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NEW ENERGY-EFFICIENT METHOD FOR PRODUCING NANOSTRUCTURED COMPOSITE SORBENT BASED ON PLANT BYPASS (COFFEE HUSKS) AND MONTMORILLONITE CLAY FROM PROVINCE OF LAM DONG

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Abstract

This article presents a new energy-efficient method for producing nanostructured composite sorbent based on plant bypass (coffee husks) and montmorillonite clay from province of Lam Dong. The composite sorbent is received by pyrolysis in the oxidizing (air) atmosphere that allows to exclude use of vacuum and expensive inert gases. The pyrolysis process occurs montmorillonite crystal lattice modification by partial degidroksilization and its interaction with the pyrolysis products of plant bypass. Thus the micro mesoporous structure of a sorbent with big number of ion-exchange groups at the expense of what there is an effective sorption of various pollyutant is formed. It is established that composite sorbents have high sorption ability in relation to iron (III) ions which reaches 97.07%, in relation to the methylene blue – 82.6%. The developed adsorbents have pronounced antimicrobial activity against Enterococcus feacalis, Proteus mirabilis, Pseudomonas aerugenosa, and Salmonella typhimurium. Experimental sorbents compared with activated carbon exhibit high grade MC inhibitory effect on Escherichia coli, Staphylococcus aureus and Candida albicans. Empirically established the high effectiveness of the binding of herbicide (glyphosate) experimental sorbent in soil, with its joint application with the seeds of the test plants. The effectiveness of sorption of glyphosate from the soil estimated by bioindication the test culture (pea). In control plots peas (without making glyphosate and sorbent) germination rate was only 58%, when applied to the soil only glyphosate germination was 16%, with the introduction of the sorbent Only germination was 100%, which is conclusive evidence of the efficiency of absorption of the herbicide. The composite sorbent has a high moisture capacity, which in turn contributes to long-term retention of water in the fertile soil layer, stimulating the growth and development of the green mass. At the same time the nitrogen status of the highest rates comparable to the control. This material can be used in the production of glass fibers, catalysts, conductors.

Key words: montmorillonite clay, coffee husks, composite sorbent, heavy metal ions, antimicrobial activity, glyphosate.

Introduction

Nowadays, Russian Federation and the socialist Republic of Vietnam faced with the global environmental problem, such as environmental pollution, in particular, natural, drinking and waste water, radionuclides, heavy metals, arsenic, natural and industrial hydrocarbons, surfactants, pesticides, nitrates, nitrites, exciter of zooantroponosis. It prompts an increase of morbidity and mortality of population, at the expense of accumulation in the organism of harmful materials for the health benefit organic and inorganic origin.

Constantly increasing scales of production and elevation of requirements to quality of water dictate the search for effective methods of cleaning natural, drinking and waste water. Among the methods, successfully applied for solution this problem and appearing one of the most effective, can be called sorption on absorbent carbons and other materials that allow to reduce the content of the toxic contaminants in water to the maximum permissible concentration [1]. Traditionally in the practice of water purification serve the purpose high efficiency, but expensive absorbent carbons such types as AG-OB-5, SKD-515, DAK, KAD, MIY-C (Miusorb) [2]. Despite the obvious advantages of these materials, their use for deep extraction of water dissolved organic compounds is limited by the need to create sufficient large height of the layer filter. It explains due to the specificity of the porous structure of absorbent carbons, a significant portion of which compose meso - and macropores, limiting diffusion's speed of molecules of sorbate inside the grain of the sorbent. That is why these sorbents are most effectively used for cleaning large water expenses in the absorbers with large square and height of filter's layer at relatively low requirements for reclaimed water. To get effective sorbents it can be used apicomplexans planar materials (cotton wool, fabrics, felt, etc.) which are reactive with different methods. Received new composite materials combine well filtration, adsorption and ion-exchange properties and have advantages over the granulated sorbents when placing them in the machine [2, 3]. Advanced materials for promotion of water quality should be considered natural, mineral sorbents: various clays, silica clay, zeolites, zeolite-containing rocks, etc. The advantage of such materials, in comparison with other sorbents, to begin with, are their natural origin, cheapness, availability of extraction and elaboration, significant reserves in Russia and other countries, such as Vietnam, China, Kazakhstan. A unique complex of technological properties of sorption, ion-exchangeable, molecular sieve and, also, the possibility of their modification, recycling, regeneration make these materials are indispensable in sorption technology.

As the solution purification's problem of natural, waste and drinking water we have developed a compositional sorption-active material on the basis of montmorillonite-containing clay, modified with products of pyrolysis of coffee husk. This material was tested in laboratory conditions with positive effect in the quality of absorbent of heavy metal ions, organic dye-ware colors and pathogenic bacteria in the gastro-intestinal group.

Methods and Materials

In the quality of raw materials used montmorillonite-containing clays deposits «Tam Bo» (Vietnam, province Lam Dong), which have been assigned the following labels BT 1.1, BT 1.2, BT 1.3, BT 6 and coffee husk which were provided by the Institute of environmental technologies Vietnam Academy of science and technologies. The coffee husk is a waste of production, so secondary use as a component of compositional sorption-active material would help to solve the problem of its disposal.

The material composition of raw materials and products of synthesis were studied with methods of x-ray phase and roentgenofluorescence analyses with use of x-ray workstation ARL 9900 series X-ray workstation with CoKa1 anode, at the intention of U=60 kV. Sorption characteristics determined by a spectrophotometric method. To determine sorption's capacity in relation to organic dye-ware colors performed testing of the absorption capacity clays' samples in relation to dye-ware colors of methylene blue and Congo red. When it was investigation introduced the following experimental parameters: the mass of a sample weight of 1 g sorbent, the volume of the working solution of 20 ml, the concentration of methylene blue (Congo red) 20 mg/l, contact time of 24 hours, repeated three times. The efficiency of adsorption was calculated by equation (1):

$$\alpha = \frac{(C_{ish} - C_k)}{C_{ish}} \times 100\,\% \tag{1}$$

C ish is the initial concentration of methylene blue (Congo red) in solution, mg/l; Ck is the concentration of methylene blue (Congo red) in solution after sorption process, mg/l.

To determine the efficiency of sorption cations of iron, organic dye-ware colors and quantitative characteristics the process of sorption on the experimental sorptions used a static method. Used natural clays disintegrated preliminarily and emphasized fraction with a grain size of 1 – 2 mm. With method of dilution from the solution of iron chloride (III) were prepared model solutions with different concentrations of cations Fe^{3+} [4 - 6]. In the process of investigations pH if the solutions was not corrected and was not added oxidants. The concentration of iron cations was determined before and after the sorption process by the photometric method on the spectrophotometer «SPECORD 210 PLUS» by a standard method [7]. To research the process of sorption of iron ions Fe^{3+} with experimental sorbents built sorption curves (Figure 1), reflecting the character of sorption. Such curves are constructed in the job [8].

Results and Discussion

The determination of chemical and mineralogical compositions of the samples of clays in province Lam Dong was performed with using of material with roentgenofluorescence and X-ray diffraction method of analysis of powder materials. It is established that the submitted samples contain in the composition oxides of silicon, aluminum and calcium, typical of clays on the basis of minerals of the montmorillonite group, namely, aluminum dioctahedral montmorillonite with ions of alkaline-earth metals, in this case, the ions Ca^{2+} in interpacket positions. The relatively high content of aluminum's oxide is characteristic for montmorillonite- kaolinitic clays. In the presented samples it has high content of iron's oxide (Fe_2O_3), ranging from 3.58 to 8.57 wt. % and sodium's oxide from 0.745 to 3.931 mass. %. It is established by methods of x-ray phase analysis (table 1) that the studied samples of the clays refer to montmorillonite-illite (sample VT 6) and illite-montmorillonite (sample VT 1.1, VT 1.2 and VT 1.3). (Table 1).

Table 1. Mineralogical composition of the samples of clays in province Lam Dong.

Mineral	**Content, mass**. %			
	VT 1.1	**VT 1.2**	**VT 1.3**	**VT 6**
Montmorillonite	25	23	13	47
Kaolin mineral	7	6	3	12
Illite	44	37	40	10
Bitter-spar	3	8	10	4
Calc spar	no contact	8	10	no contact
Quartz	10	7	7	21
Feldspar	remains	3	3	remains
Goethite	6	5	6	3
Peach	5	3	8	3
Sum	100	100	100	100

The results of determination of prevailing participle size of the studied clays are presented in Table 2.

It is established that the samples VT 1.1, VT 1.2, VT 1.3 consist primarily from particles with a size of 3 to 15 um, 2 to 15 um and 4 to 30 um, respectively. Samples VT 1.3 and VT 6 contain particle size from 4 to 30 um and from 1.5 to 6 um, respectively.

Table 2. Prevailing participle size samples of clays.

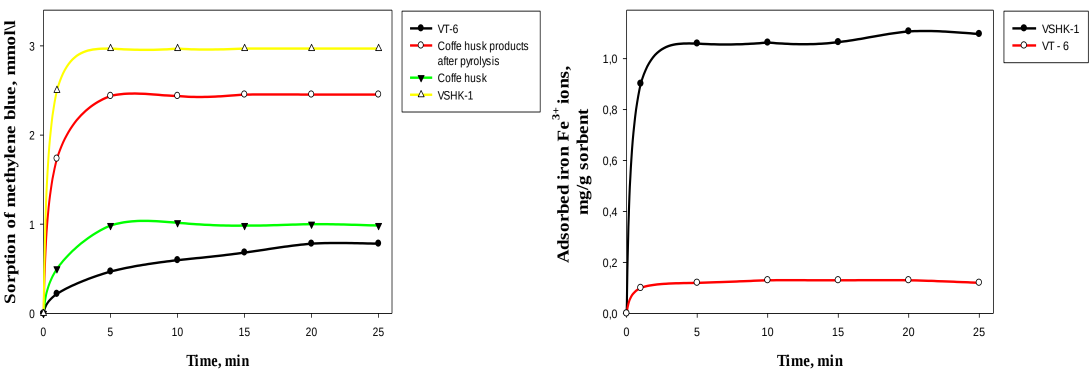
Sample	Participle size, um
VT 1.1	3- 15
VT 1.2	2 - 15
VT 1.3	4 - 30
VT 6	1,5 – 6

Composite sorbent got from montmorillonite clay and coffee husk of Vietnamese origin, joint subjected to carbonization in a muffle furnace. By method of energy dispersive analysis it was established chemical composition of the products of pyrolysis of coffee husk which confirmed a carbon basis (53 wt. %) sorbent and the presence of such biogenic elements as calcium (1.49 wt. %), potassium (3.72 wt. %), iron (0.25 wt. %) and silicon (0.51 wt. %). This composite material is given issue slip VSHK-1. Sorption characteristics determined in relation to organic dye-ware colors by a spectrophotometric method. The results of determination the sorption capacity of the composite sorbent in relation to iron's ions (Fe^{3+}) methylene blue and Congo red are presented in Table 3.

Table 3. Sorption characteristics of experimental sorbents.

Name of sample	The effectiveness of sorption of methylene blue, %	The effectiveness of sorption of Congo red, %	The effectiveness of sorption iron's ions (Fe^{3+}) %
VT 6	80.5	17.2	81.57
VSHK-1	82.5	38.5	97.36

It is established that compositional sorbent VSHK-1 has high sorption capacity in relation to methylene blue from 82.5%, and increased by 21.3% sorption capacity in relation to Congo red, in comparison with the best clays in Lam Dong and high sorption capacity in relation to iron's ions (Fe^{3+}) which composes 97.36 %. The kinetic characteristics of the sorption of methylene blue and iron's ions (Fe^{3+}) by experimental sorbents are presented in Figures 1 a and 1 b.



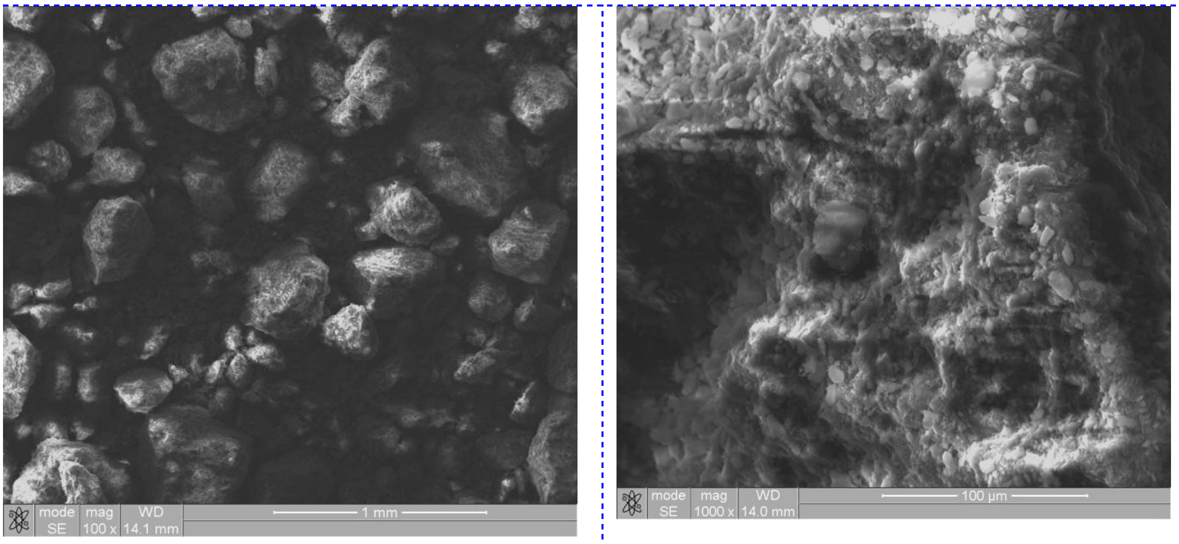
(a) **(b)**

Figure 1. Sorption of (a) methylene blue and b) iron ions (Fe^{3+}) experimental sorbents.

Structural-morphological characteristics of compositional sorbent VSHK-1 were investigated by means of scanning electronic microscopy (Quanta 200 3D) (figure 2).

It is revealed that the products of pyrolysis of coffee husk have the form of granules with crystallographically perfect equal edges (Figure 2 a). It is established that the crystals of montmorillonite insphere the products of pyrolysis of coffee husk and are situated along the grooves which are situated on the surface of the pyrolysis products of coffee husk (Figure 2 b).

Empirically established the high effectiveness of the binding of herbicide (glyphosate), when combined with the experimental introduction of the sorbent. The effectiveness of sorption of glyphosate from the soil estimated by bioindication the test culture (pea). In control plots peas (without making glyphosate and sorbent) germination rate was only 58%, when applied to the soil only glyphosate germination rate was 16%, while making only sorbent germination rate was 100%, which is conclusive evidence of the efficiency of absorption of the herbicide, which has a high moisture capacity, that, in turn, contributes to long-term retention of water in the fertile layer, stimulating the growth and development of the green mass. This material can be used in the production of glass fibers, catalysts, conductors.



(a) **(b)**

Figure 2. Electronic microphotographs of the powder material VSHK-1: a) general microstructure of montmorillonite clay modified products of pyrolysis of coffee husk; b) the surface of montmorillonite clay modified products of pyrolysis of coffee husk

Conclusion

As a result of conducted work was received compositional sorbent VSHK-1 based on montmorillonite clay which is modified by products of pyrolysis of coffee husk. It is established that compositional sorbent VSHK-1 has a high sorption capacity in relation to methylene blue – 82.5 %. The high sorption capacity of montmorillonite clay, which is included in the composition of the sorbent due to the fact that it has a negative electrokinetic potential, while methylene blue has positive. It is established that compositional sorbent VSHK-1 has a high sorptive capacity in relation to iron's ions (Fe^{3+}), which is 97.36 %. Developed sorbent extends the scope of applicability of mineral sorbents due to the effective sorption of organic pollutants, and helps to solve the issue of utilization and recycling of waste coffee.

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