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Biodegradation of Toxic Aromatic Amines in Industrial Site Soils

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Abstract **-** Method of biological remediation of industrial site soils contaminated with toxic aromatic amines (aniline) is substantiated by theoretical and experimental research. Peculiarities of grain-size composition and agrochemical properties of industrial soil have been studied, the results of aniline concentration assessment presented. A model of transformation and mass transfer of aniline in the soil profile have been discussed. Efficiency of bio-stimulation and bio-supplement methods for decontamination of industrial sites soil contaminated with aniline is proved. Results of mathematical analysis for identification of optimal parameters of aniline biodegradation are presented.

Keywords**:** Soil, Aromatic amines, Biodegradation, Remediation, Activated sludge.

1. Introduction

After emergency spills of toxic organic substances, the special methods are needed for effective and quick soil rehabilitation. Similar problems arise when there is need to rehabilitate the disturbed and contaminated industrial sites while changing their usage type, for instance, during transferring of industrial areas to areas for residential building or urban planning. Excavation of contaminated soil followed by thermal decontamination or by physical and chemical treatment is well-known cleaning method for the soil contaminated with toxic organic substances with anthropogenic origin. But in most cases these methods are economically unreasonable for decontamination of local industrial sites. Currently, a promising method for remediation of contaminated sites is a biotechnological approach, namely, bio-supplement and bio-stimulation methods. These methods are based on the injection of biological products containing the different groups of microorganisms, capable to biodegradation of contaminants, and the stimulation of natural microflora of contaminated soils. One of the methods of stimulation of native soil microflora is the use of organic substrate: compost, biohumus, protein-vitamin concentrates, waste of yeast production, etc. Remediation method for contaminated areas with the introduction of sewage sludge and activated sludge from biological treatment facilities has good perspectives. This method promotes the supply of metabolically active microorganisms, macroelements and microelements that are important for biological processes in the soil. It is necessary to consider, that sludge mass injected into the soil must have a high vitality and should neither be pathogenic nor contain toxic substances such as heavy metals in the normal range.

2. Object of Research

The object of the current research is industrial soils from industrial site of the production complex of aromatic amines, particularly, aniline. The field and laboratory studies were performed for choosing a remediation method for contaminated areas; mathematical analysis methods was used for studying the essential amount of reagent from activated sludge, adapted to the priority industrial pollutant.

2. 1. Characteristic of Contaminant

Aniline is referred to the toxic organic substances (second hazard class), but despite the environment danger, it is easily decomposed by biodegradation and can be partially oxidized by atmospheric oxygen.

Aniline has weak basic properties, so it is subjected to chemical bonding in acidic conditions. In alkaline conditions reaction of formation of bound residues of aniline is reversible, what leads to its accumulation in soil. Aniline has low solubility in water (3.3% wt. at 20°C), so it does not migrate deeply into the ground and accumulates in the topsoil (Shvetcova et al., 2013). It is known that microorganisms are able to use aniline as a carbon source and maintain the decomposition process at a depth of about three meters, which proves the possibility of biodegradability of aniline at anaerobic conditions. The addition of mineral fertilizer increases the initial rate of decomposition (Kosson et al., 1995; Roy et al., 1997; Kuznetsov, Gradova, 2006; Linkova et al., 2011). The bioavailability of aniline confirms the possibility of using the biological method as the main method of soil decontamination.

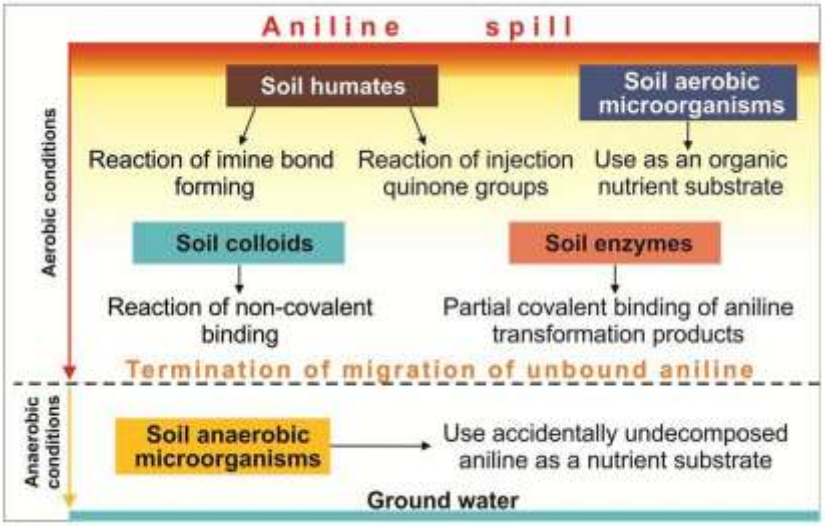

Fig. 1. Model of transformation and mass transfer of aniline in the soil.

2. 2. Ranking of Soil Contamination at Industrial Site

According to the results of the engineering and environmental studies, the industrial site is characterized by local aniline contamination on a depth of 30 cm (the concentration of amines in terms of aniline in soils were as follows: at a depth of 10 cm – up to 50.35 mg / kg of the dry soil, at a depth of 10-30 cm – up to 132.11 mg / kg). According to the norms of aniline content in soils (Web-1), 42% of the area is subject to mandatory decontamination, the rest of soil is suitable only for industrial use.

2. 3. Soil Conditions at the Research Site

In order to assess the aniline migration in the soil profile of the industrial site, the particle size distribution and agrochemical parameters were analyzed.

It has been revealed that the investigated industrial soils are characterized by the following morphological common features:

1) Abundance of inclusions at the top layer (0-0.5 m), major of which is construction waste (crushed stone, gravel, decorative and construction tiles, etc.);
2) Expressed inhomogeneity of horizons which is caused by serious mechanical violations of profile;
3) Grain-size composition relatively lightweight, how in the profile as well as within the top layer (from 0 m to 0.3-0.4);
4) Small thickness of the humus layer (from 0 to 0.05-0.1 m);
5) Presence of sand layer, underlying humus horizon, with capacity from 0.05 to 0.07-0.13 m.

According to the analysis of grain-size composition, the studied soils have low water absorption and low moisture capacity, which may have contributed to the contaminant migration in the soil profile.

The results of agrochemical analysis are shown in Table 1. In comparison to zonal soil, these soils has low humus content (0.15-4.17%) and exchangeable bases (Ca – 2.25-10.25 mEq /100g; Mg – 0.45-1.45 mEq / 100g), therefore detoxification of the aniline is low. Soil pH was in the range of 6.5-7.5.

Table. 1. Agrochemical parameters of the investigated and zonal soils.

Depth of sampling	pH		Humus content, %	Exchangeable bases, mEq /100g			P_2O_5 mg/kg	NO_3^- mg/kg	NH_4^+ mg/kg
	H_2O	KCl		Ca^{2+}	Mg^{2+}	Sum			
Area sampling 1									
0-10	7.43	7.07	4.17	8.45	0.45	8.90	12.4	2.3	13.7
10-20)	7.54	7.04	1.84	10.25	0.65	10.90	59.2	1.5	6.1
40-50	7.43	7.16	1.05	7.05	1.45	8.50	74.6	1.7	9.9
70-80	7.44	6.83	0.23	7.50	1.00	5.50	48.0	1.6	7.6
Area sampling 2									
0-10	7.39	7.24	3.40	5.55	0.70	6.25	41.1	2.0	8.2
10-20	7.88	7.56	1.40	5.45	0.70	6.15	25.7	1.5	6.2
45-55	7.59	7.02	0.61	8.35	0.60	8.95	62.9	0.0	6.0
90-100	7.25	6.47	0.15	5.90	0.60	6.50	108.6	0.0	8.2
Area sampling 3									
0-4	6.99	6.70	1.87	3.20	0.75	3.95	31.5	1.7	7.9
7-17	7.47	7.37	0.15	2.25	0.05	2.30	20.4	1.8	6.4
18-28	7.90	7.39	0.58	8.95	1.10	10.05	48.6	1.6	6.3
Zonal soils									
Sandy soil	6.0-6.5	5.51 - 5.8	1.8-2.2	от 4	0.66-0.82	not less than 4.7	150-200	7 - 15	6 - 8
Sandy-loam soil	6.5-7.0	5.51 - 6.2	2.0-2.5		1.00-1.23	not less than 5	200-250		

The maximal aniline concentrations are detected at about 30 cm and are caused by its poor ability to migrate in water. Supposed doses of aniline spills were quite high – therefore, despite good soil aeration, natural soil cleaning process was not full. That resulted in accumulation of large amounts of aniline (up to 132.1 ± 18.2 mg/kg).

3. Choice of Aniline Biodegradation Method

Decomposition and a significant decrease of the aniline concentration in the contaminated soil can be achieved by addition of the special cultures of microorganisms-destructors and various complex biologics (Pat. 2193464; Pat. 2198748; Pat. 2183142; Pat. 2398640). The advantage of bio-supplement technique is in its selectivity and possibility of cultivation of special strains of microorganisms. Efficiency of this method increases during additional agricultural activities: plowing the cultures into the soil, periodic use of fertilizers, temperature conditions higher than 15^0C. The process takes, in average, two or three seasons.

Equally effective way is bio-stimulation of microflora of native soil, which is aimed at artificial creation of an optimal environment for development of certain microorganisms' groups which can

decompose pollutant. This is achieved by entering of fertilizers, changing temperature, humidity, acidity of the soil environment and agrotechnical receptions (Odokuma, Dickson, 2003).

The activated sludge adapted to a substance-contaminant can be used for methods of bio-stimulation and bio-supplement.

4. Determination of Biodegradation Aniline Parameters

The series of laboratory experiments on determining the effectiveness of aniline concentration reduction in the samples of industrial and background soil were performed for obtaining the optimal parameters of land recultivation. Under the experimental conditions, the small and large aniline spills have been modeled (from 100 to 10,000 mg of aniline per 1 kg of industrial soil). The following model conditions of bio-supplement and bio-stimulation were examined:

– Aniline degradation by addition of adapted to contaminant activated sludge;

– Activation of soil microorganisms by mineral fertilizers;

– Aniline degradation by addition of adapted activated sludge and mineral fertilizer simultaneously.

The results of the experiments (Fig.2 and Fig.3) have shown that when using 2 g/m^2 of sludge, aniline concentration at anthropogenic soils decreases by 90-99% wt. in 15 days. When using 4 g/m^2 of sludge the biodegradation will be less effective. The necessity of use of mineral fertilizers for intensification of the aniline biodestruction has been confirmed.

The mathematical dependence of the decomposition rate of aniline in soil conditions on the activated sludge dosage and the exposure time is the following:

$$C(t,I) = C_0 e^{(-0.07663 - 0.24632I + 0.05266I^2)t} \quad (1)$$

To determine the exact sludge dosage for achieving a maximum rate of aniline concentration decrease in the soils, the mathematical dependence (1) was analyzed. The exponent of the function (1) describes the rate of substance decomposition, thus, the maximum biodegradation rate will correspond to the extreme value of a rate function. For identification of extreme value a rate function has been differentiated and was equated to zero (2):

$$\frac{dk(I)}{dI} = a_1 + 2a_2 I = -0.24632 + 0.10532I = 0 \quad (2)$$

The solution of this equation has allowed to obtain a value of the optimal sludge dose (I*) 7.7 g/kg (in presence of the optimum ratio of biogenic elements: nitrogen – not less than 6.3 mg, phosphorus – 4.7mg, potassium – 2.9 mg).

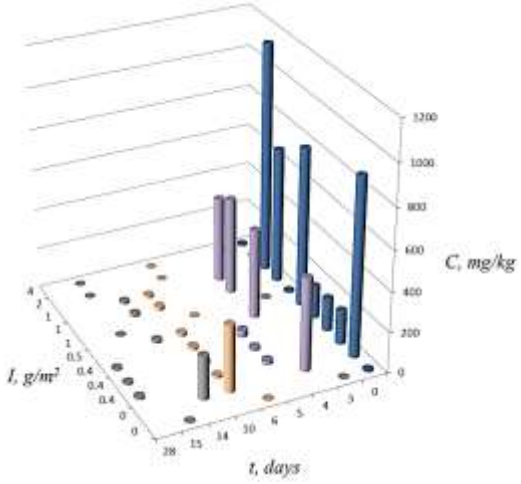

Fig. 2. Results of experimental studies on the biodegradation of different aniline amounts (C) by adding different dosages of adapted activated sludge (I) at different exposure time (t)

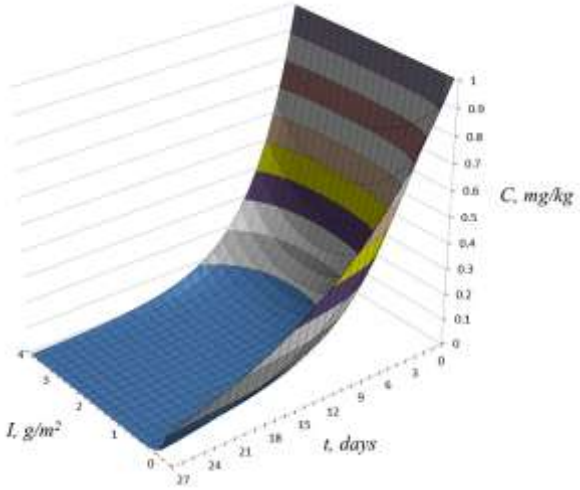

Fig. 3. Approximation of the experiment result
C – aniline concentration in the soil (mg/kg), I – sludge dose (g/m^2), t - exposure time (days)

Considering the size of area subject to recultivation (about 5 ha) and identified consumption of activated sludge, the resource potential of 117 kg of waste activated sludge will be used for aniline biodegradation.

Surplus activated sludge from aniline producer enterprise has been used in the current studies. This sludge was adapted to aniline in industrial conditions (Shvetcova et al., 2013). Activated sludge, which was adapted to pollutant substances in laboratory conditions, can also be used.

5. Conclusions

The process of natural and activated biodegradation of toxic aromatic amines in soils was analyzed on the example of aniline. The effectiveness of bio-stimulation and bio-supplement methods for purification of the industrial soils from aniline has been proven. The optimal dosage of activated sludge for sustaining the maximum decrease rate of aniline concentration in the industrial soils was determined by mathematical analysis method. The experimental data was used to develop the fundamental technological purification schemes for studied soils using wet and dry activated sludge biomass.

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