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HUMIC ACIDS OF SOLID FOSSIL FUELS – PERSPECTIVES FOR APPLICATION IN TECHNOLOGY AND ENVIRONMENT PROTECTION*

Humic acids of solid fossil fuels are very perspective for application in many areas of mining, and also for derivation of advanced technology products for agriculture, production, medicine, etc. Ability of humic acids to bind toxic elements (including heavy metals and radioactive elemens) contained in technogenic soils and waters of mining companies and plants allow them to be used in the area of environment protection and reclamation. Drilling fluids with humic substances as polymeric fillers have rheological properties close to properties of systems that are used for water, oil and gas wells horizontal and deep drilling. Moreover, such solutions allow to reduce the unfavorable effects at the environment. In agriculture, humic acids are primarily used as potassium, calcium and sodium humates as additives for enhancement of plants growth and crop yield enhancers. In construction, humic acids and their derivatives could be used as fillers for improving of cement and concrete Humic acids could find a potentially wide application in the area of medicine. This is reasoned by a number of unique properties such as inflammatory and antiviral ones, sorption, etc. Perspective direction of humic acids in medicine is targeted drug delivery. Some researchers showed that humic acids could suppress growth of cancer cells. In veterinary, humic acids and their derivatives are used as nutrition additives that help to enhance animals' immune system and activate metabolism along with increase of stress resistance. However currently there exist no sufficient and reliable information on features of humic acids structure and properties with respect to their origin. This considerably complicates humic acids and their derivatives wide utilization in Technology and environment protection. Authors of this paper believe that the solution of such problem could be found by development of humic acids classification based on revealing the most relevant characteristics responsible for humic acids behavior in different processes.

Key words: *humic acids, peat, coal, sapropel, mining, drilling fluids, agriculture, medicine, environment protection*
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Introduction

The last few decades became a break-through in studying of humic acids (HA) and their derivatives structure, composition and applicability in various fields of science and technology. HA are a mixture of organic acid-like substances that, in bound state, could be found in soils, peats, lignites, sapropels, etc. The largest source of HA and other humic substances are lignites, peats, sapropels and oxidized bituminous coals. HA demonstrate high chemical and biological activity which determines an extremely wide area of their proposed application: mining, namely purification of soils and waters of the mining plants from toxic elements, and also derivation of new advanced technology products for agriculture, veterinary, construction, medicine, etc. The aim of the current work is to summarize the main areas of the possible utilization of humic acids depending on their origin, and also to give information on the primary problems that arise during the attempts of HA introduction to production.

Proposed areas of humic acids utilization in Mining

Functioning of the Mining industry plants is connected with serious ecological pressure at the environment, namely pollution of soils and waters by toxic elements. The last decades revealed that there exist an increase in attention to utilization of humic acids of solid fossil fuels for purification of technogenic soils and waters. This became possible due to such most important characteristics of humic acids as their sorption properties, namely tendency to form stable complexes with heavy metals ions and other pollutants [1–8]. This decreases bioaccessibility of heavy metals stored in, for example, soils [2, 3]. Moreover, some studies were devoted to prove the radioactive and trace elements binding by HA [2, 6]. Processing of soils contaminated with oil-production waste by humic acids as components of peat and lignite-based reactants revealed detox properties of HA and allowed obtaining data on biostimulation characteristics of such reactants for soils reclamation [7]. Introduction of HA to polluted soils allows to remediate their structure, to enhance sorption and buffer properties as well as to decrease migration of pollutant agents to underground water [3]. Therefore, this allows to use HA at technogenic soils reclamation [2, 3, 9]. On the other hand, the aforementioned properties allow to use HA in processes of wastewater treatment, for example, in [4, 5, 10] the possibility was shown for solid fossil fuels humic acids to be a basis of efficient and cost-efficient filtration agents for purification of wastewaters from heavy metals, oil production waste, coloring agents and other pollutants. Some patents and copyrights of authorship were issued describing means for Mining industry plants waters and soils purification of toxic elements [11–14]. But it was also shown that fulvic acids presence in the HA reactants based on

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solid fossil fuels might decrease the efficiency of humic acids application for contaminated soils and waters purification. It is well-known that fulvic acids form stable complexes with heavy metals ions [8]. Unfortunately, such complexes may be as insoluble as soluble in water, depending on the reactant fulvic acids molecular mass. In the latter case the bioaccessibility of heavy metals may increase. In [5] authors demonstrated that there exists an efficient method for decreasing of fulvic acids negative effects. This method is based on such preparation of peat-based HA reactant so that the mechanical activation of peat is performed in presence of calcium hydroxide. This effect is, presumably, connected with fulvic acids deactivation by calcium ions. HA reactants obtained by such method of preparation were found to be perspective for toxic metals contaminated waters treatment [15–16].

Efficiency of well-drilling highly depends on drilling agent quality and composition. Common drilling fluids were based on synthetic lubricants that have shown their high toxicity [17]. Therefore, the primary part of advanced countries have developed regulatory documents that narrows utilization of such drilling fluids, especially for the cases of marine wells. Polymeric drilling fluids based on additives of natural origin are widely spread nowadays because they do not implement any negative environmental effects [18]. The latest studies have shown the applicability of humates for production of drilling fluids [19, 20]. Rheological parameters of such solutions are close to the standard properties of systems that are used for water, oil and gas wells horizontal and deep drilling [20]. Humic acids within such solutions allow to reduce the unfavorable effects at environment.

Perspectives of solid fossil fuels humic acids application at derivation of advanced technology products

It should be noted that humic acids and their derivatives synthesized from solid fossil fuels and partially renewable feedstocks could be used for derivation of advanced technology products utilized in agriculture, medicine and veterinary. As mentioned in [21], in agriculture, humic substances are primarily used as potassium, calcium and sodium humates as additives for enhancement of plants growth. Studies revealed positive effects of such humates at plants, namely, increase of plant seeds germination after their processing by humates and crop yield increase at plants processing during growth stage [22, 23]. But such effects were observed only at using of exact optimum dosage for humates supply [22]. The fact that humic acids derivatives allow improvement of plants growth and yield could be explained by the following. Such substances increases plant cell membranes permeability providing a better supply with water and microelements [24]. Furthermore, HA and their derivatives enhance the photosynthesis processes by increasing the velocity of carbon dioxide sorption [25]. Also, they stimulate the nutrition substances supply to fruits [23]. In addition, HA and derivatives show protective properties towards plants under stress conditions [22]. This is reasoned by formation of stable complexes with toxic elements in soil and also by direct action at plants for stimulating of their physiological activity [22]. HA are also widely used as nutrition additives for animals [26]. It was found that HA-based substances enhance animals' immune system and activate metabolism along with increase of stress resistance.

Development of new construction techniques require novel approaches for cement and concrete production. Unique properties of HA, namely, high chemical activity and tendency to form stable complexes with different molecules and ions allow them to be used as fillers for enhancing some properties of concrete and cement. For example, research works and patents were made for using the HA-based substances to improve the concrete strength [27], cement plasticity [28] and assist with cement fluid loss control [29], although HA in their natural state are assumed to cause the destruction of cement and concrete-based constructions at interaction with soil [30].

HA molecules have a high biological activity, which was observed firstly for plants and animals. The last few years' studies revealed a proposition by Dr. Visser [31] on anti-inflammatory [32, 33], antioxidant [34] and antiviral [35] effects of HA and derivatives, which proves applicability of such substances in medicine. Chemical and physical properties of humic substances also give a wide range of opportunities to be applied in area of the modern targeted drug delivery techniques [36-41]. Researchers report on stabilization of nanoparticles by HA for improvement of their antibacterial and sorption properties (e.g. see [36, 37]). Scientists also give proofs for application of humic substances-improved nanoparticles for cancer [38] and even HIV therapy [39]. Another perspective direction of HA application in medicine is using as stabilizing agents of nanomagnetic particles suspensions aimed at targeted drug delivery [40, 41]. In the aforementioned context, HA are not toxic and are being removed from the human organism in unaltered condition [40]. Analysis presented in [41] demonstrated that magnetic Fe_2O_3 nanoparticles and their suspension in HA solution are not cytotoxic for fibroblasts cells culture. This shows the possibility for development of new medical magnetic substances based on iron compounds (III) and HA, but their efficiency was not pre-clinically and clinically proved. Despite the aforementioned research results on uniqueness of HA properties for medicine, there exist no reliable data on the exact chemical structure of humic acids and even on their exact molecular weight. This fact leads to impossibility of HA-based medical substances certification and production.

Unfortunately, although many efforts were made in direction of humic acid properties study and seeking for the areas of their successful application, there exists a problem connected with variation of structure and properties of HA depending on their origin [42]. Solving of any technological or ecological problem connected with humic acids utilization is closely connected with a question of choosing the indicators responsible for efficiency and safety of their application. The authors of the current paper believe that the solution of the problem could be found by development of humic acids classification based on revealing the most relevant characteristics responsible for humic acids behavior in different processes. This will allow to maximally use the humic acids potential in construction, agriculture, medicine and environment protection.

Conclusion

Humic acids and their derivatives could be used in various areas like mining for purification and reclamation of technogenic soils and waters, as components of drilling fluids, also for derivation of advanced technology products utilized in agriculture, veterinary and medicine, construction, etc. Humic substances are non-toxic, show sorption, biostimulating, antioxidant, anti-inflammatory any other properties. However currently there exist no sufficient and reliable information on features of humic acids structure and properties with respect to their origin. Solution of such problem could be found by introduction of approaches for classification of humic acids with respect to their origin and properties. Such classification should be based on indicators responsible for HA behavior during the processes of sorption, ion exchange, solutions stabilization, plants growth, etc. This will allow to use the full potential of humic acids in construction, agriculture, medicine and environment protection.

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