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MINISTRY
OF ENVIRONMENT
OF THE SLOVAK REPUBLIC
SLOVAK
ENVIRONMENT
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This publication has been prepared by the Slovak Environment Agency
in the close cooperation with the Ministry of Environment of the Slovak Republic.

PUBLISHED BY:
Slovak Environment Agency
Tajovského 28
975 90 Banská Bystrica
SLOVAKIA
Tel.: + 421 48 4374 287
www.sazp.sk
contaminated-sites2020.sazp.sk

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Document completed in December 2020.
1st edition, 140 pages

ISBN: 978-80-8213-030-3

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THIS DOCUMENT SHOULD BE CITED AS:
Slovak Environment Agency. International Conference Contaminated sites 2020. Conference Papers. Banská Bystrica, November 2020. ISBN: 978-80-8213-030-3.
Available on the Internet: http://contaminated-sites2020.sazp.sk/

The activity has been implemented within the framework of the national project
Information and providing advice on improving the quality of environment in Slovakia.
The project is co-financed by Cohesion Fund of the EU under the Operational programme Quality of Environment (2014–2020).

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SYNTHESIS OF ORGANOCLAYS AND STUDY OF THEIR SORPTION PROPERTIES IN RELATION TO INORGANIC AND ORGANIC POLLUTANTS

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KEYWORDS

Clay minerals, organic substances, clay modification, adsorption, heavy metals, humic substances

ABSTRACT

The review on the synthesis and use of a new class of sorbents based on clay minerals and organic substances – organoclays is given. The mechanisms of interaction between minerals with an expanding and non-expanding structural cell and organic substances are shown. Data on the effective adsorption of organic and inorganic pollutants by organoclays are presented. An adsorption of heavy metals by kaolinite in the presence of fulvic acids has been studied.

Adsorption is one of the most effective processes used for wastewater treatment and the immobilization of pollutants in soils and grounds. The main adsorbents that have shown satisfactory results in the immobilization of inorganic and organic toxicants include: zeolites (activated and natural) (Syafalni et al., 2014), natural clay minerals (Singh et al., 2018), modified clay minerals (Yadav et al., 2019; Han et al., 2019), activated carbons (Singh et al., 2018; Mirmohseni, 2012), agricultural waste (Anastopoulos and Kyzas, 2018; Ahmad and Danish, 2018), biochar (Gorovtsov et al., 2020; Premarathna et al., 2019), industrial waste and sludge materials (Zhao et al., 2016; Anastopoulos et al., 2017), polymer resins (Singh et al., 2018; Rivas and Muñoz, 2009). To increase the efficiency and selectivity of mineral sorbents, they are modified by inorganic (Perelomov et al., 2016) and organic (Sarkar et al., 2019, etc.) substances.

The interaction of organic substances with clay minerals is a complex process, depending on the chemical nature of the surface and structural parameters of the minerals, physical and chemical properties of organic substances and environmental conditions. Organic substances have a significant effect on minerals, modifying their surface due to the formation of both chemical compounds and intermolecular agglomerates built by hydrogen bonds and other long-range forces, as well as coagulation contacts. As a result, the physical, chemical, and physico-chemical properties of organo-mineral systems that include organic substances and clay minerals differ markedly from the properties of individual components both in terms of the electrical properties of the double electric layer of colloidal particles and the number of functional groups available for interaction with inorganic and organic pollutants.

Organoclays, which are the product of the interaction of clays and organic substances, combine the useful characteristics of clay minerals and organic substances in one adsorbent. Organo-clay composite materials based on layered silicates can be divided into three large groups: (i) microcomposites, phase separated, (ii) intercalated nanocomposites, and (iii) exfoliated nanocomposites (Mukhopadhyay and De, 2014). Organoclays are understood as clays modified with organic substances, while modification does not lead to exfoliation of silicates, i.e. the filler is organic matter, and the surface structures of the clay mineral acts as a matrix.

The ability of clay minerals to modify is due to the fact that the outer and inner surfaces of the layered silicates are hydrophilic and polar. This facilitates the wetting and penetration of both low- and high-molecular compounds containing polar groups, such as acetone and its derivatives (Sohn and Kim, 2000), methyl methacrylate, proteins and amino acids (Ding and Henrichs, 2002), and other compounds with hydroxyl (Yu et al., 2003) and nitrile groups (Farkas and Dekany, 2003) into the interlayer space of the layered silicates. The minerals of the montmorillonite group are also intercalated by substances containing ester groups due to their specific interaction with cations and hydroxyl groups on the surface of silicate plates (Park et al., 2002). At the same time, the polarity of the silicate surface hinders the interaction of montmorillonite with non-polar and weakly polar polymers (Rashid et al., 1972).

Among the known methods for modifying clays by organic substances (according to Gerasin et al., 2013) are:

1) Ion exchange of clay cations to organic cations;
2) Adsorption of polyvinyl alcohol, polyacrylamide, alkyl ketones, acrylonitrile and other compounds that form complexes with the clay surface or exchangeable cations;

3) Adsorption of anions, in particular polyacrylates, on the side faces of silicate plates at $pH < 5$ as a result of protonation of hydroxyl groups;
4) Inoculation of organosilanes onto the clay surface;
5) Introduction of organic molecules capable to Van der Waals or ion-dipole interaction with the clay surface, for example, alkyl ammonium cations, for which the affinity for clay decreases in the series $RNH^+ > RNH_2^+ > RNH_3^+$ and increases with increasing length of the aliphatic ion chain.

The simplest alkyl ammonium cations Me_4N^+ and alkyl amines $MeNH_2$, Me_2NH and Me_3N effectively displace Na^+ ions from montmorillonite, making the surface of the clay mineral organophilic, which ensures its compatibility with macromolecules (Snircova et al., 2009).

The geometry of the interaction of organic substances with clay minerals may be showed by the example of structures formed during the modification of clays with an expanding structural cell by surface-active substances. It is known that surfactants, including one aliphatic chain or having a plane molecular structure, are absorbed by clay, forming one or two adsorption layers with parallel orientation of the chains relative to the plane of the silicate plates and increasing the interlayer distance. With a large cation exchange capacity of clay material, molecules of primary amines with an aliphatic chain exceeding a certain length form “pseudo-triple” layers. Quaternary ammonium salts molecules containing two long aliphatic chains can form “paraffin” mono- and bilayers, which are located in the interplanar space of montmorillonite at a certain angle to the surface of the layered silicate and are attached to one or different plates (Gerasin et al., 2013).

However, apparently, intercalation of organic matter in clay minerals in vivo occurs in rare cases. Probably, the sizes of a significant part of macromolecules, such as humic or fulvic acids, are larger than the interlayer spaces in clays. Therefore, for this type of interaction, the properties of the outer surface are much more important for the binding of organic matter than the internal crystalline structure of clays (Kayugin and Zhuravsky, 2009). In this regard, it is logical to assume that intercalation of humic acids will be more effective when their concentration in solution is significantly lower than the critical micelle concentration.

Currently, various polymers are used to synthesize organoclays based on layered silicates, such as polyvinyl chloride, epoxies, polyurethanes, polyesters, polypropylene, polystyrene, chitosan, etc. Recently, the ability of organoclays to immobilize inorganic and organic pollutants in the environment has been widely studied. So, Sarkar et al. (2010) investigated the detoxification of hexavalent chromium by adsorbing it with the organoclay composed of bentonite and commercial alkyl ammonium surfactant Arquad®. The synthesized organoclay effectively adsorbed the toxicant from the solution, and the amount of adsorbed chromium increased with an increase in the amount of modifier. The introduction of this organoclay into the soil also reduced the bioavailability of arsenic (Sarkar et al., 2012). Jin et al. (2016) studied the simultaneous sorption of 2,4-dichlorophenol and Cu (II) ions from a mixture by organoclay based on bentonite and humic acids. The experiment showed the non-competitive nature of the adsorption of inorganic and organic pollutants. The composite based on montmorillonite and acrylamide, synthesized by treatment with an aryldiazonium salt and photopolymerization, selectively removed lead from the solution (Msaadi et al., 2017). Modification of montmorillonite with poly-4-vinylpyridine copolymerized with styrene was effective for removing atrazine (Zadaka et al., 2009). Xu et al. (2018) synthesized the organoclay based on chitin, which removed up to 99.99 % of methylene blue from the solution.

However, some quaternary ammonium salts are toxic to soil microorganisms (Sarkar et al., 2013). These compounds showed toxicity to anaerobic bacteria, and the toxic effect increased with decreasing alkyl chain length (Tezel et al., 2006). The LD50 values of the hexadecyltrimethylammonium cation in an aqueous solution for heterotrophic soil bacteria vary from 1.14 to 146.26 mg/L, and Gram negative bacteria are more sensitive to this compound compared to Gram positive bacteria (Nye et al., 1994). Quaternary ammonium salts exhibit both acute and chronic toxicity, and DNA damage and a mutagenic effect can be considered (Ferk et al., 2007). Thus, the use of synthetic quaternary ammonium salts for the synthesis of organoclays can cause significant harm to biota, therefore, additional studies of their toxic properties are necessary.

Within the frame of the project for study the effect of natural and modified humic substances on the adsorption of heavy metals by clay minerals we have studied the adsorption of Zn by a mineral with non-expanding structural cell – kaolinite, modified with natural fulvic acids isolated from lowland peat. The experiment was carried out under the following conditions: mass of the mineral – 0.2 g, the concentration of fulvic acid – 0.2 g/l, the range of metal concentrations – 0.05 – 0.8 mmol/l (3.27 – 52.08 g/l) , electrolyte – 20 mmol KNO_3, pHin – 5, the ratio of solid and liquid phases – 0.2 g : 25 ml. The experiment was carried out for 4 hours with constant stirring on a magnetic stirrer (500 rpm). After reaching equilibrium, the solutions were centrifuged for 15 min at 8,000 rpm and then filtered through a syringe filter with a pore size of 45 µm. The experiment was carried out in triplicate. To study the effect of pH on the adsorption process, experiments were carried out with the pH of the initial solution 3, 4 and 5 at a constant zinc concentration of 52.08 g/l. We also studied the effect of the sequence of fulvic acids and Zn addition on the adsorption process at the maximum concentration of the element.

The adsorption of Zn by kaolinite and kaolinite in the presence of natural fulvic acids is satisfactorily approximated by the Langmuir equation. Under the conditions of our experiment, fulvic acids enhanced the adsorption of zinc ions. Our results show that there is a tendency towards an increase in the adsorption of zinc ions by kaolinite with an increase in pH under acidic conditions. Modification of kaolinite with fulvic acids forms new sites with different functional groups for the sorption of microelements.

Thus, the synthesis of organoclays based on clay minerals and natural organic substances, including humic substances, can be a promising direction in the development of effective and cheap sorbents for inorganic and organic pollutants.

ACKNOWLEDGMENTS

The study was supported by the Russian Foundation for Basic Research (Projects No. 18-04-00274).

TRACE ELEMENTS IN THE ALLUVIAL SOILS NEAR INDUSTRIAL CITY

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KEYWORDS

Heavy metals, urban soils, floodplain, soil pollution

ABSTRACT

Concentrations and profile distribution of a total content and forms of heavy metals in the alluvial soils near Tula city were studied. In the soils near the industrial center the concentrations of heavy metals may not exceed hygiene standards due to intensive removal and accumulation in immobile forms. Agricultural use can cause uniform distribution of total and mobile forms of heavy metals. A content, distribution and speciation of heavy metals in the fluvisols depend not only on industrial load value, but also on the soil properties and the ratio of the processes of metal input to and removal from the soils.

Alluvial soils, as a rule, have higher fertility compared to zonal soils due to the better supply of moisture, nutrients and good structure; therefore they are intensively used in agriculture, primarily for growing vegetable crops that are most demanding on nutrition and moisturizing conditions. Fluvisols occupy 590 million hectares on Earth and provide food for about 25 % of the world's population (Kellogg and Orvedal, 1969). Heavy metals (HM) are well-known environmental pollutants. HM come into alluvial soils by agricultural, urban and industrial sources and by mining and smelting activities (Cappuyns and Swennen, 2007). The specifics of accumulation and transformation of HM in fluvisols are determined by soil genesis, including location in a subordinate landscape, the effects of the alluvial process, and bedding with carbonate rocks. In arable soils, these processes are affected by watering, the application of high doses of mineral and organic fertilizers and chemical plant protection products. Due to the significant technogenic emission of harmful substances, suburban and urban alluvial agricultural soils should be subject to continuous environmental monitoring (Mensik et al. 2020).

In the study concentrations and profile distribution of the total content of heavy metals and their forms in alluvial meadow soils of Upa river near Tula city (Central Russia) and assessment of they use for safe agricultural products were investigated. The study was carried out in two plots in the floodplain of Upa river in the vicinity of industrial Tula city (near 54°17` and 37°67`). One site is occupied by natural meadow vegetation. Another site is represented by agricultural soil used to grow row crops. The plots are located in close proximity to each other, at a distance of about 3 km from the metallurgical plant.

The total Mn concentration in the soil under the meadow is slightly higher than its content in arable soils for all the studied depths (Table). This may be due to both technogenic deposition and active participation in the biological cycle in natural ecosystems. In arable soil, both total and mobile forms of Mn are more evenly distributed in depth. A decrease in the concentration of mobile Mn in the upper layer of agricultural soil can be due to migration to deeper horizons, lateral removal or removal with a crop.

Tab. 1 Heavy metal concentrations in studied alluvial soils

Site	**Depth cm**	**Concentration of heavy metals, mg/kg**											
		Mn total	**Mn mobile**	**Fe total**	**Fe mobile**	**Pb total**	**Pb mobile**	**Zn total**	**Zn mobile**	**Cd total**	**Cd mobile**	**Ni total**	**Ni mobile**
Upa floodplain, meadow	0–20	760	128.3	33,000	81.8	15.0	0.8	100	12.2	0.35	0.16	24.5	0.60
	0–40	600	14.1	22,500	18.2	15.0	0.4	120	5.1	0.30	0.06	28.5	0.10
	0–60	700	9.9	25,000	10.2	17.5	0.1	125	2.3	0.25	0.05	25.5	0.05
Upa floodplain, arable	0–20	580	22.3	31,500	21.9	15.0	0.5	225	13.2	0.40	0.13	27.5	0.05
	20–40	560	18.1	27,000	30.1	15.5	0.5	115	10.9	0.35	0.11	22.5	0.05
	40–60	540	19.8	23,500	43.7	15.0	0.5	95	23.1	0.25	0.08	21.0	0.30
Approximate permissible concentrations (2009)						**130**		**220**		**2**		**80**	
Maximum permissible concentrations (2006)		**1500**	**100–140**	**22,300**		**32**	**6**	**100**	**23**				**4**

The total Fe content in the 0–60 cm layer in natural and arable soils is comparable and exceeds clark value for soils (Alekseenko and Alekseenko, 2013) in the 0–20 cm layer (Table). The maximum accumulation of Fe in the upper layer of these soils does not relate either with the content of humus, or with the fraction of physical clay, or with acidity and may be due to aerotechnogenic input from the metallurgical plant. In the arable soil in a layer of 0–40 cm, total Fe is distributed more evenly. The concentration of mobile forms of Fe is maximal in the upper layer of natural soil and decreases with depth; in arable soil, on the contrary, it increases with depth.

The total Pb concentrations are same in both arable soil and soil under the meadow at different depths (Table). One of the main sources of Pb in urban soils, away from the point sources of its emission, is motor vehicles. The studied sites are located at a considerable distance from the major highways of the city. The total stock of mobile forms of Pb in the layer of 0–60 cm in both soils is comparable. In arable fluvisol the element is distributed more evenly. In the natural soil, its concentration is maximal in the upper layer and decreases with depth.

The concentration of Zn both in natural soil under the meadow and in arable soil, in general, is within the limits of the existing hygiene standards (Approximate… 2009; Maximum… 2006), but exceeds the more strong standards that were existed in the USSR (Maximum… 1990) (Table). Its maximum concentration is noted in arable soil in a layer of 0–20 cm and slightly exceeds the approximate permissible concentrations in the Russia. This occurs despite the heavier particle size and higher soil humus content under the meadow and similar acidity. The source of Zn can be organic fertilizers, aerotechnogenic fallout, as well as fluff brought during floods. It is logical to assume that during floods in arable soil, due to their better water permeability, a higher amount of the element is retained. In the soil under the meadow, the element concentrations slightly increase with depth, while on the arable soil they decrease. The distribution of mobile forms is the opposite and in the layer of 40–60 cm in arable soil reaches a value of estimated permissible concentrations. Since high concentrations of Zn cause the greatest concern, its forms associated with various soil components were studied for upper horizons of natural soil and arable alluvial soil according to Tessier method (Tessier et al. 1979) (Figure). The element concentrations in the exchangeable fraction were lower than the sensitivity level of the device. The largest amount of Zn in the upper layer of the soils is in the residual fraction and the fraction associated with oxides and hydroxides of Fe and Mn (Figure). Karathanasis and Pils (2005) also note that residual forms were most important for the retention of Zn in alluvial soils. The retention of Zn in the Fe-Mn oxide fraction is explained by the high stability constants of Zn oxides and the ability of Zn to replace Mn in the oxide surface (Ma and Rao 1997). In fractions strongly bound to organic matter and extracted with sodium acetate (bound to carbonates), approximately the same amount of element is present, regardless of the nature of soil use. The increase in Zn concentration in the upper horizon of arable soil is due to a significant increase in its content in the residual fraction. The metals that make up this fraction are represented by inert compounds in the primary and clay minerals and are not able to pass into the soil solution and be uptake by plants.

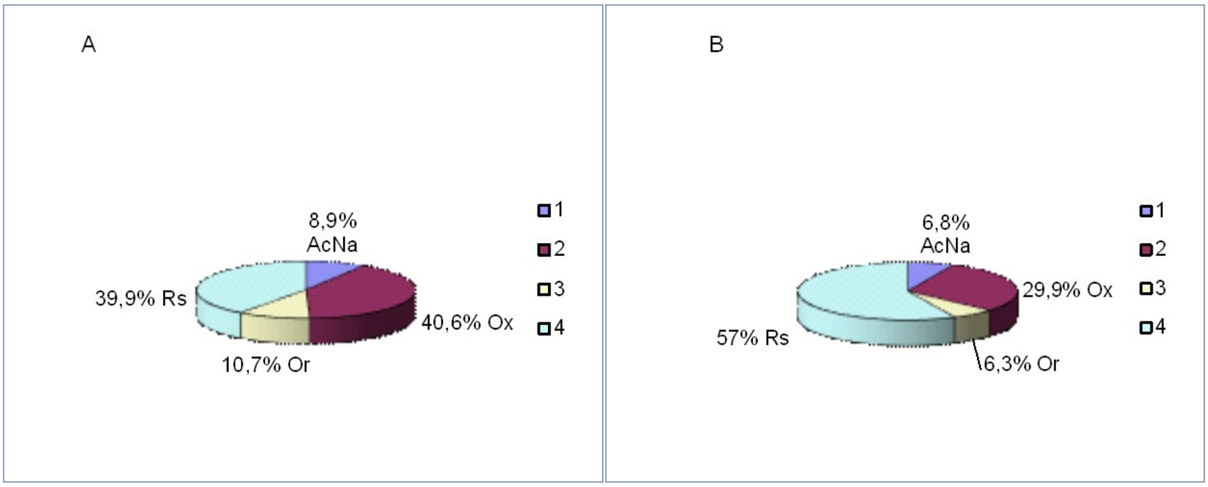

Fig. Zn speciation in natural under meadow (A) and arable (B) alluvial soils (% from total). AcNa – carbonate-bound fraction, Org – organic-bound fraction, Ox – Fe-Mn oxide-bound fraction, Res – residual fraction

There were no essential differences in the contents of total Cd and total Ni between arable and natural soils; their concentrations are within the established standards (Table). In both soils, the maximum concentrations of total and mobile Cd are characteristic of the upper layer and decrease with depth. The greatest number of mobile Cd and Ni is observed in the soil samples with highest humus concentration and content of physical clay. In arable soils in the layer of 0-40 cm the concentrations of mobile Ni are minimal and aligned in depth.

So, despite being on the outskirts of the industrial city, concentrations of most HM, with the exception of Zn and Fe, in the natural and arable alluvial meadow soils of Upa river is within the established standards and clark values, which may be due to the predominance of the removal of these elements over the input. In the fluvisol under meadow, the maximum amount of total Fe and Mn is observed in comparison with arable soil. The maximum concentrations of HM mobile form (with the exception of Zn) are in the upper layer of natural soil under meadow, which has the highest content of humus and physical clay and a salt pH close to neutral. Agricultural use can cause a change in depth distribution of total and mobile forms of heavy metals, which is often expressed in their most uniform distribution. The increase in Zn concentrations in agricultural soils is due to an increase in its content in conservative fractions and is safe for transition along food chains at the present soil conditions. Nonetheless, floodplain agricultural soils should be a permanent subject of environmental monitoring.