Review article

Advantages of lignite addition in purification process of soil polluted by heavy metals

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Abstract: *Environmental contamination by heavy metals represents a potential threat for plants, animal and humans. The metals do not undergo biodegradation. Many of them are soluble in water, therefore become more available for living systems and accumulate in the environment, especially in soil. This paper presents properties of brown coal(lignite) which show that this substance can be use as cheap and efficient sorbent in soil contaminated by heavy metals.*

Key words: *lignite, brown coal, contaminated soil, heavy metals.*

Introduction

Growing awareness of the environmental pollution makes need to do regular analyses of the toxic substances content and elements in air, water and soil [1]. As the result of civilization development, in many cases natural ecological balance has been disrupted.

In recent years the reduction of dust and gases emission have been observed. This is the result of rational environment management. However, destruction of natural resources is very far advanced and very often economic problems does not allow to change the situation [2]. The dynamic development of industry, irrational use of substances for plant protection in agriculture, sludge and industrial waste contributes to the excessive accumulation of trace elements in soil and plants which can be dangerous for animal and human [2,3].

Among the substances which can have a negative impact on environment, the increasing interest of heavy metals is still observed. During long-term contact with heavy metals it is observed that they are accumulated in living organisms [4]. The health effects of regular consumption of even small amounts of harmful trace elements can be observed after many months, and even years. Extremely sensitive for the toxic effects of heavy metals are the children [5].

Natural source of heavy metals for people and animals are plants. Many researches proved that the highest concentration of toxic substances is observed in the roots of plants, especially growing in contaminated soil [6].

The concentration of heavy metals in plants does not depend directly on concentration of those elements in soil. It is more complicated and depends on many different factors such as: pH, activity of soil microorganisms, content of water and air in soil, solubility and forms of metals and many others [7,8]. However, the most important part of soil which is responsible for immobilization and bioavailability of trace elements for plants is organic matter [9,10]. Generally, if the content of organic matter in soil is higher the concentration of heavy metals in plants is lower. Because of the fact, that positive impact of organic matter on soil was proved many times in many researches it seems to be good solution to use cheap and effective substance with high content of organic carbon to make soil more rich in humus substance.

As a result we can expect better quality of soil and lower content of harmful substances in vegetables which are growing on this soil what makes them more safety for human. The good example of substance which can be use for such function is lignite.

Properties and characterization of brown coal

Brown coal is an organic rock formed from plant material. The process of lignite formation depends on many conditions, including the development of flora and microorganisms, climate and morphology of the area. The main substances from which lignite was built were proteins, fats, carbohydrates, lignin, waxes, resins and other substances and their conversion to brown coal were carried out in many biological processes. The intensity of these processes depended on content of water and oxygen, pH and the amount of bounded nitrogen. However, the main factors were time, pressure and temperature. The living organisms also played a role in creating of brown coal [11,28].

Lignite is described as a substance with high water content. There is about from 6.0-37.0% in hard coals to 40.0-60.0% in earthy coals. Much of the water, especially in the earthy coals is mechanically connected (free water), which relatively quickly evaporates. The rest of water (hygroscopic water) is characteristic for each type of brown coal and depends on fragmentation and size of the particles. High fragmentation of the particles shows that lignite is a solid colloid. It has impact on water content, wetting and sorption properties and also the ability to form the sol from gel [12,13].

High content of water in brown coal makes really good conditions for microorganisms growth. Microorganisms which live in soil are able to produce many metabolites, some of them are toxic such as hydrogen cyanide, antibiotics, mycotoxins etc., but most of them are hormones of growth, vitamins and substances involved in the uptake of trace elements [14].

During decomposition processes of organic matter, a lot of chemical functional groups is produced, for example –COOH, -OH, -C=O, $-OCH_3$. These substances are carbon and nitrogen sources for soil microorganisms.

There are no pathogens in brown coal. Weakly acidic pH and a large surface can affect on increase of microbial activity what is important for many soil processes. Better growth of *Azotobacter* and *Clostridium* has an impact on nitrogen transformation [15].

Brown coal is known as a good buffering material and it is able to regulate soil pH in acidic and alkaline conditions [16]. The buffering properties are results of high concentration of hydrogen ions which react with hydroxide ions of alkaline solutions and the other hand with cations of metals which cause neutralization of hydrogen ions in acidic solution [15].

It is necessary to remember that lignite which is used as soil amendment is able to prevent soil structure from physical modification, increasing soil aggregates, improving water infiltration aeration and reducing erosion and runoff. Most of the positive properties of brown coal is the result of high content of humic acids which play main role in many different processes in soil.

Humic substances in lignite

Humic and fulvic acids are the final break-down constituent in the natural decay of plant and animal materials. Humic substances improve the physical, physicochemical (including sorption) and biological properties of soil. They are also important source of nutrients for plants and regulate the concentration of trace elements in soil solution. Lignite as soil amendment prevent ground water and ecosystems from the negative effects of metal contamination [17]. It is possible because brown coal and products of its humification in soil are able to make many complexes with heavy metals. Stability of these complexes is different and depends on many environmental conditions, especially on metals, structure of humic acids, pH, sorption capacity, oxidation-reduction potential and many others [18,19]. In this case migration of heavy metals from soil profile to groundwater is not so fast as it could be in normal condition without lignite. Many forms of metals which potentially could be dangerous are bonded with organic matter and are not available for plants [15].

Humic acids which are part of lignite have similar structure as humic acids in soil (Figure 1). In both cases there are some major elements such as: aromatic core, parts which connect cores and functional groups. The most common functional groups in lignite are: -COOH,-OH,-OCH_3 and -C=O and they are responsible for bonding most of cations in the soil solution (Table 1, Table 2) [15,20,21].

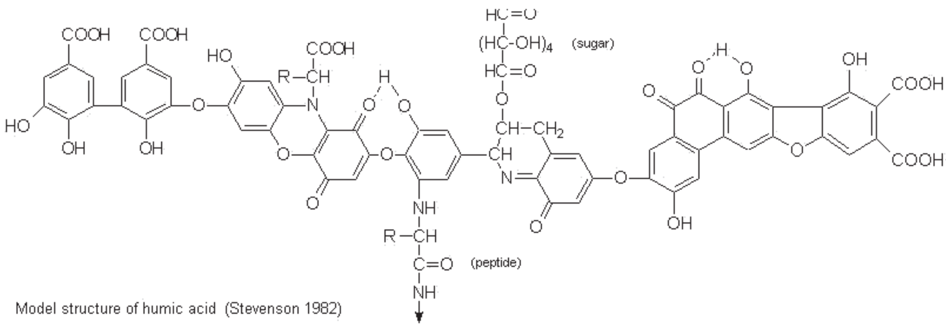

Figure 1. Model structure of humic acid

Brown coal humic acids are macromolecular, polyfunctional organic acids and their salt. Construction of humic acids depends on the type of starting material, the degree of charring and the intensity process of coal making. The content of humic acids in brown coal in Poland is relatively high: 18.3-64.7%, but variable, which depends mainly on the genesis [22]. Humic acids are build from carbon, hydrogen, oxygen and small amounts of nitrogen and sulphur. The carbon content varies between 56.0-70.0%, 3.3-6.2% hydrogen, oxygen 24.0-33.0%. Nitrogen is generally present in amounts less then 3.0%, sulfur content does not exceed 2.0% [23,24].

The complex nature of interaction between humic substances and metal cations is given by their heterogeneous, polyelectrolyte and polydispersive character of different functional groups which are located in various chemical environments of the three-dimensional structure of humic substances. The nature of the binding ranges from purely electrostatic, non-specific interaction of metal cations with the negative charge on the surface of a humic macromolecule to specific interactions during formation of complexes and chelates with the functional groups [25,26,27]. The mechanism for cations removal by the lignite includes ion exchange, complexation and sorption. The process is very efficient especially in the case of low concentrations of pollutants [29].

Table 1. Sorption properties in the Val/g of certain functional groups of humic substances [37]

Functional groups	COOH carboxylic acids	OH phenols	OH alcohols	C=O ketones	C=O quinones
Humic acids	4.5	2.1	2.8	2.5	1.9
Fulvic acids	9.1	3.3	3.6	2.5	0.6

Table 2. The complex stability constants of humic and fulvic acids [37]

	The stability constants of the complex ions
Humic acids	$Ba^{2+}<Ca^{2+}<Mg^{2+}<Co^{2+}<Ni^{2+}<Fe^{2+}<Zn^{2+}<Pb^{2+}<Cu^{2+}<Al^{3+}<Fe^{3+}$
Fulvic acids	$Mg^{2+}<Mn^{2+}<Zn^{2+}<Ca^{2+}<=Pb^{2+}<Co^{2+}<Ni^{2+}<Cu^{2+}< Al^{3+}<Fe^{3+}$

Bioavailability of heavy metals for plants and their mobility in soil often depends on interaction with other trace elements. In acidic soil most of metals exist as cations, but in neutral and alkaline conditions as hydroxy complexes. Organic and inorganic complexes limit taking of metals by plants. Roots play the main role in this process. Many chemical, physical and biological changes of trace elements take place in rhizosphere zone.[30,31].

Stimulating effect of organic matter on nutrient assimilation by plant

Organic matter and humic acids have an impact on plant growth[32]. Therefore, respiration is more intensive, hormones production is higher, roots system is well developed and permeability of plasma is more efficient [33]. Positive influence of humic substances in taking of nutrient elements by plants is a result of complexes creation with metals which are not available for plants in normal conditions. If organic matter content in soil is high, the respiration of plant is much more intensive, especially when there is not enough air available for root system [15].

There is a lot of research which showed that lignite added to soil is able to accumulate iron and make it more available for plant. It is quite complicated process and depends on many different reasons such as: content of phosphor and calcium, pH, soil properties and plant species. The regulation of this mechanism is closely related to amount of HCO_3^- which is produced by roots to reduce iron accumulation. Organic matter turns the process to bond iron to the organic complexes which are more available for plants then bound with mineral matter [34].

Positive effect of brown coal amendment is also observed in the uptake of phosphorus, which is a major problem in plant nutrition. This problem is more serious than taking up other macro elements. In both cases in alkaline soil (which can be result of high amount calcium addition) and in acidic soil, phosphates become insoluble, even if they were added to the soil in form available for the plants. The phosphorus is the most available for plants in pH about 6.5 and 7.0. High content of organic matter in the soil leads to better phosphorus accumulation by plants [35].

Magnesium is one of the most important element for plants. Its uptake depends mainly on soil pH. In acidic soil there are a lot of hydrogen and aluminum ions instead of magnesium ions, which in high concentration are toxic for plants. However, in soil with regulated pH (for example with lignite addition) and rich in magnesium, the ions of this element surround the roots of plants and are available for them. The main reason why magnesium is so important for plants is the fact that it is a component of chlorophyll. Chlorophyll plays main role in photosynthesis and is also a component of many enzymes which are responsible for organic matter transformation in plants [36].

There were some experiments which showed that if brown coal is added to soil, plant are able to take up about 15.0% more nitrogen and sulphur from organic substances than in control samples without lignite addition. It is said that humic substances have impact on free nitrogen transformation what makes it available for plants [15].

Summary

Brown coal is mainly use as a energy source. Lignite can be also use in agriculture as a source of plant nutrients and organic substances (humic acids) for direct fertilization and recultivation of grounds. High content of organic substances in brown coal gives not only macro elements, but also make them available for plants. Moreover, lignite is pathogens-free therefore is not potentially dangerous for soil. Use lignite as soil amendment improves physical, chemical and biological properties, increases the water capacity and sorption ability for cations. These properties are very important in nourishment of plans, soil fertility and immobilization or stabilization of toxic compounds, especially heavy metals. Increasing addition of brown coal in many experiments [4,5] resulted in proportional decrease in heavy metals content and increase of concentrations of macro elements. As the result the higher crop yield was observed. Many authors [7,15] point to the beneficial effect of brown coal in taking up of nitrogen, phosphorus and potassium by plants and positive influence on pH stabilization in soil.

These considerations lead to conclusions that brown coal properties are visible in direct and indirect action. Direct action is strictly connected with its good chemical properties. Indirect effects are due to development of porous system, optimizing the properties of the water-air relations in soil what have the impact on the growth of microorganisms. It creates great opportunities to use brown coal in agriculture and environment protection, especially in soil contaminated by heavy metals.

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