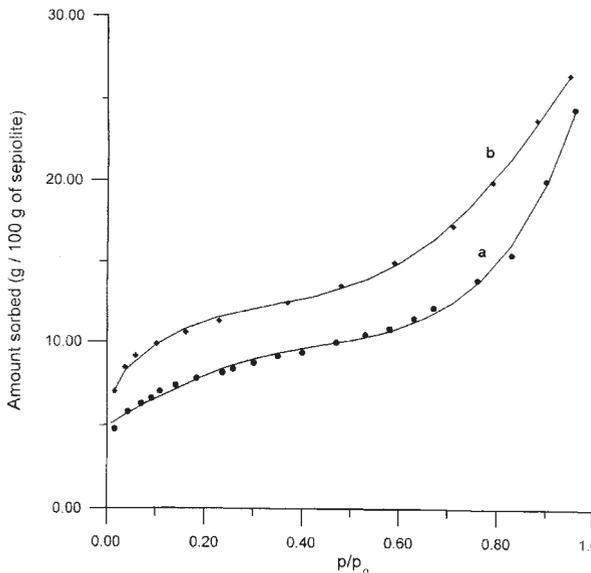

Fig. 5. Adsorption isotherms of methanol on the samples: a) S-0, and b) S-7.

All the acid treated samples had a higher specific surface areas than the original one, and it progressively increased up to 70 h reaction time. In contrast, sample S-170 had a smaller specific surface area than sample S-70. The adsorption of benzene and isooctane by these two samples was also investigated. The adsorption isotherms are plotted in Fig. 6 and Fig. 7, respec-
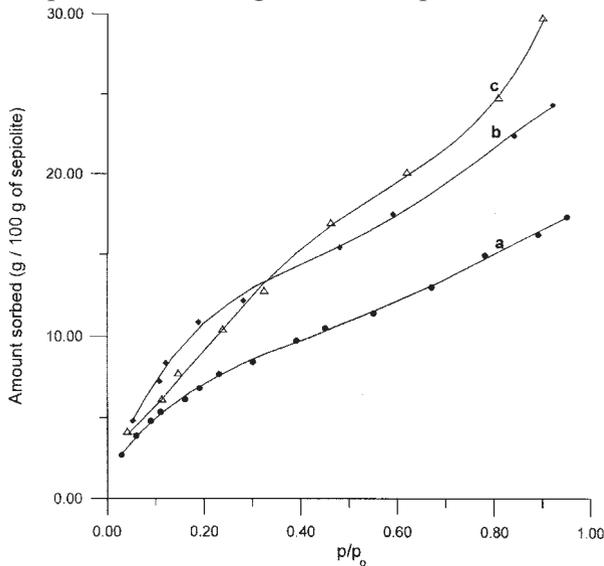

Fig. 6. Adsorption isotherms of isooctane on the samples: a) S-0, b) S-70, and c) S-170.
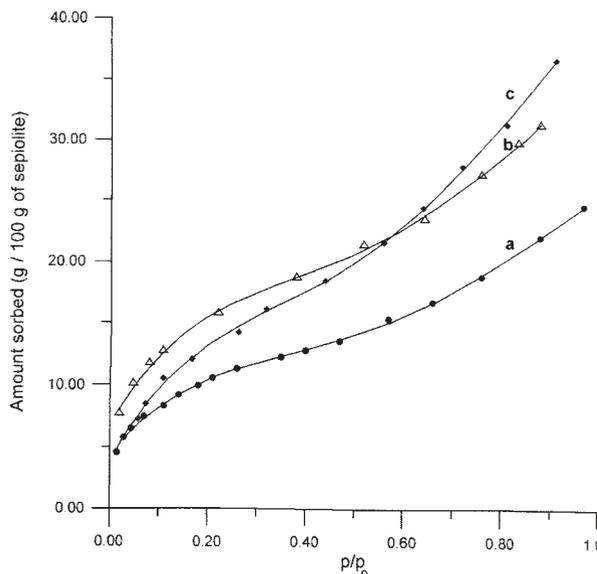
Fig. 7. Adsorption isotherms of benzene on the samples: a) S-0, b) S-70, and c) S-170.

tively, together with the adsorption isotherm of the natural sample. The plots corroborated the data presented in Table II. At lower relative pressures the sorption was the greatest on sample S-70, due to its surface area being the largest. The greatest adsorption capacity at relative pressures near 1 was shown by sample S-170, due to its greatest pore volume.

CONCLUSIONS

Chemical treatment of sepiolite from Goleš with 4 M HCl, for various periods of time, developed the pore structure and adsorption properties of the substrate, characterized by S_{BET}, micropore volume, total pore volume and f – plots, which were calculated from N_2 adsorption isotherms. Benzene, n-hexane, methanol and isooctane adsorption isotherms were also measured. It was shown that the adsorption properties of Goleš sepiolite can be improved by acid treatment. Modification of the properties of sepiolite by this method could be very important for its application as a sorbent. The results suggested that an adsorbent with optimal surface area and porosity can be produced by chemical treatment of sepiolite with 4 M HCl at 20 ºC for 70 h.

ИЗВОД

ИСПИТИВАЊЕ СЕПИОЛИТА СА ГОЛЕША (КОСОВО, ЈУГОСЛАВИЈА). II. АКТИВИРАЊЕ КИСЕЛИНОМ

МАРИНА РАДОЈЕВИЋ[а], ВИДОЈКО ЈОВИЋ[б], ДРАГОМИР КАРАУЛИЋ[а] и ДРАГОМИР ВИТОРОВИЋ[в]

[а]Институт за општу и физичку хемију, п. пр. 551, Студентски трг 12, 11000 Београд, [б]Рударско-геолошки факултет, Ђушина 7, 11000 Београд и [в]Центар за хемију-ИХТМ, Његошева 12, 11000 Београд

Испитиване су промене у структури пора и адсорпционих особина сепиолита са Голеша после обраде са 4 M HCl за различито време. Специфична површина, запремина пора и f – крива одре-

ђивани су адсорпцијом азота. Површина је прогресивно расла за време од 70 часова обраде киселином, када је постигнут максимум. Разлике у адсорпционим особинама између природног узорка и сепиолита обрађеног киселином процењиване су упоређивањем адсорпционих изотерми добијених са бензеном, *n*-хексаном, метанолом и изооктаном. Повећана адсорпција изооктана била је посебно значајна, с обзиром да је сорпција овог једињења на природном сепиолиту иначе врло ограничена. Резултати су показали да се хемијском обрадом сепиолита са 4 M HCl за време од 70 часова може добити адсорбент оптималне порозности и других адсорпционих особина.

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