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VARIABILITY OF MERCURY SPECIATION FORMS IN SOIL EXPOSED TO WASTEWATER FROM OLEOCHEMICAL PRODUCTION*

ZMIENNOŚĆ FORM SPECJACYJNYCH RTECI W GLEBIE PODDANEJ DZIAŁANIU ŚCIEKÓW Z PRODUKCJI OLEOCHEMICZNEJ

Abstract: The results of four-year research concerning variability of mercury speciation forms, contained in soil, subject to treated wastewaters from low-tonnage oleochemical production were analyzed in this paper. Doses of sewage directed to experimental patches were limited by total nitrogen concentration, with the total doses not exceeding the limit of $170 \text{ kg} \cdot (\text{ha} \cdot \text{year})^{-1}$. Every year, the experimental patches were sown with plants; in the subsequent years these were: oats, rape, triticale and mustard. Then, the plants were put into soil as green fertilizers in the whole weight. After an analysis of the fractional composition in soil samples handled with treated wastewater in the experimental period, a gradual decline of the exchangeable fractions was found. Moreover, an increase of the fraction connected with carbonates and stability of the fraction connected with hydrous iron and manganese oxides and the so-called organic connections fraction, and remaining fraction was found.

Keywords: fractional composition of mercury in soil, irrigation with wastewater, fertilization with wastewater, oleochemical production

Introduction

One of the main parameters limiting the implementation of sewage from the so-called biodegradable sector in agroutilization is the contamination with heavy metals including mercury in soil, where they could be directed [1-5]. The concentration of metals limits the suitability of the appropriate type of soil for agricultural use of sewage, including their quantity and the dose of pollutant load [1-5]. In literature, there are many examples concerning the agroutilization of sewage from vegetable or animal fats production, including the aspect of the change of total heavy metals concentrations caused by agroutilization [6-17]. However, there is no information about variability of individual fractional fields during many years of experiments with fertilization and irrigation of soils such as sewage. This question seems to be essential as the total metal concentration does not reflect changes taking place with their participation and components of wastewater pollution during long-term delivery of these substances into soil [4, 5]. Low-tonnage production processes of animal or vegetable fats manufactured for the technical issues are inextricably linked to formation of effluents, which after pretreatment can be used in agriculture for irrigation and as fertilizers because they belong to the biodegradable category [1-5]. Technological wastewaters from production of vegetable fats are usually rich in phosphorus forms but lack nitrogen compounds, whereas, technological wastewaters from production of animal fats are rich in nitrogen and potassium compounds and lack

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phosphorus compounds [2, 3]. A significant amount of fat, suspensions and colloids which are frequently in form of stable dispersions impose the necessity of the physico-chemical pretreatment [4, 5].

Experimental part

The details of the physico-chemical pretreatment of wastewaters from oleochemical production are provided in works [4, 5]. Doses of sewage directed to plots were limited by the total concentration of nitrogen with the total doses not exceeding the limit of $170 \text{ kg} \cdot (\text{ha} \cdot \text{year})^{-1}$. Every year experimental patches were sown with plants, and in the subsequent years these were: oats, rape, triticale and mustard, which in form of green fertilizers were in the whole weight implicated to soil. Samples of soil (light soils classified as Ap-Bw-Ck [18] from two experimental plots, (with the surface of 50.0 acres each)) irrigated and fertilized with defatted mixed crude and pretreated waste, were taken in accordance with PN-ISO 10381-2 from the subsurface layers of 0.0-0.20 m. The pH of the soil samples was determined using the methodology specified in PN-ISO 10390:1997. The soil material for analysis of the total mercury content was collected for 4 years at equal intervals. Air-dried soil samples underwent mineralization and extraction with a mixture of acids ($\text{HCl } \rho = 1.183 \text{ kg} \cdot \text{dm}^{-3}$ and $\text{HNO}_3 \rho = 1.341 \text{ kg} \cdot \text{dm}^{-3}$ in a volume ratio of 3 : 1) according to the standard of PN-ISO 11047:2001. Concentrations were determined by atomic absorption spectrometry technique AAS (devices: BUCK Scientific 210 VGP and Spectr AA Varian 220 SS according to the methodology of PN-ISO 16772:2009). Soil samples taken from the areas of the experimental plots also underwent the sequential extraction according to Tessier's methodology [19], using the air-dried sample weight (about 0.04 kg) which were treated with extracting solutions of increasing power according to the procedures given in [4, 5]. The results of the averaged content and the variation analysis concerning individual fractions of mercury speciation over four years of running the experiments are presented in Figure 1.

Results and discussion

The literature presents different aspects connected with implementation wastewaters from the production of vegetable and animal fats for agroutilizational purposes [6, 7, 12-17]. However, there is a lack of information concerning variation in speciation of metals including mercury during the long-term agroutilization. It could be the matter of high importance to crops technology and usability of plants grown on those irrigated areas. The presented results are continuation of the previous work [4, 5] which purpose was quantitative identification of dynamic fractional variation of heavy metals (Cd, Cr, Cu, Hg, Ni, Pb and Zn), taking place in the surface layer of soil (0.0-0.20 m) during four-year utilization of defatted raw and physico-chemically pretreated mixed wastes from oleochemical production. To compare changes taking place over time, the area of plots was irrigated and fertilized separately with mixed crude wastes after defatting and with wastes pretreated using the method described in [4, 5]. In the experimental period, the range of values of the basic parameters for the mixed crude wastes developed in accordance with the values given in Table 1 [4, 5].

Table 1

The basic parameters of crude wastes and physico-chemically pretreated wastes from low-tonnage oleochemical production

| Item | Parameter | Unit | Raw wastewater | Pretreated wastewater |
|------|---------------------------|--------------------------|----------------|-----------------------|
| 1 | Reaction | pH | 3.9-5.0 | 8.4-9.3 |
| 2 | Total nitrogen | [mg · dm ⁻³] | 175.3-720.9 | 88.8-170.7 |
| 3 | Total phosphorous | [mg · dm ⁻³] | 60.7-220.8 | 11.3-40.8 |
| 4 | Potassium | [mg · dm ⁻³] | 149.4-606.2 | 66.9-483.7 |
| 5 | Ether extract | [mg · dm ⁻³] | 703.3-5999.0 | 3.7-27.3 |
| 6 | Total suspended solids | [mg · dm ⁻³] | 477.3-2530.0 | 18.9-42.7 |
| 7 | Chemical oxygen demand | [mg · dm ⁻³] | 3348.9-10201.6 | 809.6-4405.7 |
| 8 | Biochemical oxygen demand | [mg · dm ⁻³] | 905.8-4593.9 | 467.9-2067.8 |

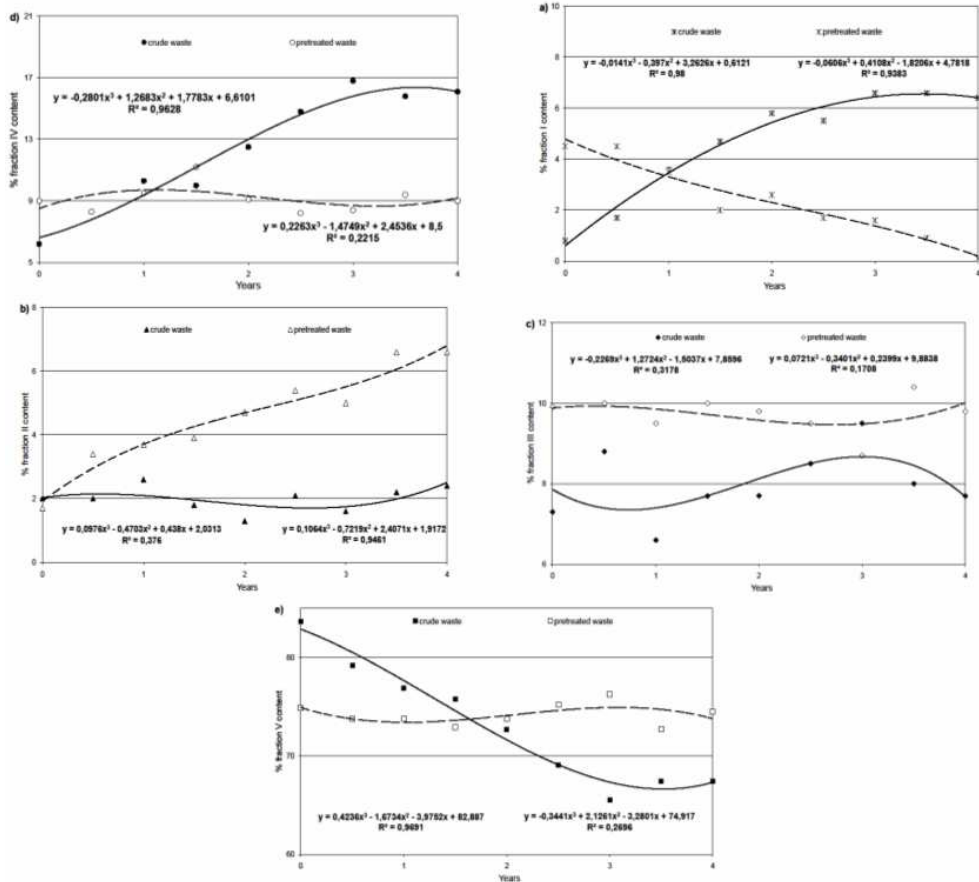


Fig. 1. Changing the fractional composition of mercury (Hg) in the surface layer of soil from the plots irrigated and fertilized with mixed waste from the oleochemical plant - crude wastes (solid trend line) and pretreated wastes (dashed trend line) ($C_{0(Hg)} - 0.5 \pm 0.3 \text{ mg} \cdot \text{kg}^{-1} \text{ TS}$). The individual fractions are given in diagrams: a) I exchangeable, b) II carbonate, c) III associated with hydrated oxides of manganese and iron, d) IV organic, e) V remaining

On the basis of the analyses of soil samples, it was found that the total concentration of mercury at the level of the natural background of these soils. In the case of soil irrigated with defatted crude wastes in accordance with a polynomial equation $C_{Hg}(t) = 0.0001 \cdot t^2 - 0.005 \cdot t + 0.4987$ ($R^2 = 0.1378$) (where: C_{Hg} - the total concentration of mercury indicated by AAS technique, and the parameter t is the experimental time in units of month). However, in the case of the soil irrigated with treated wastewaters, it was done with some approximation in accordance with the polynomial equation $C_{Hg}(t) = 9E-05 \cdot t^2 - 0.0052 \cdot t + 0.5019$ (Fig. 1) [4]. Registered in the experimental period, the mercury concentration did not exceed the level of $1.0 \text{ mg} \cdot \text{kg}^{-1}$ TS and remained within the statutory limits prescribed for light soils by $0.8 \text{ mg} \cdot \text{kg}^{-1}$ TS [1]. Slight variations of concentrations registered in the near surface indicate changes resulting from the vegetation processes of the sown plants.

Despite the usage of pretreated wastewater at $\text{pH} = 7.8\text{-}8.8$ over the four-year experiment no significant changes were found in soil from the experimental plots, since the level of this parameter was within the range $\text{pH} \approx 6.7 \pm 0.2$, during the whole period. Thus, it is the pH level at which the ionic mercury forms have a natural preference to form sparingly soluble forms of hydroxide - like $\text{M}(\text{OH})_{n(s)}$. The effect of this phenomenon was the gradual decrease in the content of fraction I which was recorded in the experimental period in the case of soil samples handled with treated wastewater. However, for the soil samples treated with defatted crude wastes, the acidification was found to change over the time of the experiment from the starting level $\text{pH}_0 \approx 6.7 \pm 0.3$ to the final value $\text{pH}_K \approx 5.9 \pm 0.4$ (no liming the plot was carried out, and after degreasing crude wastes had $\text{pH} \approx 3.9\text{-}5.0$). This caused an increase in the content of the exchangeable fraction (Fig. 1a). This phenomenon can be caused by the fact that there appear suitable conditions for releasing the soluble forms, possibly in the form of aqua complexes $[\text{M}(\text{H}_2\text{O})]^{+m}$ and organic products of changes in soil, especially in the low molecular weight acids in time of vegetation (eg. deriving from micro and mycological soil transformations of polysaccharides and oligosaccharides, eg glycogen provided from wastes). This group contains both complex constructions $[\text{M}(\text{R})]^{+m+n}$ (where: R - organic ligands, eg products of poly sugar hydrolysis: monosaccharides or dextrans; soil metabolism products: low-molecular acid, poly acid, low molecular condensation products etc., a m and n - mercury load and organic ligands) as well as different organic, non-coordinating soluble forms [5, 20-22]. Creating metal-organic connections is also justified by the constant supply of organic substance delivered to the soil, and in consequence increasing transformation processes with the participation of those substances and products of their decomposition, especially during vegetation [20-22]. In the case of fraction II (mercury connected with carbonate forms), no significant changes are found. Whereas, in the case of samples handled with treated wastes, an obvious increase of this fraction content can be seen (Fig. 1b). In the case of fraction III (associated with the hydrated forms of oxides of manganese and iron) for soil samples handled with defatted crude wastes, high stability of this fraction was found, understood as a permanent tendency to maintain a similar level of the content to the natural background in the course of the experiment (Fig. 1c). This indicates that substance composition contained in the wastewater has no effect on total changes of concentration in this fractional pool. However, in the case of soil samples handled with pretreated waste, no statistical tendency or trend providing the

course possible to define the nature of the change was registered. This indicates high instability of the content of this fraction; it can also be the result of composition changes or may be the result of different vegetation processes of plants grown on the soil. Defatted crude technological wastes and pretreated wastes from the oleochemical production is free from heavy metals, and in pollution loads there are mainly low molecular weight soluble substances of vegetable origin (for example: proteins, lecithin, glycerides, sterols, tocopherols, aldehydes, ketones, lactones) or animal origin (for example, amino acids, protein degradation products, simple sugars and oligosaccharides) [12, 15]. On the basis of the obtained research results it can be concluded that they have no quantitative impact on the fractions III, which should be regarded as a desirable effect of agroutilizing impact of wastes on soil quality. In the cases of analyzed soil samples handled with defatted crude wastes, an obvious increase of fraction IV content was estimated (so-called: the combination of organic substances). This increase was recorded at the level of ca 280% (Fig. 1d). Certainly, the dynamics and the nature of humification processes involving organic external substances supplied with wastes affected such a significant change in relation to the initial conditions. The dynamics of change in the concentration of this fraction in the case of soil samples handled with pretreated wastes was shaped differently - no increase in content of this fraction was found (Fig. 1d). Analyzing the fractional composition of the soil samples treated with wastes, definitely the highest percentage recorded in this case is the so-called remaining fraction (fraction V). In the case of fraction V, which is the remaining pool for soil samples treated with defatted crude wastes in the case of mercury, there is a quantitative reduction in content registered at the time of 20-35% (Fig. 1e). Fraction V is the least defined pool in terms of the qualitative and structural composition and its properties depend to the high extent on soil formation and the local environmental conditions, which makes it difficult to describe the interpretation only on the basis of quantitative changes in time. To sum up, it can be suggested that in the case of soil samples handled with pretreated wastes no obvious evidence of a significant change in the quantitative relations concerning individual fractional pools resulted from the increase of properties and the buffer capacity of the soil presented, for which no significant changes in pH were recorded (except for periodic minimal variations - 0.3 values), and this parameter is important in the case of almost all chemical and biochemical soil transformations. In the case of mercury, the phenomenon of the wide variety of percentage shares in fractional pools in time, should be also evaluated in terms of random scatter of the results, taking into consideration the relatively low concentration of this element in soil (for $Hg_{(0)} = 0.5 (\pm 0.3) \text{ mg} \cdot \text{kg}^{-1} \text{ TS}$), and thus the statistical evaluation of the obtained results.

Conclusion

During the four-year agroutilization of the pretreated mixed wastes no significant change in the total mercury content in irrigated and fertilized surface layer of soil was recorded. Analyzing the experimental period, the fractional composition in soil samples handled with pretreated wastes, a gradual decline of the exchangeable fraction was found, whereas the increase in the fraction related to the forms of carbonate and the stability of the fraction concerning hydrated iron and manganese oxides and the fraction of the so-called organic compounds, and the remaining fraction.

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ZMIENNOŚĆ FORM SPECJACYJNYCH RTĘCI W GLEBIE PODDANEJ DZIAŁANIU ŚCIEKÓW Z PRODUKCJI OLEOCHEMICZNEJ

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Abstrakt: Przedstawiono wyniki czteroletnich badań nad zmiennością form specjacyjnych rtęci oznaczanej w glebie poddanej działaniu podczyszczonych ścieków z mało tonażowej produkcji oleochemicznej. Dawki ścieków kierowanych na poletka doświadczalne limitowano stężeniem azotu ogółem, w łącznych porcjach nieprzekraczających granicznej ilości $170 \text{ kg} \cdot (\text{ha} \cdot \text{rok})^{-1}$. Poletka doświadczalne corocznie były obsiewane roślinnością, w kolejnych latach: owsem, rzepakiem, pszenżytem i gorczycą, które w formie zielonego nawozu były w całej masie wprowadzane do gleb. Analizując w okresie doświadczalnym skład frakcyjny w próbkach gleby traktowanej ściekami podczyszczonymi, stwierdzono sukcesywny spadek zawartości frakcji wymywalnej, natomiast wzrost frakcji związanej z formami węglanowymi oraz stabilność frakcji związanej z uwodnionymi tlenkami żelaza i manganu oraz frakcji tzw. połączeń organicznych i pozostałej.

Słowa kluczowe: skład frakcyjny rtęci w glebie, nawadnianie ściekami, nawożenie ściekami, produkcja oleochemiczna

