



The Interaction of Metals with Humic Acid of Activated Sludge and Biological Treatment Facilities Sludge

Irina Zykova¹, Maksim Rebezov^{2*}, Nikolai Maksimiuk³,
Natalya Kuramshina⁴

¹Department of fundamental and applied chemistry, Yaroslav-the-Wise Novgorod State University, 173003 Veliky Novgorod, 41 B. Sankt-Petersburgskaya str., Russia

²Department of Applied Biotechnology, South Ural State University, 454081 Chelyabinsk, 76, Lenin prospekt, Russia

³Department of biology and biological chemistry, Yaroslav-the-Wise Novgorod State University, 173003 Veliky Novgorod, 41 B. Sankt-Petersburgskaya str., Russia

⁴Department of Environmental Protection and Rational Use of Natural Resources of the Ufa State University of Economics and Service, 450078 Ufa, 145, Chernyshevskogo str., Russia

Abstract: Sludge and wastewater sediments generated during biological treatment, contain significant concentrations of heavy metals which prevents the recycling of nutrients in sludge. In order to develop technologies of neutralization of heavy metals in sludge and wastewater sediments it is necessary to study the mechanisms of binding heavy metals with sludge components. The values of conditional stability constants of humic acid with metals allow us to make an assumption about the possibility of a reverse process provided certain conditions are met.

Key words: sludge, biological treatment, metals, humic acid, stability constants.

Introduction

Contamination of water ecosystems by toxic substances including heavy metals takes place in a variety of ways - surface and groundwater runoff from contaminated areas, industrial wastewater, municipal wastewater, etc. Heavy metals are not subject to transformation in the environment and can accumulate in sediments, in microorganisms, higher aquatic plants and spread throughout the food chain, having a negative impact on living organisms.

When using biological methods of wastewater treatment the concentration of heavy metals in the activated sludge components can increase hundreds and thousands times contaminating the surplus sludge and thereby preventing the recycling of sludge nutrients.

Such surplus sludge is incinerated or disposed of in landfills which is environmentally unsound. When using thermal or thermochemical methods of treatment of surplus sludge and sediment the organic matter synthesized by microorganisms is destroyed, the atmosphere is polluted in a varying degree, and the formation of secondary waste water is possible. For these reasons the thermal methods of treatment in the future will have limited application.

At the same time, activated sludge contains significant amount of proteins, polysaccharides, minerals, B vitamins, and its use as a high-grade product suitable for feeding animals, birds, fish, as a fertilizer in agriculture is very promising [1, 2].

Consequently, it is essential to search for methods of neutralisation of heavy metals in surplus sludge and sediments.

When using activated sludge and sewage sediments in agriculture they must comply with standards established both in Russia and the EU (Table 1) [3].

Table (1): Medium- and long-term plans for permissible content of heavy metals in sewage sludge used in agriculture

Index	Medium-term plans till 2015		Long-term plans till 2025	
	Permitted content of heavy metals			
	in sediments used in agriculture, mg/kg of dry matter	which can be introduced into the soil for 10 years, g/(ha-year)	in sediments used in agriculture, mg/kg of dry matter	which can be introduced into the soil for 10 years, g/(ha-year)
Cadmium	5	15	2	6
Chromium	800	2400	600	1800
Copper	800	2400	600	1800
Mercury	5	15	2	6
Nickel	200	600	100	300
Lead	500	1500	200	600
Zinc	2000	6000	1500	4500

Material and Methods

The object of the study was the surplus activated sludge produced after secondary settling tanks of the biological treatment plant in Veliky Novgorod with moisture content of 98.5% and ash content of 28%.

Analysis was performed manually by burning ash in quartz tubes in oxygen atmosphere at a temperature of 750 °C for 40 minutes.

Analysis of the metal content was carried out using ICP - OES, Perkin Elmer and mass spectrometer of X-Series ICP - MS, Perkin Elmer.

Analysis of the metal content was preceded by solid phase sample preparation, which was conducted by "wet combustion" in an autoclave under pressure. The "wet combustion" process involved a sequential treatment by concentrated sulfuric acid, then aqua regia, and then perchloric and hydrofluoric acids.

Humic substances (HS) were extracted from the sludge by 0.1 M sodium hydroxide. Dissolved humic substances containing impurities of low molecular weight substances, were purified by passing through a column of cation exchange KU-2-8 in the H-form, and precipitated with nitric acid (pH = 2) to isolate the humic acid (HA).

To obtain reliable experimental data for each point of the series we used 3 - 5 samples. For each sample we carried out 10 - 15 measurements which were then processed to filter out emissions by criterion 3σ . Statistical processing of results was carried out using software packages such as STATGRAPHICS Plus, MathCAD, and typical software for implementation of linear and non-linear regression.

Experiments were conducted with active sludges containing a total concentration of metals in the following ranges (Table 2).

Table (2): Total concentration of metals in the activated sludge (mg/kg)

Object	Zn	Mn	Cr	Fe	Cu
Sludge	2360±300	1108±500	116±40	23720±1000	1372±400

Results and Discussion

By analyzing infrared spectra of the sludge, HS, and HA shown in Figure 1, one can see almost complete coincidence of the main characteristic lines, which indicates the presence of identical functional groups involved in the binding of heavy metals.

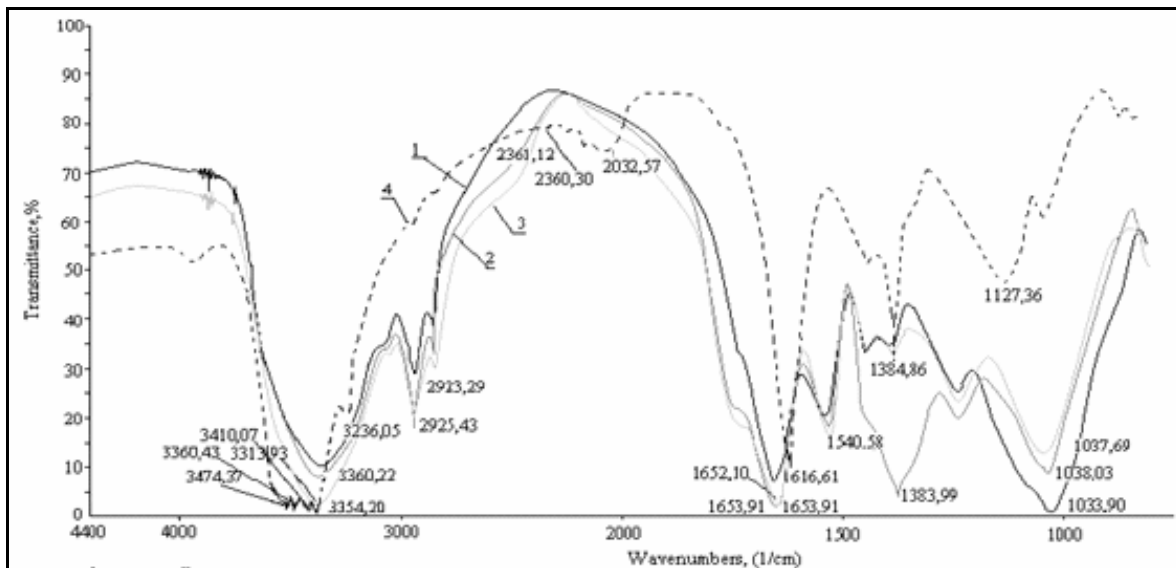


Fig: (1). Infrared spectra of the activated sludge (1), humic substances (2), humic acid of the sludge (3) and sodium humate of known elemental composition (4)

However, comparing the infrared spectra of these substances with the spectrum of sodium humate of the following elemental composition: C – 60 H – 7,1, N – below the detection limit, S + O – 32,7% (S – 7–8%) shown in Figure 1, we conclude that the humic acid of the sludge differs considerably from natural humic acids of different origins. Therefore, it seems necessary to examine the nature of the interaction of metals with humic acids of the sludge.

The synthesis of biopolymers proceeds according to a given genetic code. In contrast to it, the formation of humic substances follows the stochastic principles. For this reason, the humic substances (HS) are a mixture of macromolecules of variable composition and irregular structure [4–7].

There are two main approaches to the study of interactions of metals with humic acid. One is to study the interaction of metals with solid preparations of HA. The other is to study the interaction of HA with the metals in solutions [8–12].

To study the interaction of metals with a solid preparation of HA we selected concentration range from 2 to 25 mg/dm³ (Table 3).

Table (3): The maximum sorption of certain metals by sludge humic acid

Object	Sludge			
	Cu (II)	Ni (II)	Pb (II)	Cr (III)
a _m , mmol/g	0,22	0,16	0,19	0,18

The calculated values of the maximum adsorption capacity reveal the ability of the solid HA preparation to sorb heavy metals. However, studies of sorption with the solid preparation have some disadvantages. Firstly, such studies can be carried out only in a sufficiently acid medium, otherwise HA begins to dissolve. Secondly, the maximum sorption may vary depending on the degree of grinding of HA, and therefore it could be not a characteristic of HA proper. Therefore, it is common to study the interaction of metals with HA in solutions.

The interaction of HA with metal salts in solutions is possible in two ways: the formation of soluble and insoluble humates. The insoluble humates are formed at a sufficiently large ratio (more than 1 mmol/g) metal:HA. At lower ratios, the soluble complexes are formed. Natural and waste waters are characterized by small metal:HA ratio, therefore the formation of the complexes is the most probable way of interaction between metals and HA in the environment. The problem of determining the stability constants is complicated by the inability to establish the stoichiometry of the interaction between HA-metal, due to the polyelectrolyte nature and chemical heterogeneity of HA, as well as the inability to correctly calculate the molar concentration of HA, due to their polydispersity.

Works [13–17] proposed an approach to the description of the interaction of HA with metals. It is based on the fact that HA is considered as a set of independent reaction-binding centers (RBC). In this case, when calculating the stability constants of metal humates the molar concentration of HA can be replaced by the molar concentration of RBC. This allows to assume the stoichiometry of interaction of metal:HA as 1:1. Consequently, the interaction of HA with metals can be described by the equation:



In this case, the apparent stability constant of the complex:

$$K(\text{RBC}) = \frac{[\text{MeRBC}]}{[\text{Me}^{2+}] \cdot [\text{RBC}]} \quad (2)$$

where $[\text{MeRBC}]$ means concentration of the metal associated with the HA; $[\text{RBC}]$ means total RBC concentration of all types.

To determine the amount of RBC we used the ability of metals to form insoluble humates at high ratios of Me (II):HA. It can be assumed that in an abundant excess of metal all RBCs are occupied by metals. Then the metal content in the obtained humates is equivalent to the content of RBC in HA. For this purpose the saturated saline solutions Cr (III), Pb (II), Zn (II), Mn (II), Cu (II) were added to concentrated HA solutions (1.2 g / dm³). As a result, pH decreased to 2.3 – 2.5 (Table 4).

Table (4): RBC amount in sludge HA

Metal	Cr (III)	Pb (II)	Zn (II)	Mn (II)	Cu (II)
RBC, mmol/g	2	2.2	2.4	3.6	1.5

The comparison of the obtained data with the results of experiments on the adsorption with solid HA shows that solid HA sorbs by far less metals than the amount of HA that can be linked when humates precipitate from solutions.

The determining of conditional stability constants of HA complexes with metals was carried out at low degrees of filling RBC. This constant allows us to characterize the strongest RBCs which determine the reactivity of HA in natural environment. For this purpose the saline solutions diluted to 10⁻⁶ - 10⁻⁷ mol / dm³ were added to concentrated HA solutions (1.2 g / dm³). Equilibration time 24 hours. The results of conditional stability constants are summarized in Table 5.

Table (5): Conditional stability constants of HA with some metals

Metal	Cr (III)	Pb (II)	Zn (II)	Mn (II)	Cu (II)
K (RBC)	$2.1 \cdot 10^5$	$3.2 \cdot 10^4$	$5.4 \cdot 10^4$	$7.1 \cdot 10^4$	$3.8 \cdot 10^4$

The example of Cu (II) shows an attempt to establish the relationship between the structure of the reactive binding fragment and stability constants of the respective ligands with Cu (II). For this purpose we analyzed the data on stability constants of Cu (II) with 109 organic oxide-donors.

All oxide-donors were divided into 12 types according to the configuration of the copper-binding fragment (table 6) [18]. The same table shows model ligands for each type (the most common ligands having the given configuration of the reactive binding fragment) and the range of the stability constants of complexes of Cu (II) with ligands of this type.

Table (6): The main types of configuration of copper-binding oxide-donor fragments and their properties

Type name (number of ligands)	Characteristic	Model ligand	Range of lgK ₁
Benzoate (5)	Aromatic carboxylate	Benzoate	1.66 – 3.01
Glyoxylate (2)	Carboxylate with keto group in α -position	2-ketoacetate	2.57
Acetate (26)	Aliphatic carboxylate	Acetate	0.87 – 2.81
Glycolate (6)	Carboxylate with OH group in α -position	2-hydroxy acetate	2.65 – 3.71
Succinate (14)	2 carboxylates at adjacent C atoms	Succinate	3.45 – 5.3
Phthalate (6)	2 carboxylate at adjacent C atoms of the aromatic ring	Phthalate	3.8 – 5.7
Maleate (2)	2 carboxylates at adjacent C atoms linked by a double bond	Maleate	4.35 – 5.05
Phenol (2)	Aromatic hydroxylate	Phenolate	5.3 – 6.3
Malonate (17)	2 carboxylates at one C atom	Malonate	4.77 – 6.18
β -diketones (2)	2 carboxyls with intermediate carbon atom containing at least one hydrogen atom	Acetyl-acetone	8.47 – 9.05
Salicylate(5)	Hydroxylate and carboxylate at adjacent atoms of the aromatic ring	Salicylate	10.3 – 12.4
Pyrocatechol (7)	2 hydroxylates at adjacent carbon atoms of the aromatic ring	Catechol	12.8 – 14.5

For each type, the range of constant values is not more than two orders of magnitude, as the table shows. On the one hand, knowing the configuration of the reactive binding fragment allows us to predict the order of stability constants of the metal complex with a ligand, and on the other hand - to solve the opposite problem, i.e. to select most probable configuration of the metal-binding site by using the value of stability constants.

Comparing the calculated conditional stability constants of copper with HA and stability constants of copper with low molecular weight ligands we assume that a fragment of either succinate or phthalate type can act independently as a reactive binding fragment. However, given the large proportion of aliphatic fragments in sludge HA, the most likely configuration of the copper-binding site is of the succinate type. If RBC has two reactive binding fragments then one of them may be of the benzoate type and the other – of the acetate type.

Conclusion

Values of conditional stability constants of the humic acid with metals allow us to make the assumption about the possibility of the reverse process - the extraction of heavy metals from the activated sludge and biological treatment sludge with the creation of certain conditions of non-toxic metals concentrations in the system.

Findings

- Identified the maximum sorption of metals (Cr (III), Pb (II), Ni (II), Cu (II)) by solid preparations of humic acid extracted from sludge.
- Identified the amounts of RBCs in humic acids of the sludge for metals (Cr (III), Pb (II), Zn (II), Mn (II), Cu (II)).
- Identified the conditional stability constants of humic acids with the metals (Cr (III), Pb (II), Zn (II), Mn (II), Cu (II)).
- Made the attempt to establish the nature of the reactive-binding centers of humic acid using Cu (II) as an example.

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