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The activity has been implemented within the framework of national project
***Information and providing advice on improving the quality of environment in Slovakia**.*
The project is cofinanced by Cohesion Fund of the EU under Operational programme Quality of Environment.

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ADSORPTION OF HEAVY METALS BY NATURAL AND MODIFIED HUMIC SUBSTANCES

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Humic substances are widespread in the environment and comprise the most abundant pool of nonliving organics. They compose from 50 to 80% of the organic carbon of soils, natural waters and bottom sediments.

Source	μmol C/L	mg C/L
Groundwater	60	0.7
River	580	7.0
Oligotrophic Lake	180	2.2
Eutrophic Lake	1000	12
Marsh	1420	17.0
Bog	2750	33.0

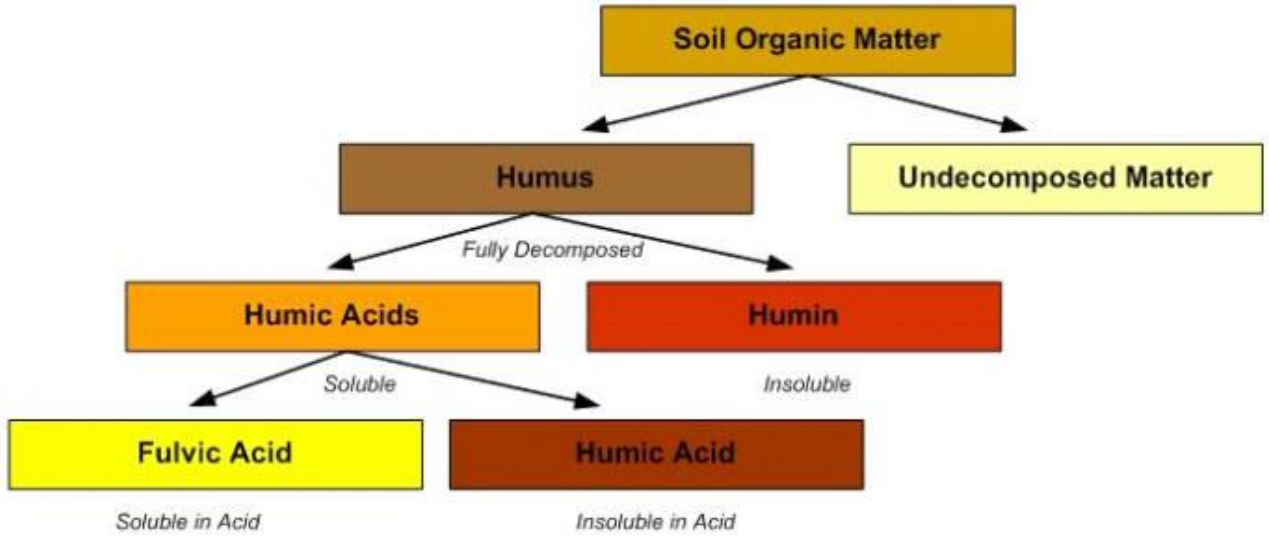
Organic carbon content in natural waters (Thurman, 1985)

RESERVES OF HUMIC MATERIALS OF INDUSTRIAL VALUE (LOU, 2003)

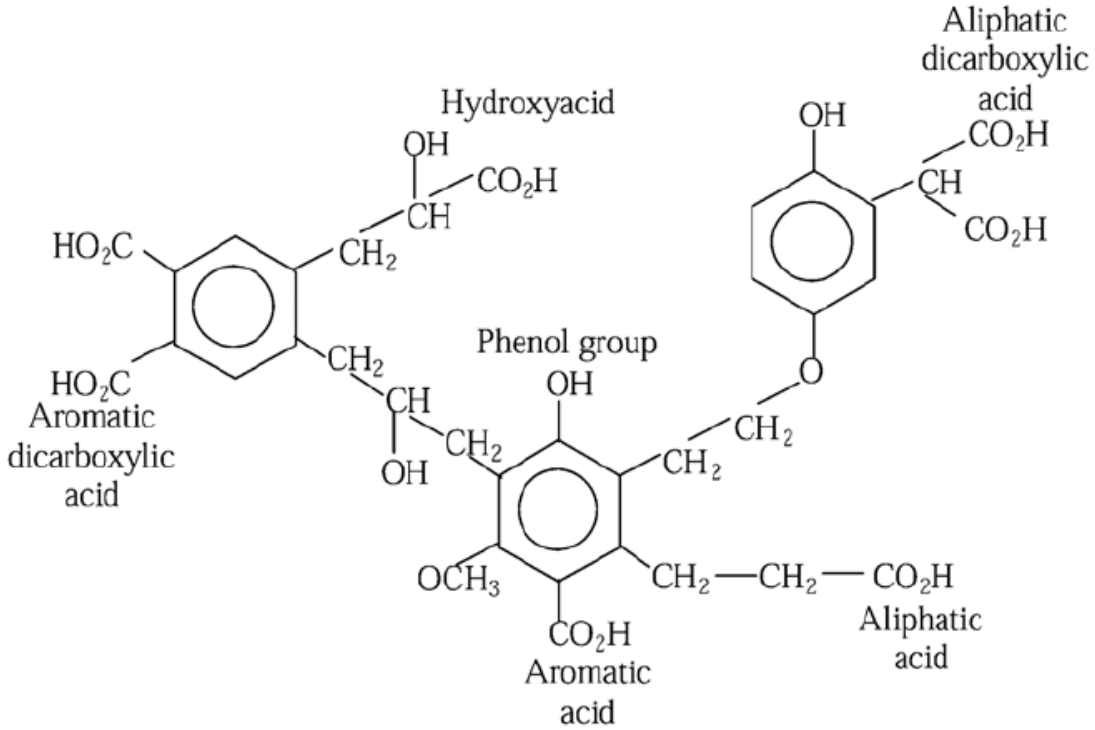
Source	Amount, Gton C
Lignite and Subbituminous coal (Total/Recovered)	1120/512
Anthracite and Bituminous coal (Total/Recovered)	3880/571
Peat	400-500
Sapropel	800

Humic substances are usually derived on an industrial scale from peat, sapropel and coal

Because of its great complexity, the organic fraction usually has been classified operationally rather than chemically into 3 fractions: **humin**, which is insoluble in both acid and alkaline solutions; **humic acid**, which is soluble in alkaline solution but insoluble in strong acid; and **fulvic acid**, which is soluble in both strongly acid and alkaline solutions



The main functional groups present in humic materials are **carboxylic acids, alcohols, phenols, carbonyls, phosphates, sulfates, amides, and sulfides**; and all of these groups are able to interact with metal species in solution (Senesi, 1992).



The ability of humic acids to bind cationic metals and form complexes makes them useful in various applications, such as

- the transport of micronutrients from the soil to plants,
- **the removal of heavy metals from soil and water,**
- the inhibition of the formation of free radicals by metal catalysis ,
- reduction and stabilization of metal nanoparticles

Multiple interactions between humic substances and heavy metals include:

- **binding interactions** that impact chemical speciation and bioavailability of the pollutants;

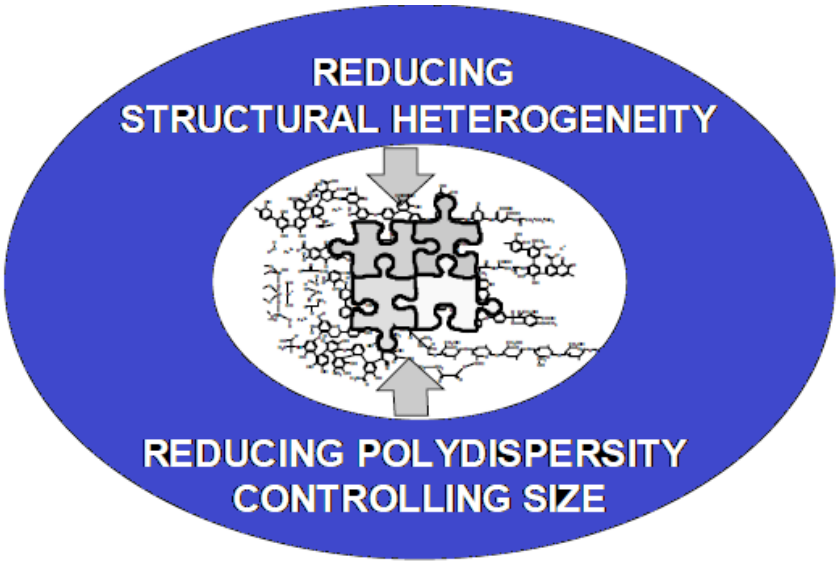
- **sorptive interactions** affecting physical speciation or interphase partitioning of the metals;

-**redox interactions** that impact metabolic pathways of elements

(Perminova and Hatfield, 2005).

Despite the diverse protective functions, application of humics-based products for remediation remains limited. Humics are **polydisperse** and **heterogeneous**, which translates into properties that vary between natural sources and between industrial suppliers.

Conceptual model for designing reactive humic materials based on idea of reducing structural heterogenity and polydispersity (Perminova and Hatfield, 2005)



Also modern technologies of remediation require novel materials having **increased uptake capacity** and **high selectivity**.

Purposeful chemical modification of humic substances may change the composition and increase the content of the desired functional groups and thereby improve their sorption properties.

Among the possible methods for modifying of humic substances are:

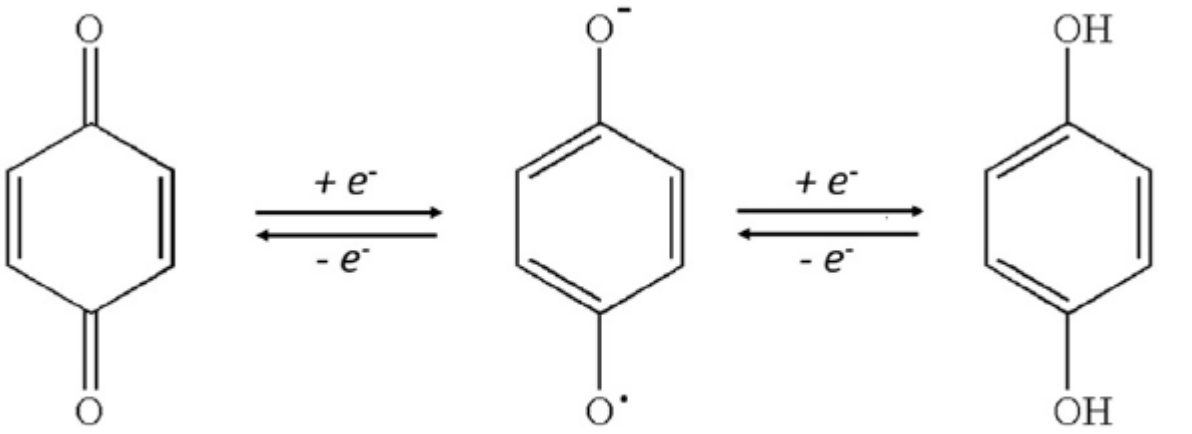
- reduction,
- oxidation (oxidative degradation, oxidation of phenolic groups, oxidative polymerization),
- introduction of fragments of organic molecules into the structures of humic substances

Oxidative methods have been frequently and successfully used to degradation and modification of humic substances.

The most widely used methods of humic substances **hard oxidation** include reactions with permanganate-ion, hypochlorite, metal oxides, nitrobenzene, peracetic acid, nitric acid etc.

Different organic substances as results of oxidation may be obtained.

Soft oxidizing agents to humic acids oxidation: hydrogen peroxide or OH radical (Fenton's reagent), organic peroxides, iodic acid (HJO_4), persulfates, lead tetraacetate and potassium nitrosodisulfonate (Fremy's salt) oxidize phenols causing their hydroxylation, quinone formation and polymerization

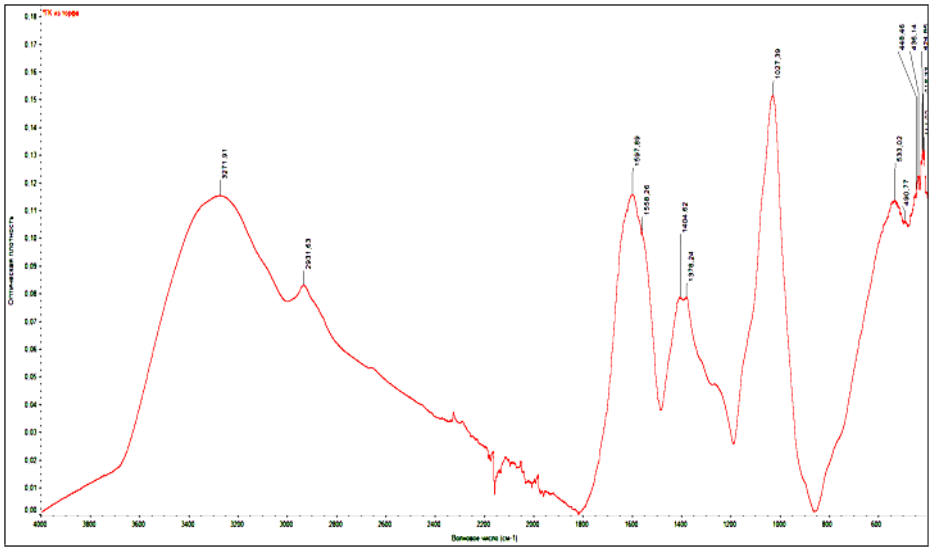


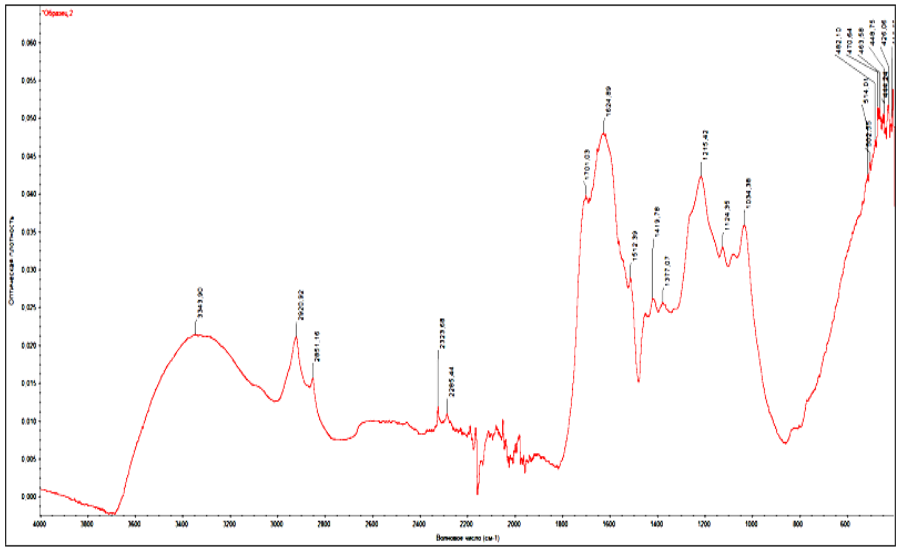
Oxidation of the humic acids increases sorption capacity to cations in comparison with unmodified acids (Zherebtsov et al., 2017).

Structural moiety	Type of related interaction
- COOH	ion-exchange, complexation
- OH	complexation, hydrogen bonding
>C=O	reduction-oxidation
	donor-acceptor interaction (charge transfer complexes)
- CH_n	hydrophobic interaction

1. Enrichment of humic acids with phenolic hydroxyls by oxidizing (Elbs persulfate oxidation)

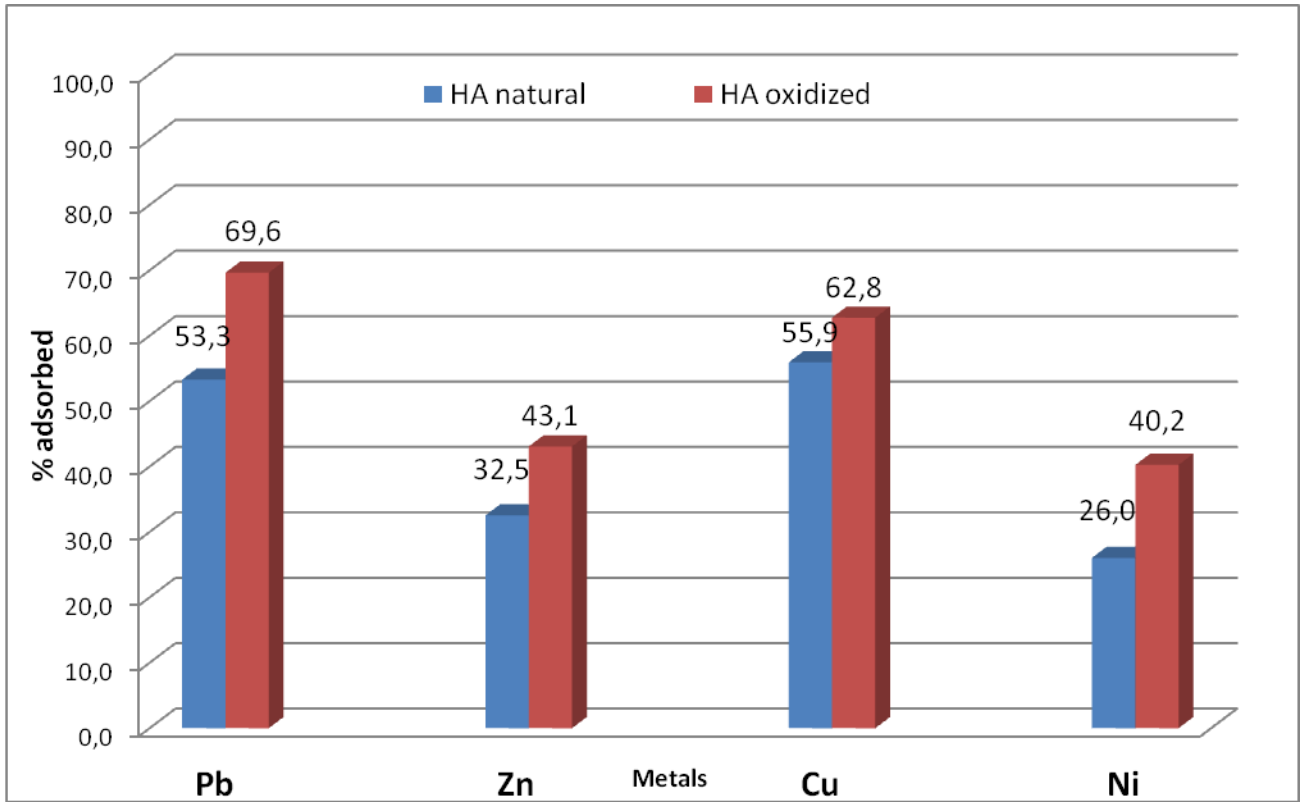
The Elbs persulfate oxidation is the reaction of phenols with potassium persulfate under alkaline conditions to form para-diphenols.

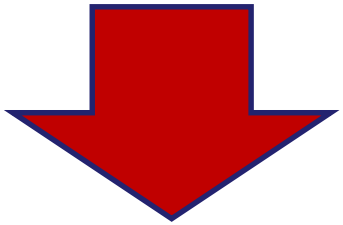




Adsorption of heavy metals by natural and oxidized humic acids

(at an initial metal concentration 4 mmol/l)

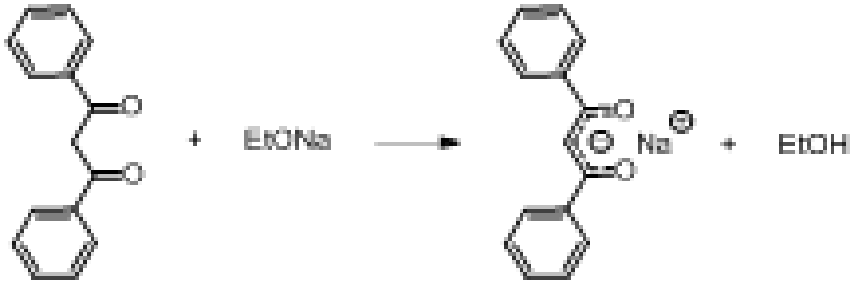




Thus, a simple procedure of chemical modification of humic acids by oxidation able significantly increase the absorption efficiency of these widely available and accessible substances in relation to heavy metals, especially to **Ni** and **Pb**

2. Chemical modification of natural humic acids by dibenzoylmethane

(1)



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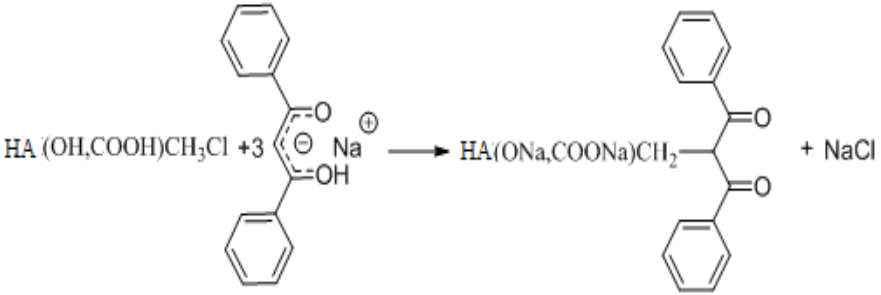

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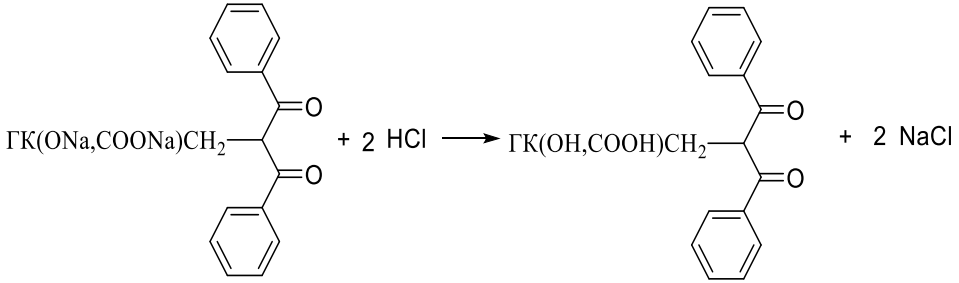
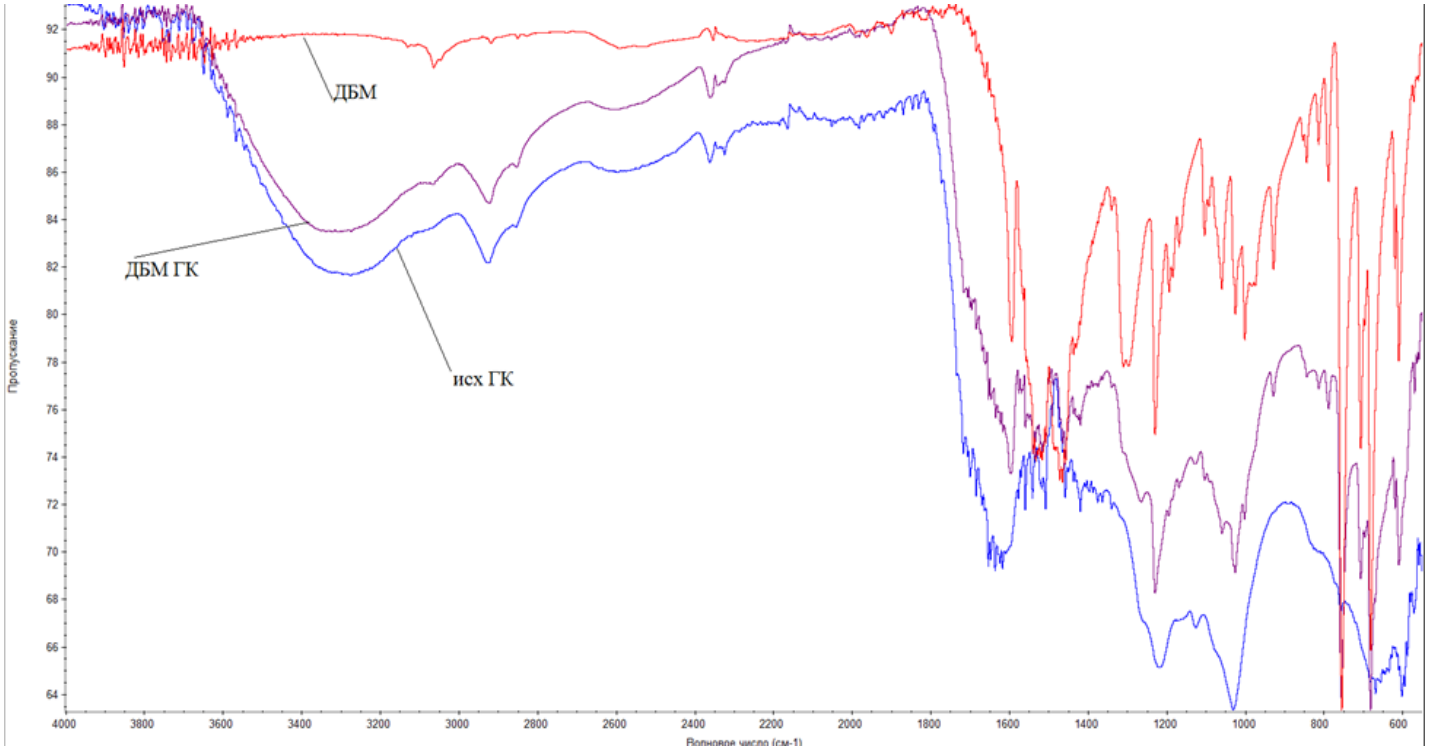
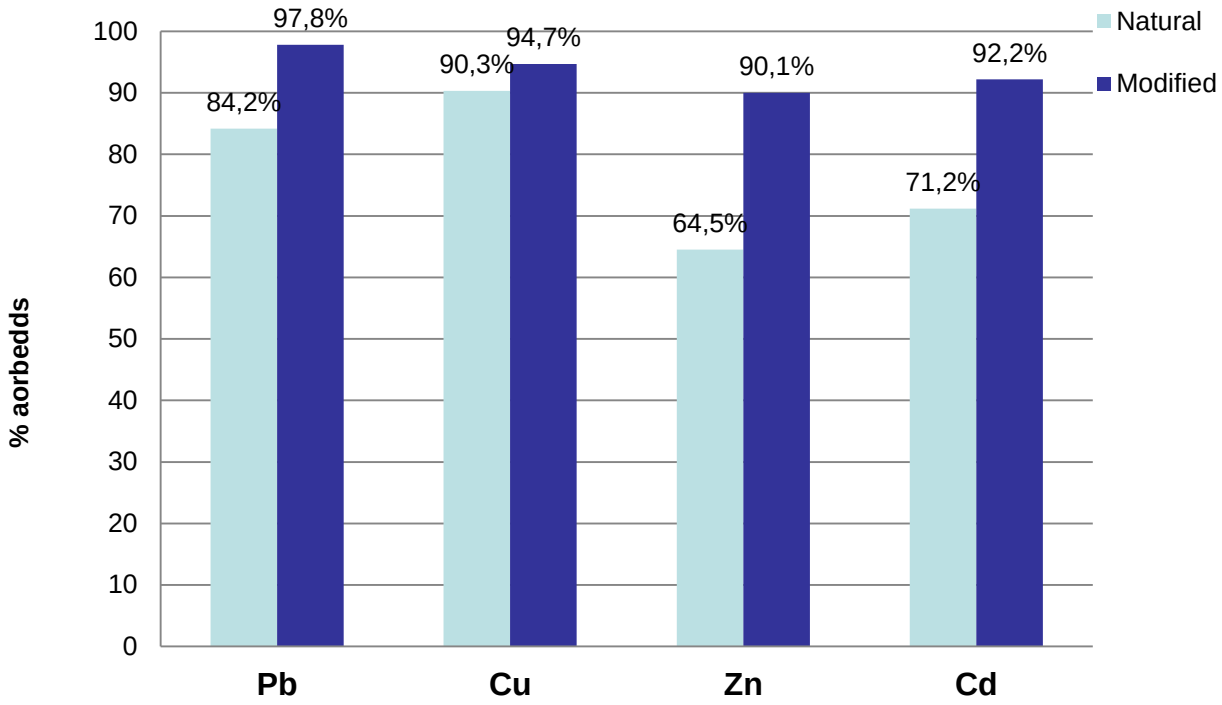


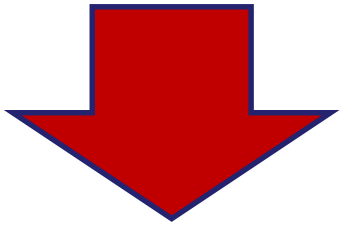
IR spectra of the natural humic acids (blue), dibenzoylmethane (red) and modified humic acids (lilac)



Adsorption of heavy metals by natural and chemically modified humic acids

(at an initial metal concentration 1 mmol/l)





The adsorption of **all** heavy metals by chemically modified humic acids increased as compared to the initial natural organic substances.

Conclusions:

Binding interactions of natural and chemically modified humic substances with heavy metals are of particular importance in remediation, as such interactions reduce concentrations of freely dissolved metals and as a result make contaminant less available to living organisms.

Widespread of humic substances, easiness of their extraction and modification make these organic substances are very promising for the cleaning of contaminated sites.

Department of Chemistry, Tula State University is working on the development and implementation into practice:

- preparations based on humic acids for immobilization of heavy metals;
- preparations based on humic acids for the oxidation and reduction of arsenic and chromium compounds;
- preparations based on chemically modified humus substances that stimulate plant growth;
- schemes for selective extraction of organic substances from humic substances

and invites everyone to collaboration

The study was supported by Russian Foundation for Basic Research.

Project number is 18-04-00274

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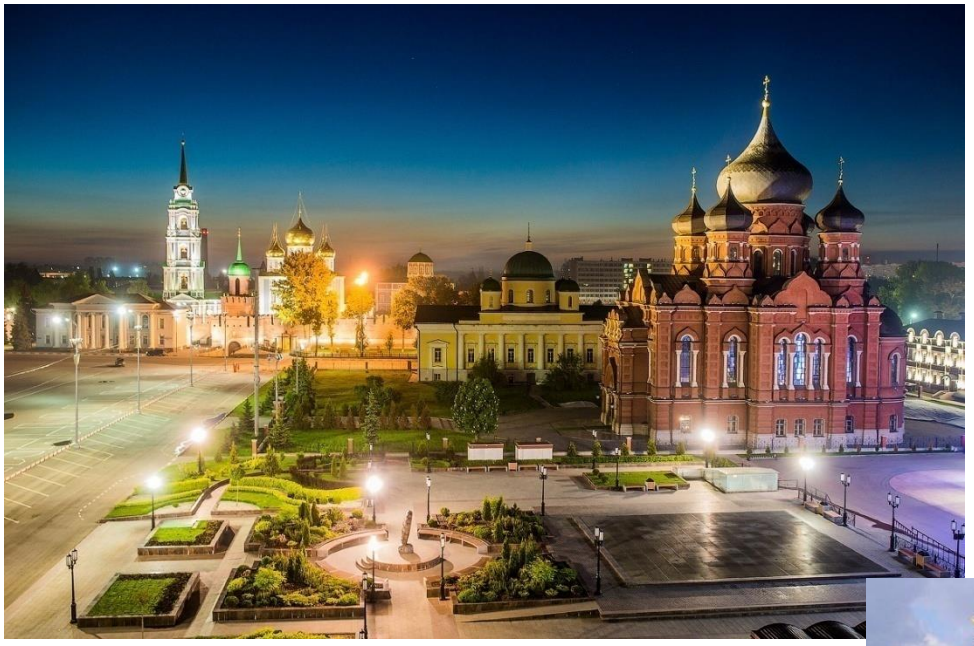
Tula and Banska Bystrica are twin cities



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