MAGNETO SUSCEPTIBLE ADSORBENTS OBTAINED BY THERMOCHEMICAL ACTIVATION OF HYDROLYTIC LIGNIN WITH IRON(III) HYDROXIDE

*Nikolai Bogdanovich[1, *], Mikhail Arkhilin[1], Anna Menshina[1],*
Lidiya Kuznetsova[1], Albert Kanarskii[2], Nadezda Voropaeva[3], Oleg Figovsky[4]

Abstract. Magnetosusceptible adsorbents (MSA) were obtained by method of thermochemical activation of lignin and precipitated on its surface iron(III) hydroxide. Dependence of magnetic susceptibility and porous structure parameters were investigated. Optimal conditions of synthesis for output parameters in determined interval of factors variation were found. Structural characteristics of MSA were compared with industrial activated carbon BAU-A and OU-B. It was demonstrated that pores volume of MSA does not inferior to values for the activated carbons.

Keywords: hydrolytic lignin, thermochemical activation, magnetosusceptible, adsorbent, iron(III) hydroxide.

1. Introduction

Adsorption processes are widely used in modern technology. Processes rate is determined by dispersity of adsorbent as well as technological method of used adsorbent separation from a purified medium. The usage of powdered adsorbents with average size less than 100 μm for adsorption processes intensification is highly recommended. However, powders with such dispersity cannot be efficiently separated from purified medium. A promising method for high-disperse powder adsorbents separation is a method of electromagnetic separation, that can be implemented by magnetization of adsorbents. Obtained adsorbents are magnetosusceptible (MSA) [1]. Development of such adsorbents passes extensively [2-6], but industrial production of MSA is still absent. Magnetic sorbents used in petroleum industry are not MSA, because they are macroporous materials, adsorbing oil spills by a mechanism of adhesion and with the help of capillary forces.

Following methods are used for obtaining MSA:
– modification of activated carbon by magnetic nanoparticles [2];
– pyrolysis of synthetic polymers with Fe, Ni, Co salts [3,4,5];
– pyrolysis of metal-polymer composites [6];
– covering of magnetic particles by mesoporous carbon [7];
– synthesis of porous magghemite γ-Fe_2O_3 [8];
– activation of carbon precursors with both $FeCl_3$ and $ZnCl_2$ [9].

It is important to note formerly suggested methods of synthesis [1]: caking of ferrites with activated carbon and sodium silicate, synthesis of ferrites in pores of activated carbon, and electrolytic precipitation of Fe and Ni on the surface of activated carbons.

Pyrolysis of carbon precursor with $Fe(OH)_3$ is the most effective method for obtaining MSA. Iron hydroxide works as an activator and source of magnetic forms of iron – magnetite Fe_3O_4, iron α-Fe and cementite Fe_3C [10]. The adsorbents possess both magnetic and adsorption activity. Efficiency of this method of MSA synthesis is represented in [11, 12].

It is important to note that obtaining of MSA is not a cheap technological process and usage of organic wastes for magnetization allows cutting down expenses [13]. In this case the development of MSA obtaining technology on the basis of recycled resources of mechanical and chemical wood processing, in particular, hydrolytic lignin, can be reasonable.

The objective of this research is optimization of MSA obtaining by thermochemical activation of hyd-

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[1] Institute of Nature Science and Technologies,
Northern (Arctic) Federal University named after M. V. Lomonosov,
17, Severnaya Dvina Emb., 163002 Arkhangelsk, Russia
[2] Kazan National Research Technological University
68, K. Marks Str., 420034 Kazan, Russia
[3] Federal State Budgetary Scientific Institution,
All-Russian Rapeseed Research Institute,
26, Boyevoy proezd, 398037 Lipetsk, Russia
[4] Polymate Ltd. – International Nanotechnology Research Center,
Migdal HaEmek 23100, Israel
[*] n.bogdanovich@narfu.ru

rolytic lignin with iron(III) hydroxide *via* determination of influence of Fe_2O_3 dosage, pH of $Fe(OH)_3$ precipitation and temperature of thermochemical activation of hydrolytic lignin on magnetic and adsorption properties, porous structure parameters, and yield of MSA.

2. Experimental

For obtaining MSA, hydrolytic lignin from disposal area of JSC Hydrolysis Plant Arkhangelsk was used as the original source. It was dried to humidity of 9 %. Characterization of the lignin are [14]: Klason's lignin – 79.4 %, hard-hydrolysable polysaccharides – 12.1 %, extractives (extracted with alcohol-benzene mixture) – 14.8 %, and mineral substances – 3.9 %. Elemental composition of a.d. lignin, mass.: C – 60 %, O – 33 %, H – 7 %. First of all, water suspension of lignin was prepared. Calculated volume of iron(III) sulphate solution was added to this mixture. Then $Fe(OH)_3$ was precipitated with ammonia hydroxide. The mixture of iron(III) hydroxide and lignin was washed out by distilled water and underwent thermochemical activation. The activation was conducted in lab pipe-still heater SUOL-0,44 (MIUS, JSC, Russia) in quartz glass tube with a diameter of 30 mm and wall thickness of 2 mm in atmosphere of self steam-gas. The steam-gas was released to condensation system, where liquid products of pyrolysis were separated. Non-condensed gases were removed to atmosphere.

Synthesis and research of MSA properties were conducted by the method of planned experiment. Central compositional rotatable uniform-plan of second order for 3 factors was selected. Varied parameters are $Fe(OH)_3$ dosage (calculated on Fe_2O_3) $\omega(Fe_2O_3)$, pH of precipitation and temperature of thermochemical activation T_{act}. Values and intervals of factors' variation are presented in Table 1.

Influence of these factors on yield, magnetic and adsorption properties as well as on parameters of porous

structure were investigated. Based on experimental data, coefficients in regression equations were calculated. Adequacy of obtained equations was proved by Fisher's ratio test. Insignificant coefficients were casted out. Regression equations with significant coefficient are mathematic model of output parameters dependence on defined varied factors in coded factors values.

Output parameters in equations are yield of MSA (Y), relative magnetic susceptibility (RMS) and parameters of porous structure such as pores volume V_Σ, specific surface area S (SSA), mesopores volume V_{me}, micropores volume V_{mi}, average micropores size d_{mi} and average pores size d_{av}.

Yield of adsorbent was found gravimetrically in percents from a weight of absolutely dry mixture of lignin and iron(III) hydroxide.

Investigation of porous structure was conducted on the surface area with porosity analyzer ASAP 2020 mp (Micromeritics, USA) [15]. Samples of adsorbent were degassed in degasation port in 2 h at 623 K up to the residual pressure of 0.7 mPa. The weight of the sample was 20±2 mg. Porous characteristics of BAU-A and OU-B (NevaReaktiv Ltd., Russia), the industrial activated carbons popular in Russia, were determined for comparison.

Porous structure parameters were calculated on isotherms using software. Total volume of pores, specific surface area and average pore size were calculated using BET [16]. Micropores volume was calculated using *t*-plot method [17] and mesopores volume – using BJH method for desorption curve [18]. For calculation of the average micropores size method of Horvath-Kawazoe was used [19].

Related magnetic susceptibility (RMS) of the adsorbents was investigated on Gouy apparatus [20]. This dimensionless quantity was calculated as relation of balance deflexion to weight of sample. Weight of samples amounted 100–105 mg. Synthesized magnetite, RMS for which was 3.17, was used as a reference standard.

Table 1

Intervals of factors variation

Level of factor's variation	Varied factor		
	X_1	X_2	X_3
	$\omega(Fe_2O_3)$, %	pH	T_{act}, K
	Step, λ		
	5	1, 2	313
-1.682	21.6	6.0	1043
-1	25.0	6.8	1113
0	30.0	8.0	1133
1	35.0	9.2	1153
1.682	38.4	10.0	1183

Apart from the above mentioned small investigation of MSA surface structure was conducted in the Common Use Center of Scientific Equipment "Arktika" (Arkhangelsk, Russia) by SEM method. Research was done with SEM microscope ZEISS SIGMA VP (Carl Zeiss Inc., Switzerland) with detectors InLens and SE2 at boosting voltage 2 and 20 kV. Preliminary sample of MSA was freeze-dried on plant FreeZone 2,5L (Labconco Corp., USA). To improve quality of image sample was deposited with 5 nm Au/Pd film using evaporation plant Q150T ES (Quorum Technologies Ltd., GB).

3. Results and Discussion

Calculated values of F did not exceed critical values F_{crit} for $\alpha = 0.05$. It means that all regression equations with significant coefficients were adequate. In this case one can regard the equations for mathematic models of synthesis of MSA. The equations are represented below:

$$RMS = 11 - 1.3X_2 - 2.6X_1X_2 + 1.6X_1X_3 + 0.9X_2^2 + X_3^2; F = 2.19; F_{crit} = 4.77 \quad (1)$$

$$Y = 44 - 1.2X_3 - 0.5X_2^2 - 0.8X_3^2;$$
$$F = 2.38; F_{crit} = 4.70 \quad (2)$$

$$V_\Sigma = 0.26 + 0.03X_1 + 0.04X_2 - 0.041X_2X_3 + 0.042X_1^2 - 0.018X_2^2 - 0.018X_3^2; F = 2.11;$$
$$F_{crit} = 4.83 \quad (3)$$

$$V_{mi} = 0.088 - 0.006X_1 - 0.007X_2 + 0.009X_3 - 0.007X_1X_3 - 0.01X_1^2;$$
$$F = 0.695; F_{crit} = 4.83 \quad (4)$$

$$V_{me} = 0.16 + 0.027X_1 + 0.038X_2 - 0.019X_3 - 0.069X_2X_3 + 0.048X_1^2 - 0.014X_3^2;$$
$$F = 2.80; F_{crit} = 4.82 \quad (5)$$

$$SSA = 103 + 44X_2 - 20X_3 - 48X_2X_3 + 27X_1^2 - 4.8X_2^2; F = 4.64; F_{crit} = 4.70 \quad (6)$$

$$d_{mi} = 1.126 + 0.005X_1 + 0.005X_2 - 0.004X_2X_3 - 0.001X_3^2; F = 0.59;$$
$$F_{crit} = 4.83 \quad (7)$$

$$d_{av} = 3.59 + 0.69X_1 + 0.38X_2 - 0.44X_3 - 0.65X_2X_3 + 0.78X_1^2 - 0.29X_3^2; F = 3.61,$$
$$F_{crit} = 4.83 \quad (8)$$

Analysis of the equations is presented further. Response surfaces were plotted for clarity.

Enhance of $\omega(Fe_2O_3)$ leads to decrease of RMS (Eq. (1), Fig. 1).

Dependence of RMS on T_{act} passes through a minimum. pH and $\omega(Fe_2O_3)$ were found to be the antagonistic factors. Synchronous increasing or decreasing of these two factors leads to declination of magnetic susceptibility. RMS value for the best sample exceeds almost 10 times RMS for magnetite (3.17) and reaches 30.3 at $\omega(Fe_2O_3) = 38.4\%$, pH = 6.0, $T_{act} = 1183$ K. Probably it is bound with the presence of more magnetoactive compound than magnetite – α-iron.
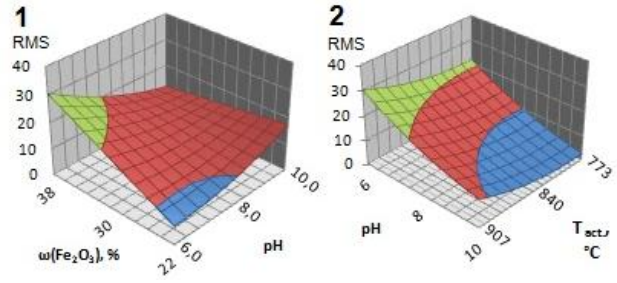

Fig. 1. Influence of $\omega(Fe_2O_3)$, pH and $T_{act.}$ on RMS: $T_{act} = 1183$ K (1) and $\omega(Fe_2O_3) = 38.4\%$ (2)

Enhance of pyrolysis temperature leads to the decrease in the yield of adsorbents. Smaller yield may be observed at central values of $\omega(Fe_2O_3)$ and at margin pH values (Eq. (2)). Yield of adsorbents is high owing to higher content of a non-volatile mineral component – iron. It is varied between 40 and 44 %. In this connection yield does not have particular importance in comparison with porous structure. Maximum yield is observed at pH = 8.0, $T_{act} = 1043$ K and $\omega(Fe_2O_3) = 21.4\%$.

It is known that total pores volume defines a total content of pores, taking part in adsorption – micropores and mesopores. Macropores do not adsorb N_2, but they play a role of transport channels, that provide free traffic of adsorbate (N_2) within porous body. In this case macropores volume cannot be investigated by this research method. One can see (Eq. (3), Fig. 2) that total pores volume has minimum at $\omega(Fe_2O_3)$ average values and its dependence on T_{act} and pH has complex nature because of hese factors interference. Analyzing Eq. (3), one can find optima in studied interval of factor variation: $\omega(Fe_2O_3) = 38.4\%$, pH = 10, $T_{act} = 1043$ K, and under these conditions $V_\Sigma = 0.51$ cm³/g.
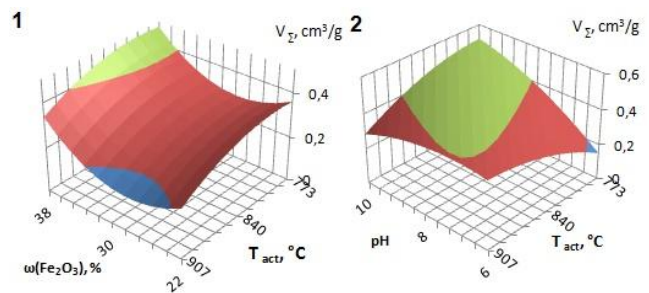

Fig. 2. Influence of $\omega(Fe_2O_3)$, pH and T_{act} on total pores volume: pH = 9.2 (1) and $\omega(Fe_2O_3) = 38.4\%$ (2)

Micropores volume enhances significantly when activation temperature is increased (Eq. (4), Fig. 3). It is increased at increasing pH, as well. Dependence of V_{mi} on Fe_2O_3 dosage has a maximum. Optimal conditions are: $\omega(Fe_2O_3) = 26\%$, pH = 6.0, $T_{act} = 1183$ K, $V_{mi} = 0.12$ cm³/g.

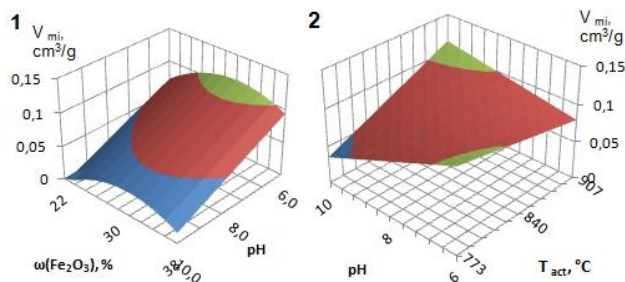**Fig. 3.** Influence of $\omega(Fe_2O_3)$, pH and T_{act} on micropores volume: T_{act} = 1043 K (1) and $\omega(Fe_2O_3)$ = 31.3 % (2)

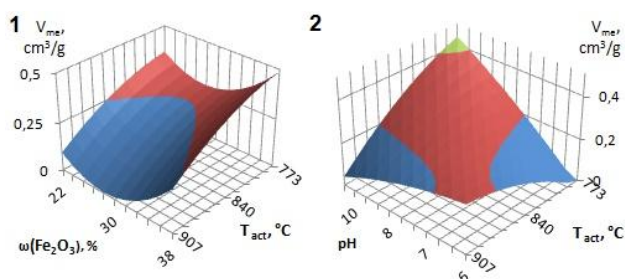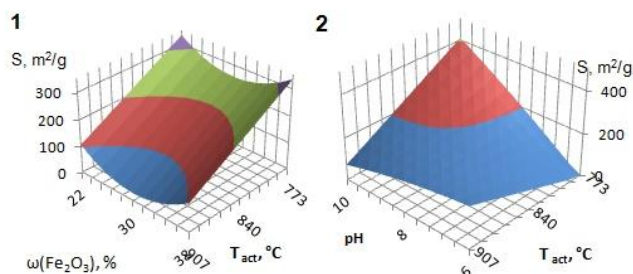**Fig. 4.** Influence of $\omega(Fe_2O_3)$, pH and T_{act} on mesopores volume: pH = 10.0 (1) and $\omega(Fe_2O_3)$ = 21.4 % (2)

Fig. 5. Influence of $\omega(Fe_2O_3)$, pH and T_{act} on specific surface area: pH = 9.2 (1) and $\omega(Fe_2O_3)$ = 38.4 % (2)

Values of V_{me} have a positive correlation with pH (Eq. (5), Fig. 4). Dependence on the temperature is more complicated. Particularly, at high values of pH the value of V_{me} decreases with the decrease of T_{act}, and at low pH value they increase. Influence of Fe_2O_3 dosage on V_{me} was not observed. The optimal conditions for mesoporous MSA are: $\omega(Fe_2O_3)$ = 21.4 %, pH = 10, T_{act} = 1043 K. V_{me} under these conditions reaches 0.42 cm^3/g.

Change of specific area of MSA depending on parameters of MSA synthesis is similar to change of total pores volume (Eq. (6), Fig. 5). Value of SSA increases with the increase of pH and T_{act}, dependence on Fe_2O_3 dosage also has a minimum. Highest value of SSA (410 m^2/g) can be reached at $\omega(Fe_2O_3)$ = 38.4 %, pH = 9.2 and T_{act} = 1043 K. Note that these conditions are identical to the conditions for maximum total volume of pores.

The average micropores size enhances at rising of Fe_2O_3 dosage and has a complex dependence on pH and T_{act} (Eq. (7)). It must be noted that any changes in synthesis conditions can change the size of micropores insignificantly (from 1.11 to 1.15 nm). Maximum value of d_{mi} is observed at $\omega(Fe_2O_3)$ = 38.4 %, pH = 10, T_{act} = 1183 K.

The average pores size at BET is a derivative quantity and it can be calculated as relation of total pores volume to SSA. The d_{av} value enhances either at increasing or decreasing of $\omega(Fe_2O_3)$ and has a complex dependence on pH and temperature (Eq. (8)). Lowering of pH at higher temperatures and rising of pH at lower temperatures allow the increase in pores size (Fig. 2). Coarse-pored samples of MSA (d_{av} up to 9.35 nm) can be obtained at $\omega(Fe_2O_3)$ = 38.4 %, pH = 9.2, T_{act} = 1043 K. These conditions are optimal for V_Σ, too.

All the data obtained under optimal conditions for each parameter are presented in Table 2. In the researched interval of factors variation the optima in center of plan were not found. It means that going beyond the range, one can find more favorable conditions for MSA preparation. It is necessary to note that the obtained data were confirmed experimentally.

Table 2

Optimal conditions for output parameters

Output parameter	Value	Varied factor		
		$\omega(Fe_2O_3)$, %	pH	T_{act}, K
V_Σ	0.51 cm^3/g	38.4	9.2	1043
V_{mi}	0.12 cm^3/g	31.3	6.0	1043
V_{me}	0.42 cm^3/g	21.4	10.0	1043
SSA	410 м^2/g	38.4	9.2	1043
d_{mi}	1.15 nm	38.4	10.0	1183
d_Σ	9.35 nm	38.4	9.2	1043
RMS	30.3	38.4	6.0	1183
Y	44.4 %	21.4	8.0	1043

Investigation of activated carbons OU-B and BAU-A has shown that OU-B is for the most part mesoporous carbon. It possesses the following characteristics: $V_\Sigma = 0.51\ \text{cm}^3/\text{g}$, $V_{mi} = 0.25\ \text{cm}^3/\text{g}$, $V_{me} = 0.26\ \text{cm}^3/\text{g}$, $S = 697\ \text{m}^2/\text{g}$. BAU-A possesses the following parameters: $V_\Sigma = 0.38\ \text{cm}^3/\text{g}$, $V_{mi} = 0.27\ \text{cm}^3/\text{g}$, $V_{me} = 0.11\ \text{cm}^3/\text{g}$, $S = 623\ \text{m}^2/\text{g}$. Obviously, that in the ratio V_{mi}/V_{me} this adsorbent is microporous.

From the abovementioned it is clear that part of mesopores even for large-porous (clarificant) activated carbon is just over half of V_Σ. Obtained MSA consist of much more mesopores (0.42 *vs.* 0.26 cm³/g) while total pores volumes are equal. And thus MSA can be recommended to clarify solutions equally to activated carbons, and the possibility of a simple separation by the method of electromagnetic separation is an additory advantage of MSA.

One can say that specific surface area of MSA is less than for activated carbon. But this parameter is not as indicative as volume of pores since capillary condensation is the main adsorption mechanism for micropores.

Results of scanning electronic microscopy have shown that small iron-consisting clusters with sizes of 20–30 nm are situated on the adsorbent surface (Fig. 6). Such configuration of elements repeats location of Fe(OH)₃ particles precipitated on hydrolytic lignin.
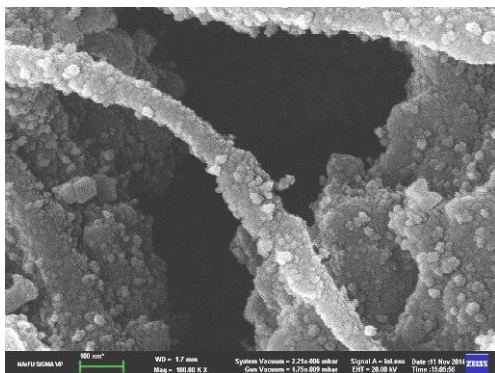

Fig. 6. SEM image of MSA (magnification of 100000x)

4. Conclusions

Summarizing the results, one can conclude the following:

– technology of MSA obtaining by the method of thermochemical activation of hydrolytic lignin and iron(III) hydroxide precipitated on its surface has been optimized; the chosen conditions are optimal only in observed interval of factors variation, so there is a potential for further improvement of the technology;

– MSA total pores volume is comparable to activated carbons BAU-A and OU-B;

– MSA are mainly mesoporous and possess high volume of mesopores and therefore they can be recommended for purification of solutions;

– the obtained MSA possesses high related magnetic susceptibility values, up to 10 times higher than for magnetite.

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МАГНЕТОСПРИЙНЯТЛИВІ АДСОРБЕНТИ, ОТРИМАНІ ТЕРМОХІМІЧНОЮ АКТИВАЦІЄЮ ГІДРОЛІЗНОГО ЛІГНІНУ ІЗ ГІДРОКСИДОМ ЗАЛІЗА(ІІІ)

Анотація. *Методом термохімічної активації лігніну та висадженого на його поверхні гідроксиду заліза(ІІІ) отримані магнетосприйнятливі адсорбенти (МСА). Досліджено залежність параметрів магнітної сприйнятливості і структури пор. Знайдено оптимальні умови синтезу для вихідних параметрів в певному інтервалі змінних чинників. Проведено порівняння структурних характеристик МСА з промисловим активованим вугіллям БАУ-А і ОУ-Б. Показано, що об'єм пор МСА відповідає значенням для активованого вугілля.*

Ключові слова: *гідролізний лігнін, термохімічна активація, магнетосприйнятливий, адсорбент, гідроксид заліза(ІІІ).*