Sych N.V., Trofymenko S.I., Tsyba M.M., Vikarchuk V.M.
Institute for Sorption and Problems of Endoecology of National Academy of Scienses, Kiev
13, General Naumov Str., 03164 Kiev, Ukraine, e-mail: nataliya_sych@ukr.net

Energy Saving Approach to Chemical Processing of Lignocellulosic Feedstock into Sorptive Materials

High porous activated carbons were prepared by microwave-induced phosphoric acid activation of lignocellulosic raw material. It was established that the parameters of porous structure of carbons obtained are increased with increasing of treatment duration and reach maximum under 3–5 min staying. Maximum BET surface area achieved during the microwave treatment with energy load 120 Wt·min/(g·mL) is 1085 m^2/g. Total pore volume reaches almost 0,7 cm^3/g. Pore size distributions indicates that carbons consists of micropores (0.9–1.1 nm) and mesopores with size 4 nm. Obtained carbons have high adsorption capacity towards copper ions from aqueous solutions at pH ≤ 4. The results proved that this process is rapid, power-efficient and economic. *Bibl. 10, Fig. 3, Tab. 1.*
Key words: microwave-induced energy, phosphoric acid activation, lignocellulosic feedstock, surface area.

The AC preparation method significantly affects the quality, properties and cost of finished product. A conventional heating method is one of the most applicable and usual technique of AC production but it has some disadvantages – the heat source is located outside bed, and the heat generated by the source is transferred to the particles by convection, conduction and radiation mechanisms. There is a temperature gradient from the surface to the interior of each particle. Heating at a high temperature is required during the pyrolysis and activation processes, which usually takes a long time and consumes much energy using the conventional thermal method [1].

In recent years, microwave has emerged as a promising alternative energy source for the AC production [2–8]. In microwave field, the materials receive energy at a molecular level through dipole rotation and ionic conduction, and the energy is dissipated in the form of heat. Microwave heating is internal and volumetric, which provides the advantages of uniform temperature distribution, rapid temperature rise and saving of energy.

Previous studies on the preparation of AC using a microwave radiation method have showed that the more significant parameters are the microwave radiation time, the microwave power level, the impregnation ratio and the agent flow rate. Accordingly, the effects of these parameters on the physical and chemical properties of AC, such as the pore structure, the adsorption capacity, the carbon yield and the surface functional groups, were discussed. In general, the physical properties of AC (adsorption capacity, pore volume and carbon yield) improved when these parameters were enhanced up to their optimum points, and then these properties decreased when these parameters were increased beyond their optimum values.

Current study was focused on the processing of lignocellulosic feedstock – dogwood stone into sorptive materials using microwave-assisted phosphoric acid activation.

Dogwood stone was grounded and sieved to obtain particle size 1.0–2.0 mm. 5 g of dried dogwood stone was impregnated with 50 mL of phosphoric acid solution with concentration adjusted to obtain desired impregnation ratio and stayed during 30 min. The microwave-induced activation treatments were conducted in a multi-mode type microwave furnace Zelmer 29Z023. Total microwave energy delivered to sample (microwave load) was 74 % of maximum power and time of irradiation was 1, 2, 3 and 5 min. After the treatment, the residual phosphoric acid was eliminated from carbon by extensive washing with hot water in Soxhlet extractor until neutral pH of wash water.

Information on carbons pore structure was derived from nitrogen adsorption isotherms obtained at −196 °C on a NOVA 2200 apparatus (Quantachrome, USA). The pore size and pore size distribution were calculated by the BJH model using desorption isotherm branch. The adsorption isotherms were determined in a conventional high accuracy volumetric adsorption rig. Prior to the measurement the samples were outgassed at 180 °C under vacuum for 2 h. Activated carbons were obtained under microwave irradiation using different amount of phosphoric acid which is presented as ra-

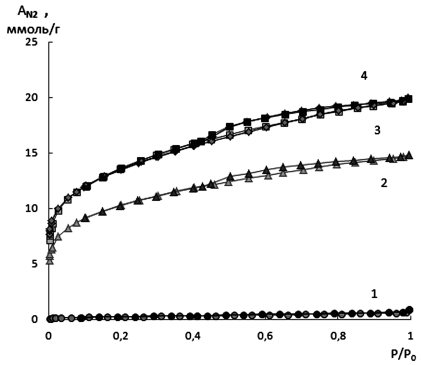

Fig.1. Adsorption-desorption isotherms of samples, obtained with phosphoric acid microwave activation (IR = 0.9, irradiation energy 74 %) with different time of exposure, min: 1 — 1; 2 — 2; 3 — 3; 4 — 5.

tio of introduced acid to sample weight. Two impregnation ratio (IR) were applied: 0.9 and 1.7. Threshold of microwave effect on development of porosity is about 40 W·min/(g·mL) for all experiments with phosphoric acid. Maximum BET surface area is achieved at 120 W·min/(g·mL) with slight decrease at higher energy delivered to the sample. Increasing impregnation ratio from 0.9 to 1.7 increases BET surface area by about 100–150 m^2/g. Maximum BET surface area is achieved during 3–5 min of microwave treatment at 74 % of maximum power provided by microwave furnace. While the value of BET surface area of microwave-activated carbons (1085 m^2/g) is less than that for conventionally heated carbon (2070 m^2/g) [9], microwave-assisted activation is much faster and needs less energy than conventional heating.

Carbon obtained by microwave-assisted phosphoric acid activation with treatment duration of 1 min does not show any significant nitrogen adsorption in entire relative pressure region that indicates negligible development of porous structure (Fig.1).

Under increasing of treatment duration up to 2 min nitrogen adsorption firstly sharply increases. Under following increasing up to 3, 5 min it almost doesn't vary. Nitrogen adsorption isotherms obtained with treatment duration of 2, 3, 5 min belong to a mixed type of IUPAC classification [10]. The initial part of the isotherms is of type I with significant uptake at low relative pressures, which corresponds to adsorption in micropores. At intermediate and high relative pressures the isotherms are of type IV with a hysteresis loop of type H4 associated with monolayer-multilayer adsorption followed by capillary condensation in narrow slit-like pores. The parameters of porous structure of carbons obtained by microwave-assisted phosphoric acid activation (Table) are increased with increasing of treatment duration and reach maximum under 3min staying — 1085 m^2/g. Total pore volume reaches almost 0,7 cm^3/g. The results proved that this process is rapid, efficient and economic.

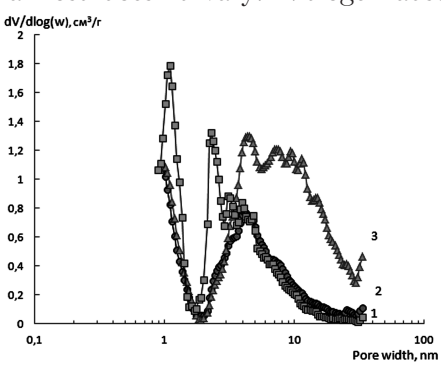

Fig. 2. Pore size distributions for: 1 — conventionally heated (T = 400 °C; IR = 1.0) and microwave-induced carbons with energy load 47 mW: 2 — IR = 0.9; 3 — IR = 1.7.

The parameters of porous structure of carbons obtained with microwave-induced phosphoric acid activation

Treatment duration, min	E, W·min/(g·mL)	S, m^2/g	V_{tot}, cm^3/g	V_{mi},		V_{me},	
				cm^3/g	%	cm^3/g	%
1	39,5	21	0,03	0,003	10	0,03	90
2	78,9	824	0,51	0,20	39	0,32	61
3	118,4	1085	0,69	0,25	37	0,44	63
5	197,3	1078	0,69	0,26	38	0,43	62

E — Energy; S — Surface area.

Porous structure of microwave-activated carbons is presented of micropores (0.9–1.1 nm) and mesopores of with size 4 nm (Fig.2).

Increasing impregnation ratio from 0.9 to 1.7 develops additional larger mesopores with size 5–11 nm. Porous structure of conventionally heated carbon is different in that main mesopore size is 2.3 nm.

Large amount of surface groups of acid character are responsible for adsorption properties towards copper ions from aqueous solutions. 0.1 g of carbon was shaken with 20 mL of 0.001 M

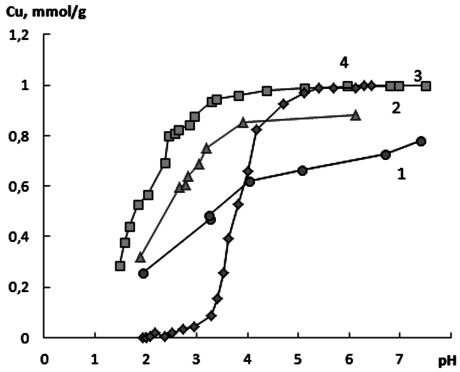

Fig. 3. pH dependence of copper binding for microwave-induced carbons, obtained at different energy load, mW: 1 — 30; 2 — 120; conventionally heated carbons — 3; and ion exchange resin with carboxylic groups (KB-4) — 4.

$Cu(NO_3)_2$ solution containing 0.1 M NaCl as background electrolyte in order to determine copper adsorption. The pH of solution was adjusted by adding different amounts of 0.1 M HCl or 0.1 M NaOH solutions. After equilibration for 24 h, the pH was measured with a pH glass electrode and copper concentration was determined by titration with standard EDTA solution.

Carbons obtained with microwave-assisted phosphoric acid activation (Fig.3) demonstrate high adsorption capacity at pH ≤ 4 as compared to ion exchange resin with carboxylic groups (KB-4). With increasing microwave load copper adsorption increases. The highest adsorption shows conventionally heated carbon.

Conclusions

Large surface area activated carbons were prepared by microwave-assisted phosphoric acid activation. It was established that the parameters of porous structure of carbons obtained are increased with increasing of treatment duration and reach maximum under 3–5 min staying. Maximum BET surface area achieved during the microwave treatment with energy load 120 W·min/(g·mL) is 1085 m^2/g. Total pore volume reaches almost 0,7 cm^3/g. Pore size distributions indicates that carbons consists of micropores (0.9–1.1 nm) and mesopores with size 4 nm. Obtained carbons have high adsorption capacity towards copper ions from aqueous solutions at pH ≤ 4. The results proved that this process is rapid, efficient and economic.

References

1. Hesas R.H., Daud W.M.A., Sahu J.N., Arami-Niya A. The effects of a microwave heating method on the production of activated carbon from agricultural waste - a review, *J. Anal. Appl. Pyrol.,* 2013, Vol. 100, pp. 1–11.
2. Jones D.A., Lelyveld T.P., Mavrofidis S.D., Kingman S.W., Miles N.J. Microwave heating applications in environmental engineering - a review, *Resour. Conserv. Recycl.,* 2002, 34, pp.75–90.
3. Liu Q.-S., Zheng T., Wang P., Guo L. Preparation and characterization of activated carbon from bamboo by microwave-induced phosphoric acid activation, *Ind. Crop. Prod.*, 2010, 31, pp. 233–238.
4. Yagmur E., Ozmak M., Aktas Z. A novel method for production of activated carbon from waste tea by chemical activation with microwave energy, *Fuel*, 2008, 87, pp. 3278–3285.
5. Ania, C.O., Parra, J.B., Menendez, J.A., Pis, J.J., Effect of microwave and conventional regeneration on the microporous and mesoporous network and on the adsorptive capacity of activated carbons, *Microporous Mesoporous Mater.*, 2005, 85, pp. 7–15.
6. Jones, D.A., Lelyveld, T.P., Mavrofidis, S.D., Kingman, S.W., Miles, N.J., Microwave heating applications in environmental engineering — A review, *Resour. Conserv. Recycl.,* 2002, 34, pp. 75–90.
7. Menendez, J.A., Menendez, E.M., Iglesias, M.J., Garcia, A., Pis, J.J., Modification of the surface chemistry of active carbons by means of microwave-inducedtreatments, *Carbon*, 1999, 37, pp. 1115–1121.
8. Liu, X.T., Quan, X., Bo, L.L., Chen, S., Zhao, Y.Z. Simultaneous pentachlorophenol decomposition and granular activated carbon regeneration assisted bymicrowave irradiation, *Carbon,* 2004, 42, pp. 415–422.
9. Sych N.V., Trofymenko S.I., Poddubnaya O.I. Tsyba M.M. Sapsay V.I. Klymchuk D.O. Puziy A.M. Porous structure and surface chemistry of phosphoric acid activated carbon from corncob, *Appl. Surf. Sci.,* 2012, 261, pp.75–82.
10. Sing K.S.W., Everett D.H., Haul R.A.W., Moscou L., Pierotti R.A., Rouquero J., Siemieniewska T., Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity, *Pure Appl. Chem.*, 1985, 57, pp. 603–619.

Received July 20, 2017

УДК 661.183.126

Сыч Н.В., Трофименко С.И., Цыба Н.Н., Викарчук В.М.
Институт сорбции и проблем эндоэкологии НАН Украины, Киев
ул. Генерала Наумова, 13, 03164 Киев, Украина, e-mail: nataliya_sych@ukr.net

Энергосберегающий подход к химической переработке лигноцеллюлозного сырья в сорбционные материалы

С использованием индуцированного микроволновой энергией фосфорнокислотного активирования лигноцеллюлозного сырья приготовлены высокопористые активированные угли. Установлено, что значения параметров пористой структуры полученных углей возрастают с увеличением длительности выдержки их в поле микроволнового воздействия и достигают максимума при 3–5-минутной выдержке. Максимальная удельная поверхность по БЭТ, полученная при микроволновом испытании с энергетической нагрузкой 120 Вт·мин/(г·мл), составляет 1085 $м^2/г$. Суммарный объем пор 0,7 $см^3/г$.

Определено, что угли состоят из микропор (0,9–1,1 нм) и мезопор (4 нм). Полученные угли обладают высокой сорбционной способностью по отношению к ионам меди при pH ≤ 4. Результаты исследований подтверждают, что процесс микроволнового активи- рования быстрый, энергоэффективный и экономичный. *Библ. 10, рис. 3, табл. 1.*

Ключевые слова: индуцированная микроволнами энергия, фосфорнокислотное активирование, лигноцеллюлозное сырье, удельная поверхность.

УДК 661.183.126

Сич Н.В., Трофименко С.І., Циба Н.Н., Вікарчук В.М.

Інститут сорбції та проблем ендоекології НАН України, Київ
вул. Генерала Наумова, 13, Київ 03164, Україна, e-mail: nataliya_sych@ukr.net

Енергозберігаючий підхід до хімічної переробки лігноцелюлозної сировини на сорбційні матеріали

З використанням індукованого мікрохвильовою енергією фосфорнокислотного активування лігноцелюлозної сировини виготовлене високопорувате активоване вугілля. Встановлено, що значення параметрів поруватої структури отриманого вугілля зростають зі збільшенням тривалості витримки їх у полі мікрохвильового впливу та досягають максимуму при 3–5-хвилинній витримці. Максимальна питома поверхня за БЕТ, отримана при мікрохвильовому тестуванні з енергетичним навантаженням 120 Вт·хв/(г·мл), складає 1085 $м^2$/г. Сумарний об'єм пор 0,7 $см^3$/г. Визначено, що вугілля містить мікропори (0,9–1,1 нм) та мезопори (4 нм). Отримане вугілля має високу сорбційну здатність по відношенню до іонів міді при pH ≤ 4. Результати досліджень підтверджують, що процес мікрохвильового активування швидкий, енергоефективний та економічний. *Бібл. 10, рис. 3, табл. 1.*

Ключові слова: індукована мікрохвилями енергія, фосфорнокислотне активування, лігноцелюлозна сировина, питома поверхня.