PREPARATION AND CHARACTERIZATION OF ACTIVATED CARBONS PREPARED FROM WOOD WASTE AND THEIR APPLICATION FOR GAS SEPARATION

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ABSTRACT

In this paper, we describe a simple, clean and low-cost technology that converts woods waste into valuable activated carbon products for environmental applications. In this work, a wide variety of industry wood waste such as Haloxylon, Apricot pits and Pine were used to prepare powders of activated carbons by a simple chemical process and thermal activation. The physical properties and surface chemistry of the activated carbons were determined by elemental analyses, scanning electron microscopy, X-ray diffraction and standard Brunauer-Emmett-Teller method. The application of the prepared activated carbons for gas separation e.g. adsorption of ammonia and of cyclohexane were studied. For the prepared activated carbons shown, physical properties and gas adsorption performance are comparable to commercial activated carbons. Finally impregnation of the activated carbons with nickel nanoparticles improved their ammonia adsorption capacity.

Key words: Activated carbon, Mesoporous materials, Gas adsorption, Wood waste.

INTRODUCTION

Activated carbons having high specific porosity and thus high surface areas are extremely versatile adsorbents of major industrial significance. Activated carbon is used in a wide range of applications concerned principally with the removal of species by adsorption from the liquid or gas phase. Almost all materials containing high fixed carbon content can potentially be activated. In most cases, activated carbons are produced from a number of precursor materials including wood, agricultural wastes, coal and synthetic resins[1-4]. All

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activated carbons contain micropores, mesopores, and macropores within their structures but the relative proportions vary considerably according to the raw material. Precursor's carbon raw materials are normally exposed to a number of different activation methods such as physical or chemical treatments in an effort to achieve carbon with the highest adsorption capacity for a particular application[1-3]. Activated carbon adsorption has been cited by the US Environmental Protection Agency (USEPA) as one of the best available environmental pollution control technologies[5]. Applications of activated carbons are enormous. Its important use is for gasoline vapour emission control canisters in automobiles. Activated carbons can act as a filter material in air cleaning filters for removal of gases and vapours in the industrial environment[6].

For the past years, one of the major challenges associated with adsorption using activated carbon is its cost-effectiveness and it is known that solid carbon is widely used in industry and all its varieties have become in deficit/Research in the recent past have mainly focused on the preparation of the activated carbon from wood low cost materials and waste materials as an alternative for the commercial activated carbon[7,8]. Consequently, numerous examples of low cost row materials have been proposed and studied and some have been fruitfully used for the preparation of activated carbon[1-3].

In this work, we describe the preparation of activated carbons based on low cost wood and mineral carbon raw materials. The prepared carbons were systematically characterized for their surface areas, chemical composition, and crystalline morphology. The prepared activated carbons were used as adsorbents for purification of gas-air mixtures from toxic compounds such as cyclohexane and ammonia. We performed a set of adsorption experiments. The results of those measurements are outlined.

The novelty of the study is that, firstly, a widely used cyclohexane solvent was used as test of the adsorptive instead of carbon tetrachloride. Secondly, wide coverage of the synthesized sorbents of wood and mineral origin (wood, nut shells, fruit stones, shungite) was carried out. Thirdly, low-temperature steam activation modes (800-850°C) were applied, which is favorable for development of a microporous structure and for preventing of burn of surface. At the end, developed technology of obtaining sorbents was adapted to local raw materials.

EXPEREMENTAL

Materials and methods

In this work, carbon-mineral low cost raw material based on shungite rocks of "Bolshevik" from east region of Kazakhstan was used. Shungite rocks-natural formations

with unique composition, structure and properties. It was formed from a natural dumps after extraction and enrichment of ores, and resources of shungite are sufficient for use it on an industrial scale.

Low cost woods raw materials were based on coconut (China), apricot stones (South region of Kazakhstan), Haloxylon (Central region of Kazakhstan) and pine wood (North region of Kazakhstan). It is well known wastes of food and paper industry.

Preparation of sorbents based on mineral raw materials

In the first step, shungite ore was crushed into particles sized lower than 70 μ musing an appropriate sieve. Next, we performed a flotation process on flotation machine FM-1M (Russia). A weight of 1.5 Kg of the crushed shungiteore was placed in a chamber of the flotation machine with 3 L water and mixed without the air supply for 10 mins. Then the flotation reagents were injected into the slurry of water - shungite and mixed without the air supply for 10 mins. Subsequently, the slurry was bubbled with air supply at a rate of 15 mL/min. In this process, we collected foam (containing the row carbon) until the colour of the slurry was changed from dark black to grey and no foams were forming any more. The concentrate carbon from the foams of the flotation processes was dried at 100 ± 5^0C for 3 hrs under stirring. The amount of carbon in the shungite samples after the flotation process was ca. $40 \pm 2\%$ as we determined from the mass difference of samples before and after thermal treatment at a temperature of 800^0C for 2.5 hrs. Cylindrical pellets of shungite were prepared by briquetting through a die hole with diameter 2 mm. The pellets were also subjected to heat treatment in an argon atmosphere at a temperature of 800^0C for 2 hrs. Finally, carbon pellets were activated by water vapour at 800-850^0C for one hr[9]. The activation process leads to increase in the specific surface area from ca. 30 to ca. 250 m^2/g as measured by BET. It is well know that the increase in the specific surface areas under steam activation is due to the combustion of hydrocarbon or tars[10].

Preparation of sorbents based on wood raw materials

For the preparation of active carbon form the wood raw materials, first the wood was crushed in to fine powders with typical crystals sizes of ca. 3-5 mm by mechanical rotary knife mill PM 120 (Russia). Carbonization and activation by water vapour were performed by the same procedure as described above for shungite.

Impregnation of the active carbon with Ni metal

The impregnation of the active carbons with nickel chloride was carried out by penetration of $NiCl_2$ solution (1 M) into the active carbon for one hour and evaporation

of the solution at 100^0C under stirring. After this impregnation the amount of Ni in the active carbons was 2% (mas.). Following this, the nickel active carbons were subjected to thermal treatment, for metal reduction, at 500^0C in a hydrogen stream to obtain carbon-Ni systems[11].

Physical-chemical characterization of the active carbon

The specific surface area and total pore volume of the carbons were determined by the standard Brunauer-Emmett-Teller (BET) method. The measurements were carried out with nitrogen at 77 K, using Quantachrome NOVA 3200E instruments. Water content in the active carbon was determined by the mass difference between the initial sample and samples after drying at 110°C for 1 hr. The ash content of the carbons was found by the mass difference from samples at room temperature and after heating to 800°C for 2.5 hrs at pH of water extract was measured after 3-min boiling of pre-micronised sorbent (5 g) in 50 mL of distilled water at reflux, followed by rapid filtration through filter paper slurry and cooling before measuring its pH. In all cases, the experiments were performed in triplicate[12].

Absorption experiments

In the first absorption experiment, we tested the sorption capacity of the active carbons to iodine. In those experiments, 20 g of the carbons were boiled for 10 mins in 200 mL of 0.2 M HCl. Then the samples were washed with distilled water and dried for 1 hr at 110°C. One gram of the carbons was shaken for 15-30 min in 100 mL of 0.1 M KI solution. Then aliquots from the solutions (10 mL) were titrated with 0.1 M sodium thiosulfate solution (indicator-starch).[13]

Absorption of ammonia gas

Sorption of ammonia was studied by a specially designed instrument. In brief, the instrument is based on a measuring tube with a diameter of 10 mm filled with 5 g of the active carbon. To this measuring tube, we supplied ammonia-air gas mixtures. Ammonia gas is produced by passing air through a solution of 50 mL of 1 M NH_4OH. The ammonia-air gas flow rate is controlled by arheometer (rate of 0.35 L/min). The sorption of ammonia gas in the active carbon is measured from the analysing the gas outlet. The outlet gas first is neutralized with 50 mL of 0.01 M of sulphuric acid solution and the amount of ammonia in neutralizing solution is determined by a method of back titration with 0.01 M NaOH solution[11].

Absorption of cyclohexane gas

Cyclohexane sorption from the gas phase was carried out at room temperature in specially designed instrument. Active carbon is put in a 5 mm diameter tube. Air-cyclohexane gas mixtures are passed through the active carbon at a rate of 1 L/min. 0055 sing a syringe pump system cyclohexane is added to the air gas at a flow rate of 90 µL/hr giving a final concentration of 300 mg/m^3 cyclohexane in the gas mixtures. The outcome gas from the active carbon was introduced into a gas chromatograph with mass spectrometric detection using Agilent 7890A/5975C with auto sampler Combi-PAL (CTC Analytics AG, Switzerland). Chromatography and detection parameters were optimized to achieve short analysis time. Optimization is found at a temperature of 115^{0}C and for the detection, we used selected ion monitoring mode, with a molecular weight of 84 for the selective detection of cyclohexane. Mass spectrometric detector interface temperature was 280^{0}C and ion source temperature 230^{0}C, temperature of quadrupole-150^{0}C. Time of one analysis was 2.5 min, and the time between successive analyses was 3 min.

Characterization techniques

Scanning electron microscope (SEM) images were obtained with a FEI instrument-Inspect S model at acceleration voltages of 5 kV, 15 kV, and 30 kV. Powder X-ray diffraction (XRD) patterns of the active carbons were acquired with a Bruker AXS D8 advance diffractometer with Cu Kα (λ = 1.5418 Å) operating at 40 kV/40 mA. Data were collected from 2θ = 10° to 70°, collected with a resolution of 0.02°. The surface area was measured at 77 K (liquid nitrogen) on a Micromeritics instrument (Gemini 2375) after the samples had been evacuated at 120°C for 12 hr. From the adsorption isotherm, the Barrett, Joyner and Halenda theory was used to calculate the surface areas, mesopore volume and its size distribution.

RESULTS AND DISCUSSION

Table 1 lists various physical values of the activated carbons prepared in those work such as surface areas and pore volumes determined for each samples.

As can be seen from Table 1, the orders of surface areas of carbons prepared by our carbonization and activation processes are in order: apricot pits > coconut shells > pine > haloxylon > shungite. The higher surface area obtained in this work is for carbon prepared from apricot pits with a relative high surface area of 815 m^2/g. However, carbon prepared from haloxylon and shungite showed relatively low surface areas that do not exceed the value of 400 m^2/g. Typically, carbons with high surface area of more than 500 m^2/g are considered as good materials for adsorption of gas and organic substances.

Table 1: Physicochemical characteristic of activated carbons

| Property	Shungite	Haloxylon	Coconut shells	Apricot pits	Pine
Surface area (m^2/g)	245	367	664	815	624
Total pore volume (cm^3/g)	0.44	0.56	0.71	0.77	0,58
Ash content (%)	27.56	4.93	5.56	5.77	4.35
Moisture content (%)	3.05	4.07	7.15	7.09	2.54
pH of aqueous extract	8.4	8.5	7.2	7.1	7.4

The pore volume of activated carbon usually exceeds 0.2 cm^3/g but in many instances can be greater than 1 cm^3/g[14,15]. All the activated carbons studied here have relatively high pore volume values, the apricot pits have the highest value of 0.77 cm^3/g and the shungite has the lowest value of 0.44 cm^3/g. This difference in pore volume values fit in with surface area and ash content of the different materials. The ash contents of the solid products depend on the chemical composition of the raw materials and the degree of carbonization. The ash content values from Table 1 indicate that the overall ash content for all wood carbonization samples has low values of ca. 5%. This attributed to lower inorganic content and higher fixed carbon. However, for the shungite activated carbon the ash content is very high (27%). This is due to the fact that shungite rocks contain the mineral part in addition to carbon content. The activated carbons based on apricot pits and coconut shells with their high surface area and total pore volume suggests the presence of micropores on its surface. The pH values of the aqueous solution after boiling of all tested samples of active carbon showed a neutral- or weak-base reaction of medium.

SEM studies of the wood activated carbons are presented in Fig. 1. The obtained images shows typical morphology of biomass-derived carbons, i.e., the cellular structure of the original wood is maintained is some of the samples see for example Fig. 1b based on haloxylon. For the SEM images, it can be deduced that the carbonization and activation process leads to the formation of various sizes of pits, which make up distinct micropores, mesopores and macropores in the activated carbons. Moreover the SEM images show that activated carbons based on coconut shells and apricot pits have high cracks and pits in a carbon matrix. The SEM images for carbon based on haloxylon shows woody tissue with lots of mesopores and macropores. The carbon matrix for carbon based on shungite has flocculent inclusions with macropores on the surface.
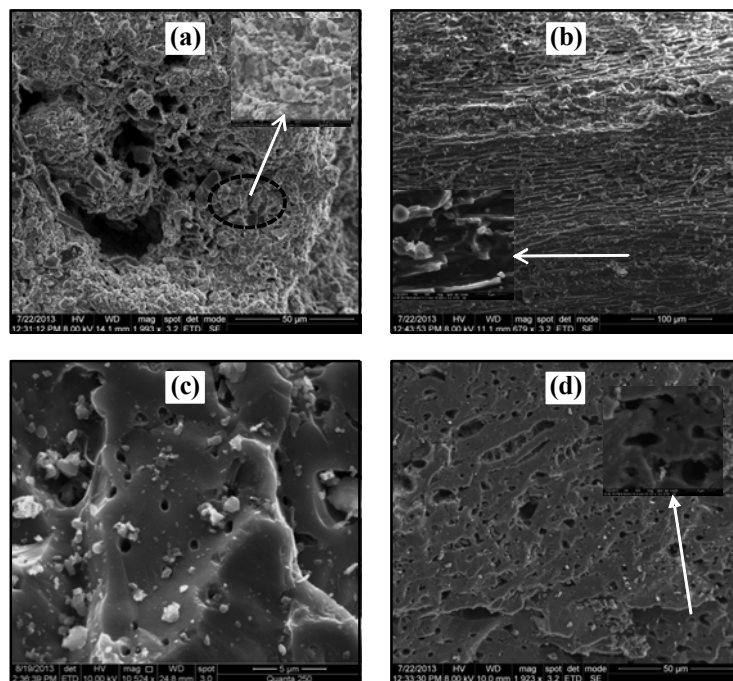
**Fig. 1: SEM micrographs of activated carbons: (a) shungite, (b) haloxylon,
(c) coconut shells, (d) apricot pits**

The XRD pattern of activated carbon based coconut shells is shown in Fig. 2. The XRD pattern of the activated carbon exhibits two broad diffraction lines, which can be attributed to the (002) and (101) planes of graphite skeleton.
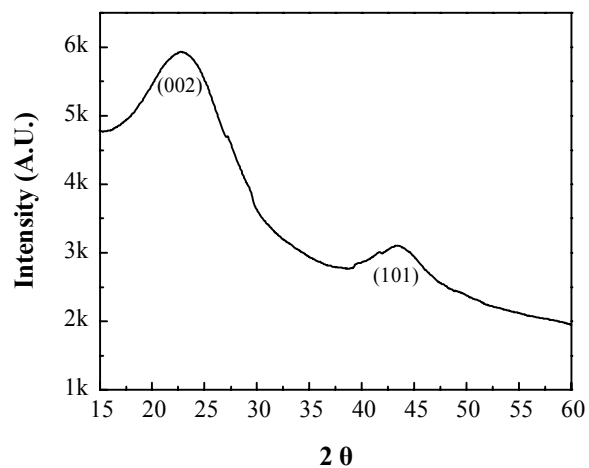
Fig. 2: XRD pattern of activated carbon of coconut shells

Moreover no crystallized compounds could be detected by XRD in the activated carbons. It should be noted that all the series of activated carbons present the same qualitative XRD patterns, so only one is presented in the Fig. 2.

To gain further knowledge of the porous structure of activated carbon, iodine adsorption from the liquid phase was adopted by us as the standard characterization of sludge-based activated carbons. The adsorption of aqueous iodine solution is considered a simple and quick test for evaluating the surface area of activated carbons associated with pores larger than 1 nm[16,17]. The iodine value, defined as the amount of iodine adsorbed per gram of activated carbon at equilibrium was measured according to the procedure described in the experimental section. The iodine values of the activated carbons are presented in the Table 2.

Table 2: The iodine values of the activated carbons

| Property	Shungite	Haloxylon	Coconut shells	Apricot pits	Pine
Iodine adsorption (mg/g)	202.6	326.4	735.8	636.6	268.2

Ammonia removal using activated carbons

In order to investigate the sorption capacity of obtained activated carbons, they were tested in purification processes of air-gas mixture of ammonia and also of cyclohexane as example of organic pollutant. Adsorption of ammonia was calculated by titrating it against 0.02 M H_2SO_4. Measurements were carried out via a batch technique at room temperature and the concentration of ammonia was determined by using titration method. The total adsorption capacity (mg/g) for the different samples as prepared is reported in Fig. 3 (Curve A).

The various prepared activated carbons showed a comparatively low adsorption capacity of ammonia. The shungite based activated carbon show the lowest capacity of ammonia (55 mg/g) and the highest capacity of ammonia is measured for the apricot samples (148 mg/g). It is well known that Ni supported on activated carbon can be prepared by excessive impregnation[14,18,19] and it has been observed that the activated carbon-supported Ni is very efficient materials for ammonia removal. Selection of nickel explained by the fact that their salts are capable of reacting with ammonia and forms ammonia complex of nickel $[Ni(NH_3)_6]^{2+}$ as a nearly white powder with a slight purple tinge, soluble in water without decomposition. In view of the above, we decided to impregnate the activated carbons with nickel chloride in order to increase the adsorption capacity of ammonia. The activated carbons were impregnated using an aqueous solution of $NiCl_2$ (1 M),

the carbons were dipped into the solution in a proportion of 10 g of carbon to 3.4 mL of solution (1 M). The samples were dried after the impregnation and subjected to thermal treatment at 500^0C under hydrogen stream[20,21].
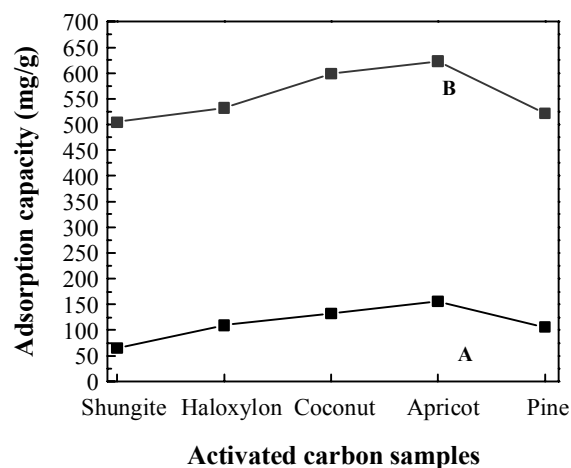
Fig. 3: Ammonia adsorption of the sorbent for the as prepared activated sample (A) and (B) after Ni impregnation

The ammonia adsorption capacity of the samples after Ni impregnation is shown in Fig. 3 (curve B). As shown in Fig. 3 (curve B) Ni impregnation significantly increased the ammonia adsorption capacity for all the activated carbons samples. For example for the haloxylon based activated carbon the ammonia adsorption capacity increased from ca. 100 mg/g without Ni impregnation to a value of 540 mg/g for the Ni impregnated sample. The experimental data suggest that the protective effect to ammonia of active carbons is increased by impregnation there with nickel salt and we can say that there are physical adsorption on carbon and chemical adsorption of reactive metal take place.

The SEM images of activated carbon sample subsequently to the impregnation with Ni are shown in Fig. 4 (a, b). In this case, of Ni impregnating, the activated carbon, the surfaces morphology is different from the untreated activated carbon and the sample surface is pitted and fragmented. Moreover after Ni impregnation the surfaces of the samples are covered by a thin layer of deposited species which resulted in the formation of an irregular surface, indicative of a high surface area. We used the Energy dispersive X-ray (EDX) method in order to determine the elemental composition of the samples. As shown in Table 3 the Ni impregnated samples contain about 10 % (Wt. %) Ni. Further more XRD patterns (not shown here) of the activated carbons treated with Ni confirms the formation of nickel and nickel oxide particles in the carbons.
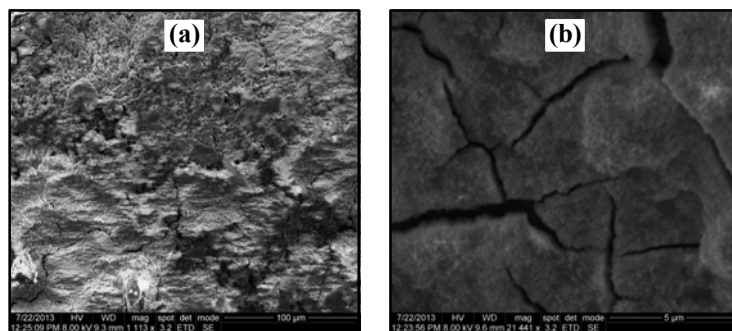
Fig. 4: SEM images of the sorbent based on the coconut shells after impregnation

Table 3: EDX analysis

Element	C	O	Ni	Cl	K
Wt. %	37.35	11.72	9.81	18.00	13.12

Cyclohexane removal using activated carbons

Activated carbons are also used for the removal of Volatile Organic Compounds (VOCs) from air and other gases. In order to explore the use of our activated carbons for the removal of VOCs, we perform a set of adsorption experiments with cyclohexane as a model for VOCs. In Fig. 5 the cyclohexane adsorption of the various activated carbons prepared in this work is shown. From Fig. 5, we can see that the maximum cyclohexane vapor adsorption capacity is measured for the coconut based activated carbon with a value of ca. 1.1 mg/g.
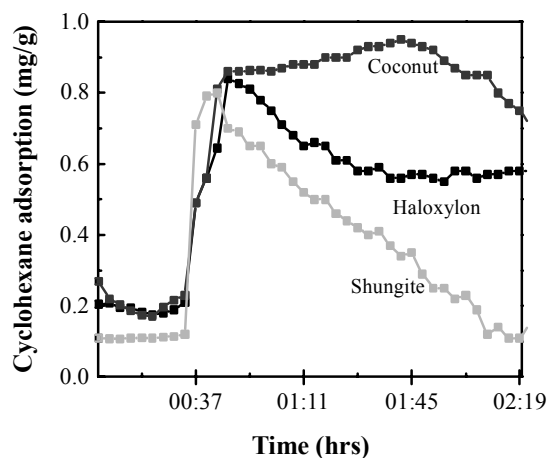
Fig. 5: Adsorption kinetics of cyclohexane on the activated carbons

CONCLUSION

The adsorption process is a powerful technique that can be used for the efficient removal or uptake of toxic materials and gasses. Activated charcoal is one of the most important adsorbents that can be employed for these purposes. In this paper, we describe a simple and effective production of activated carbon with moderate up to high surface areas from wood waste. The physical properties and surface chemistry of the activated carbon were determined by elemental analysis, SEM, XRD and BET-nitrogen adsorption. The use of the prepared activated carbons for gas separation of ammonia and cyclohexane was studied in this paper. Furthermore, it is shown that impregnation of the activated carbons with nickel improved their ammonia adsorption capacity. Overall in this paper, we describe the preparation of activated carbons based on low cost wood and mineral carbon raw materials with a simple low cost thermal and chemical process to prepare activated carbons with proprieties similar to commercially used activated carbons. Finally, it is clear that further research of the preparation and performance of our activated carbons is needed but the basic principle for their preparation and application has been presented in this article.

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REFERENCES

1.   B. Sivakumar, C. Kannan and S. Karthikeyan, Rasayan J. Chem., **5(3)**, 321-327 (2012).

2.   S. Manocha, B. Vanraj Chauhan and L. M. Manocha, Carbon Sci., **3(3)**, 133-141 (2002).

3.   S. M. Manocha, Sadhana, Acad. Proc. Eng. Sci., India, **28(1-2)**, 335-348 (2003).

4.   I. Arockiaraj, S. Karthikeyan and V. Renuga, J. Environ. Nanotechnol., **3(2)**, 09-21 (2014).

5.   J. B. Martin (USEPA) Federal Register, **77**, 58 (2012).

6.   A. Mohammad-Khah and R. Ansari, Int. J. Chem. Tech. Res., **1(4)**, 859-864 (2009).

7. S. Karthikeyan and P. Sivakumar, J. Environ. Nanotechnol., **1(1)**, 5-12 (2012).

8. M. Diasa Joana, C. M. Alvim-Ferraza Maria, F. Almeidaa Manuel, Jose´ Rivera-Utrillab and Manuel Sa´nchez-Polob, J. Environ. Manag., **85**, 833-846 (2007).

9. O. Ioannidou and A. Zabaniotou, Renew and Sustain, Energy Rev., **11**, 1966-2005 (2007).

10. S. V. Nechipurenko, V. N. Duhnitsky and S. A. Efremov, Abstr. of the 60th Repub. Sci. Conf. of Young Sci. and Stud. in the Appl. Asp. of Chem., Almaty, **51-52** (2006).

11. R. R. Tokpaev, S. V. Nechipurenko, S. A. Efremov and M. K. Nauryzbaev, Mater. of IV Int. Conf., Sorbents as a Factor of the Quality of Life and Health, Belgorod, 212-215 (2012).

12. GOST 6217-74 Crushed Active Charcoal, Technical Conditions (1974).

13. GOST 12.4.159-90 Methods of Determination of Protecting Time of Filtering-Absorbing Boxes from Gaseous Pollutants (1990).

14. V. M. Muhin and V. N. Klushin, Production and using of Carbon Adsorbents, RCTU Named by Mendeleev, Moscow (2012).

15. A. Dabrowski, Elsevier Sci. B. V., Amsterdam (1999).

16. A. Bacaoui, A. Yaacoubi, A. Dahbi, C. Bennouna, R. Phan Tan Luu, F. J. Maldonado-Hodar, J. Rivera-Utrilla and C. Moreno-Castilla, Carbon, **39(3)**, 425-432 (2001).

17. M. S. Rajeshwar, P. Y. Amar, P. P. Bhadra and P. R. Ram, Res. J. Chem. Sci., **2(10)**, 80-86 (2012).

18. Y. H. Chu, J. X. Guo, J. Liang, Q. B. Zhang and H. Q. Yin, Sci. China, Chem., **53(4)**, 846-850 (2010).

19. S. K. Verma, P. L. Walker Jr, Carbon, **30(6)**, 829-836 (1992).

20. H. Marsh, Francisco Rodriguez-Reinoso, Elsevier Sci. Technol. B. (2006).

21. G. Mul and J. A. Moulijn, Support Met. Incatal., Imperial College Press, London, **5**, 1-33 (2005).