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CHARACTERISATION OF NEW SORBENTS PRODUCED FROM BY-PRODUCT OF THE RAPESEED OIL TREATMENT.

NO RAPŠU EĻĻAS ATTĪRĪŠANAS BLAKUS PRODUKTA PAGATAVOTU JAUNU SORBENTU RAKSTUROJUMS.

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Introduction:

In rapeseed oil bleaching process, the by-product has been obtained, which consists of activated clays and rapeseed oil (30 – 40%). It has been shown that in the course of thermal treatment, the sorbent can be obtained, which is composed from alum silicate matrix (inorganic part) and rapeseed oil carbonization products (organic part). This type of materials can be used as binary sorbents, which are capable to adsorb simultaneously polar and non polar molecules from gaseous or water phase. The value of specific surface area of the investigated sorbent is up to 100 m^2/g.[1]

Experimental:

The vapor sorption isotherms at 20 ^{0}C were measured to characterize the sorbents. A complete glass adsorption device with mercury traps and a McBaine-Bakr quartz spring balance were employed [2]. The sensitivity of the quartz spring was about 2 – 3 mg/mm. A Cathetometer KM – 2 (former USSR) was used to measure elongation and shortening of the quartz spring during the adsorption and desorption of benzene and methanol vapors and to measure the

manometer level of mercury. A U–tube filled with Au powder separated the samples from other part of the device to eliminate the sorption of mercury vapor. Two different types of vapor were studied – those of non-polar benzene and polar methanol. All the investigated samples were prepared from sample No 45 representing one of typical varieties of Triassic clays from the Latvian South region (Vadakste). It was taken from a boring core (8 – 11 m depth) and consisted of clay minerals: montmorillonite (74%), hydro mica (21%) and chlorite. The chemical composition, % (by mass) was: CO_2 9.31, SiO_2 48.1, Fe_2O_3 6.72, Al_2O_3 11.9, TiO_2 0.75, CaO 10.03, MgO 4.46, SO_3 0.24, Na_2O 0.62, K_2O 1.8, P_2O_5 0.13; loss of weight at 900 ^{0}C – 14.92. The sample was kept in distilled water for about 4 – 6 months and then sieved as a suspension through a sieve of 200 mesh. The sample was activated by heating with 25% sulfuric acid solution in a water bath and then washed on a filter until the solution became neutral. In this process, from one side, H_2SO_4 dissolves minerals containing carbonate, making Ca, Mg sulfates and, from the other side, affecting the clay alum silicate matrix, making $Al_2(SO_4)_3$. The obtained product (B25S) was then divided in two series, B and M. Series B were treated thermally. The second series M was used in discoloration of vegetable oil, and then was treated thermally, as in series B, after separation from oil by filtration.

Table 1

Treatment conditions of samples.

Samples	Temperature of treatment, ^{0}C		
	250	400	600
Series B			
B 250	3 hours		
B 400	3 hours	+3 hours	
B 600	3 hours	+3 hours	+1 hour
Series M			
M 250	3 hours		
M 400	3 hours	+3 hours	
M 600	3 hours	+3 hours	+1 hour

Results and Discussion

The sorption isotherms of benzene and methanol vapor [3] are shown in fig. 1 – 4. On the X – axis the values of relative equilibrium pressure are shown. On the Y – axis – the values of adsorption [mmol/g].
As is shown at Fig. 1 – 4, adsorption isotherms do not correspond with desorption isotherms and closed reproducible hysteretic loops have been made.

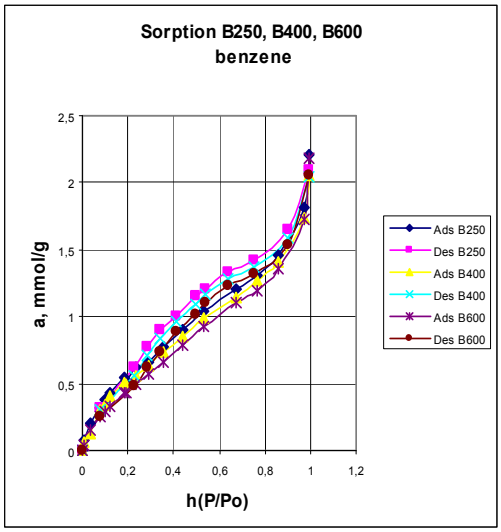

Fig.1. *Sorption isotherm of benzene vapor on the white series samples B250, B400, B600 at 20 ^{0}C.*

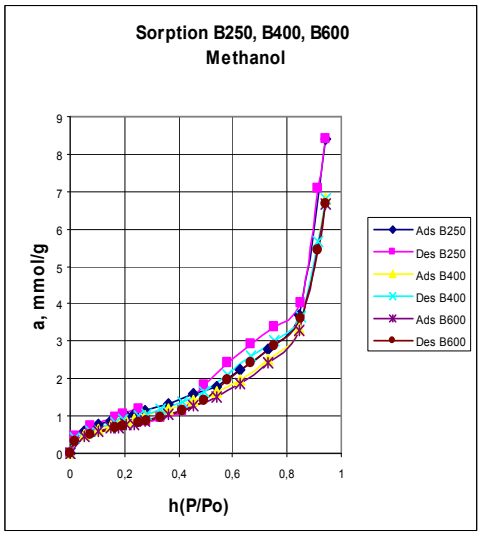

Fig.2. *Sorption isotherm of methanol vapor on the white series samples B250, B400, B600 at 20 ^{0}C.*

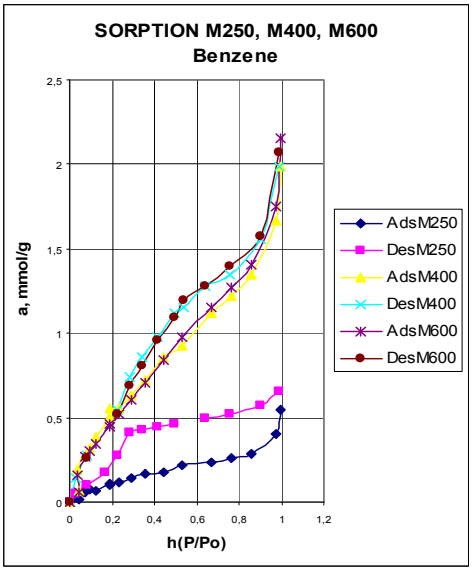

Fig.3. *Sorption isotherm of benzene vapor on the black series samples M250, M400, M600 at 20 ^{0}C.*

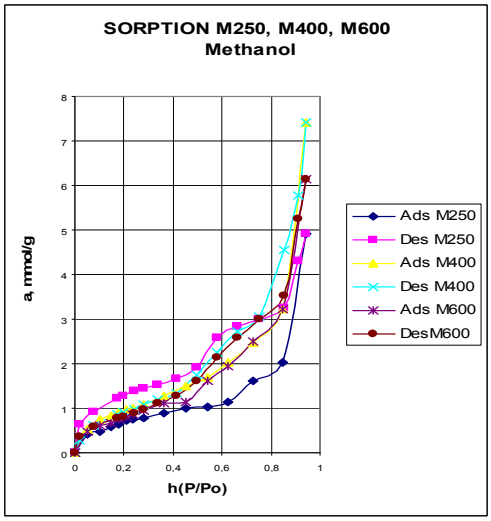

Fig.4. *Sorption isotherm of methanol vapor on the black series samples M250, M400, M600 at 20 ^{0}C.*

Adsorption isotherms may be described as S–type shaped. It was caused by multilayer adsorption and capillary condensation. The multilayer adsorption has been described by BET equation. At a relative pressure interval from 0.2 to 0.4 montmorillonite containing clays (Latvian Triassic clay seams) are characterized by typical tread on the desorption isotherm which is affined with the capillary condensation and evaporation from the pore system, is made by the plane-parallel lamellar. The adsorption and desorption isotherms were used for the calculation of sorbent parameters. The values of specific surface area of the samples were calculated following BET method. The total pore volume was estimated as the adsorption capacity of the samples at relative equilibrium pressure P/Po = 0.95. The calculated results are

shown in table 2. It has been found that specific surface area of B series samples decreases from ~ 150 (20 ^{0}C temperature) till 110 m^2/g (600 ^{0}C) when the temperature of activation increases. The values of specific surface area of M series samples are less than B series samples, however, for the sample, which was heated at the value of specific surface area is close to values of specific surface area of B series samples. The values of specific surface area of M series samples are going through maximum (128 m^2/g), as the activation temperature increases from 250 till 600 ^{0}C. It should be noted that for the sample, activated at 600 ^{0}C, the sufficiently high sorption ability is preserved (anent benzene and methanol) what determines volumes for sorbent thermal resistance.
The total pore volume of B series samples has been changed slightly, but it increases for M series samples if the temperature of activation increases.
The surface character of investigated sorbents is different for the samples of B and M series.
When the B series samples were heated till 250 ^{0}C, the adsorbed (physically contented) water has been extracted from them. In a higher temperatures, the alum silicate hydroxy- OH^- groups (chemically contented water has been extracted). Two different processes simultaneously have been made during the thermal treatment of M series samples. In fact, the sorbent which consists of two phases – inorganic (clay alum silicate matrix) and organic (the products of carbonization of rapeseed oil) is obtained. It should be noted that rapeseed oil carbonization products have the activated coal properties. This type of sorbent is capable to simultaneously adsorb polar (CH_3OH) and non-polar (C_6H_6) molecules from gaseous phase.

Table 2

Sorption characteristics of samples.

Samples	Specific surface area, m^2/g		Total pore volume, cm^3/g	
	Benzene	Methanol	Benzene	Methanol
No.45	68.4	120.0	0.089	0.154
B25S	154.4	144.0	0.177	0.247
B250	130.8	134.7	0.195	0.340
B400	128.8	122.4	0.185	0.275
B600	113.5	105.7	0.195	0.271
M250	27.9	91.8	0.044	0.198
M400	124.8	131.3	0.177	0.299
M600	121.1	116.3	0.195	0.267

Conclusions:

1. Sorption properties of new type of sorbent have been studied.
2. 2 .The sorbents have been made from the by-product of rapeseed oil bleaching during thermal treatment in temperature from 250 to 1000 ^{0}C.
3. The samples are characterized by sufficiently high sorption capacity and thermal resistance.
4. The prepared samples are characterized by sufficiently large specific surfaces, about 100 m^2/g and are capable to simultaneously adsorb polar (CH_3OH) and non-polar (C_6H_6) molecules from gaseous phase.

The results obtained serve as a basic perspective for further research.

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A.Ruplis, V.Lakevičs, L.Bērziņa–Cimdiņa. No rapšu eļļas attīrīšanas blakus produkta pagatavotu jaunu sorbentu raksturojums. *Daudzos tehnoloģiskos procesos kvalitatīvā galaprodukta iegūšana saistīta ar daudzu blakus produktu rašanos. Aktuāls ir jautājums par šo blakus produktu racionālu izmantošanu. Parādīts, ka rapšu eļļas balināšanas blakus produkti var tikt izmantoti par vērtīga divkomponentu sorbenta iegūšanu. Tas ir perspektīvs produkts, kuru var izmantot dažādu vides problēmu risināšanā. Piemērām, kaitīgu šķīdinātāju tvaiku uztveršana no gāzes fāzes, gaisa vai notekūdeņu attīrīšanā. No rapšu eļļas balināšanas blakusproduktiem izgatavoti un raksturoti materiāli ar labiem sorbcijas parametriem. Jauna tipa sorbenti sastāv no Latvijas mālu izcelsmes alumosilikāta matricas un rapšu eļļās koksēšanas (250, 400 un 600^0 C) produktiem. Izmērītas modeļvielu (metanols, benzols) adsorbcijas – desorbcijas izotermas. Adsorbcijas izotermām ir raksturīga S - veida forma, kas atbilst polimolekulārās adsorbcijas teorijai. Tā izmantota paraugu īpatnējās virsmas aprēķināšanai pēc starptautiski atzītās BET metodes. Pētīto paraugu īpatnējā virsma ir robežās no 27,9 līdz 154,4 m^2 /g. Tie adsorbē metanola un benzola tvaikus istabas temperatūrā un uzrāda augstu termisko izturību.*

Ruplis A., Lakevics V., Berzina–Cimdina L. Characterization of new sorbents produced from by-product of the rapeseed oil treatment. *In many technological processes obtaining of qualitative product results in appearance of various by-products. A vital problem is rational utilization of those. It's proven that by-products of rapeseed oil bleaching may be used for obtaining a valuable two-component sorbent. This is a perspective product which may solve some problems of the environment. For example, capturing harmful solvent vapors from gas phase, cleaning air or sewage. The materials made from rapeseed oil treatment by-products are characterized with good sorption properties. These new type sorbents consist of alumosilicate matrix of Latvian clay origin and rapeseed oil coking products (at 250, 400 and 600^0 C). Adsorption and desorption isotherms were measured for model substances (methanol and benzyl). The adsorption isotherms are S-shaped which corresponds with polymolecular adsorption theory. It is used for calculation of sample's specific surfaces with the internationally famous BET method. Specific surface of studied samples lays between 27,9 and 154,4 m2 /g They adsorb methanol and benzyl vapors at the room temperature and demonstrate high thermal resistance.*

Руплис А., Лакевич В., Берзиня–Цимдиня Л. Характеристика новых сорбентов, полученных из побочных продуктов очистки рапсового масла. *Во многих технологических процессах получение качественного конечного продукта связано с появлением многих побочных продуктов. Актуален вопрос об их рациональном использовании. Показано, что побочные продукты отбеливания рапсового масла можно использовать для получения ценного двухкомпонентного сорбента. Это перспективный продукт, который можно использовать для решения различных проблем окружающей среды. Например, улавливание вредных паров растворителей из газовой фазы, очищение воздуха или сточных вод. Из побочных продуктов отбеливания рапсового масла были получены и охарактеризованы материалы, имеющие хорошие сорбционные параметры. Сорбенты нового типа состоят из алюмосиликатной матрицы латвийских глин и продуктов коксования рапсового масла (при 250, 400 и 600^0 С). Измерены изотермы адсорбции и десорбции модельных веществ (метанол, бензол). Для изотермы адсорбции характерна S-образная форма, что соответствует теории полимолекулярной адсорбции. Она использована для расчета удельной поверхности по международно признанному методу BET. Площадь удельной поверхности исследованных образцов лежит в промежутке от 27.9 и до 154.4 м^2 /г. Они адсорбируют пары метанола и бензола при комнатной температуре и показывают высокую термическую устойчивость.*