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THE INFLUENCE OF TREATED OLEO-CHEMICAL WASTEWATER APPLICATIONS ON THE METAL SPECIATION FORMS IN SOILS

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Abstract. This paper presents a developed method of pretreating wastewaters coming from small-tonnage oleo-chemical production and also the research results on the variability of concentrations of heavy metals (Cd, Cr, Cu, Ni, Pb, Zn) in the soil irrigated and fertilized with wastewater from this production. The processing wastewater pretreatment was carried out at two stages. The first stage eliminated fatty substances by using dispersed air flotation aided with hydrogen peroxide as an oxidizer. The second stage included coagulation and chemical precipitation with milk of lime, flocculation, final dissolved air flotation (DAF), and also oxidation with hydrogen peroxide. Field experiments, the aim of which was to compare variability levels for speciation fractions of heavy metals, were carried out according to Tessier's method for four years. The study revealed that the average concentrations of the given metals fractions in soil samples where raw wastewaters were directed did not significantly change during the experiment, which clearly justifies the need for their physical–chemical pretreatment and further agro-utilization without the risk of soil environment degradation. The successive decrease of exchangeable fraction, the increase in the content of the fraction bound with carbonate forms, and stability of the fraction bound with hydrated iron and manganese oxides as well as organic and residual fractions were found in soil samples treated with pretreated wastewaters.

Keywords: irrigation and fertilization with oleo-chemical plant processing wastewater; heavy metal fractional content; flotation.

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Introduction

Small oleo-chemical plants generally deal with manufacturing fatty products such as vegetable and animal technical greases and technical fatty acids. The plants are located mainly in rural areas and their products are designed for biodiesel production, surface-active agents (SAA) synthesis, feed enrichment, and cosmetic industry (Meher *et al.* 2006; Tashtoush *et al.* 2004; Ullmanns Encyclopedia of Industrial Chemistry 1992; Haas *et al.* 2000; Angenent *et al.* 2004; Baltrenas, Kvasauskas 2008). Basic raw materials used for oleo-chemical production mostly come from the postproduction of animal fats (raw materials of the third class) from meat factories and include pork, beef, and poultry fats (e.g. tallow, inguinal fat, intestinal fat, etc.) (Commission Regulation (EC) No 92/2005; Żak 2005; Żak, Pawlak 2006a). As regards fats of plant origin, they are post-refining wastes, soapstock wastes, wastes from the process of degumming, fats from gravitational separators, post-flotation fats, fats recovered from bleaching soils, etc. (Żak 2005; Żak, Pawlak 2006b). The production processes regarding fats of animal or vegetable origin are inextricably linked with the formation of industrial wastewaters which after pretreatment can be utilized in plant farming by irrigation and fertilization because they are biodegradable (Kvasauskas, Baltrenas 2009; Aikaite-Stanaitiene *et al.* 2010; Directive 76/464/EEC). Technological wastewaters from vegetable fat production are rich in phosphorus compounds and poor in nitrogen compounds (Rüffer, Rosenwinkel 1991). The industrial wastewaters from animal fat production are rich in nitrogen compounds and potassium, and poor in forms of phosphorus (Rüffer, Rosenwinkel 1991; Londong, Rosenwinkel 2007). Therefore, it is possible to optimize and regulate the proportions N:P:K in the mixed wastewaters, pretreated

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or directed for watering and fertilization of soils. Due to the significant contents of fats, suspensions and colloids generally found in form of stable dispersions, it is necessary to use physical–chemical pretreatment (Aktas *et al.* 2001). A basic way of pretreating wastewaters from such production is their chemical treatment by using flocculation-aided coagulation and flotation (Rüffer, Rosenwinkel 1991; Londong, Rosenwinkel 2007; Ng *et al.* 1988; Mittal 2006; Żak, Zabłocki 2005; Rubio *et al.* 2002; Żak 2008b). One of the main parameters limiting the agro-utilization of the tested wastewaters is the content of heavy metals in soils where wastewaters are found (Directive 76/464/EEC). The concentration level of wastewaters, including their volume, dosages, and loads of pollutants (Directive 76/464/EEC; Lepp 1981; Ociepa *et al.* 2008), affects a given type of soil and limits their use in agriculture. A total volume of the post-pretreated substances contains mainly dissolved and colloidal proteins and polyoses which, after being introduced into the soil, undergo complex chemical and biochemical processes (Lepp 1981; Rattan *et al.* 2005). In literature, one can find various aspects of the agricultural use of wastewater from animal and plant fat production (Russell *et al.* 1993), but there is no discussion on issues concerning speciation variability of metals during multiyear agro-utilization. These aspects seem to be crucial, considering the mobility of individual metal ions and transport of some of their forms in a plant system during vegetation (Vaišis, Šuksta 2010). The problem may become important as regards cultivation technology and practical usability of plants cultivated on such irrigated arable grounds (Lepp 1981). The investigated production of technical fats of vegetable and animal origin was carried out by a small oleo-chemical factory in the countryside and the research results presented here are the continuation of the previous study (Żak, Rauckyte 2008b).

The aim of the present study was to compare the level of the content and the changeability of heavy metals (Cd, Cr, Cu, Ni, Pb, Zn) in the surface layer of soil (0.0–20.0 cm) during the four-year agro-utilization of the defatted raw and physico-chemically pretreated mixed wastewaters from oleo-chemical production.

1. Experimental part

1.1. Field plot trial

The soil samples taken from the experiment plots were classified as light soil (with its grain-size distribution at the plough-humic horizon – loamy sand). The investigated soils came from boulder clays and had a sequence of genetic horizons appropriate for Cambisols, the soil profile: Ap-Bw-Ck (IUSS WRB 2006). Before the experiment started, the pH of soil was acidic, pH in 1 M KCl 3.7 $\pm$ 0.2 and the active acidity (in distilled H_2O), measured potentiometrically was pH 6.7 $\pm$ 0.2. The average content of humus in depositional levels was 13.206 $g \cdot kg^{-1}$, organic carbon amounted 7.66 $g \cdot kg^{-1}$, and the total content of: nitrogen 0.70 $g \cdot kg^{-1}$, phosphorus (expressed as P_2O_5) 52 $mg \cdot kg^{-1}$, potassium (as K_2O) 27 $mg \cdot kg^{-1}$, and magnesium 14 $mg \cdot kg^{-1}$.

The doses directed to experimental plots were limited by the total nitrogen concentration in all wastewater batches, not exceeding the limit account of 170 kgN/ha $\times$ year. The following plants were sown on the experimental plots every year: oat, rape, triticale, and mustard, which were introduced into soil in the form of total mass of green manure.

Soil samples (the so-called light soils) from two experimental plots (50.0 ares each), irrigated and fertilized with defatted mixed raw and pretreated wastewaters at autumn every year, were taken from a surface soil layer at 0.0–20.0 cm. Defatted raw and processing wastewaters from oleo-chemical production used for fertilization were free from heavy metals.

The wastewaters used in the experiments originated from the oleo-chemical facility, category III, functioning in accordance with Directive 1774/EEC, and located in the Urszulewo Plain (315.16) of the physico-geographical mezoregion in the eastern part of Chełmno-Dobrzyń Lake District, Poland. The experimental plots were located in the arable areas near the facility.

Data-sets of investigated soils

Soil material for the analysis of the total contents of heavy metals was sampled for four years, in equal intervals – one series every six months (one in April, the second one in October) from the experimental plots. Air-dried soil samples were mineralized and extracted with a mixture of acids (HCl, ρ = 1.1830 g/ml, and HNO_3, ρ = 1.3410 g/ml in volume ratio 3:1), according to the Polish Standard PN-ISO 11047:2001. The concentrations were determined by using the atomic absorption spectrophotometry AAS (apparatus: BUCK Scientific 210 VGP or Spectr AA Varian 220 SS).

1.2. Measurement methods

Soil samples collected from the areas of experimental plots were also sequentially extracted according to Tessier's method (Tessier *et al.* 1979), by using air-dried analytical samples (40.0 g each) which were treated with extracting solutions of increasing extraction power.

After filtering solid parts, the filtrate was analyzed by using AAS.

The soil specimens, washed with water and dried, were used at the next stage of the extraction – at II–IV fractions. The results of the filtrate analyses for the contents of heavy metals in individual speciation

fractions during four experimental years are presented in Figures 2–7.

1.3. Experimental technological equipment

Figure 1 presents a simplified flowchart of a physico-chemical treatment system where the pretreatment of mixed wastewaters from the tested oleo-chemical production was carried out (Żak, Rauckyte 2008b).

Post-processing wastewaters from the vegetable (CW1) and animal (CW2) fat plant were directed into a preliminary chamber of wastewater equalization, volume 5.0 m^3, equipped with a bypass (1.1), and after that the averaged wastewater was pumped into an aerated chamber (1.3), volume 50.0 m^3 (the first stage of pretreatment), equipped with fatty flotate skimmer (1.6).

Then, hydrogen peroxide was introduced from the station (12) into the chamber in doses 150.0–175.0 gH_2O_2 per m^3 of wastewater mixed with this agent in a preliminary pipe reactor (2).

The second, chemical stage of pretreatment was conducted in a batch reactor (4) equipped with a vertical gate agitator (4.1) and a circulating mixing set with a pipe reactor (3) where lime milk was introduced from station (11) in dose of 1.25–1.50 kg CaO/m^3 of the defatted mixed wastewaters and finally enhanced by flocculation with 0.3% solution of Praestol 859 BC Stockhausen added from station (10) in dose 50.0 g of pure agent per m^3 of wastewater.

The process was additionally enhanced by dissolved air flotation (DAF) (saturation station (5)) (saturation time: 10.0 min, saturation pressure: 500 kPa, pretreated wastewater recirculation at 20%) aided by oxidation with hydrogen peroxide added from station (12) in dose of 250.0 gH_2O_2/m^3 of wastewaters. After oxidation and separation of phases, a flotate was directed into an additional tank for thickening (7), and then into a frame filter press in order to be dewatered (8), and the obtained filtrate was recirculated periodically to the aerated tank (1.3).

1.4. Wastewater

Wastewater parameters were determined according to the following standards: reaction/acidity (pH) – PN-90/C-04540/01, total nitrogen (TN) – PN-73/C-04576/12, total phosphorus (TP) – PN-EN 1189-2000,

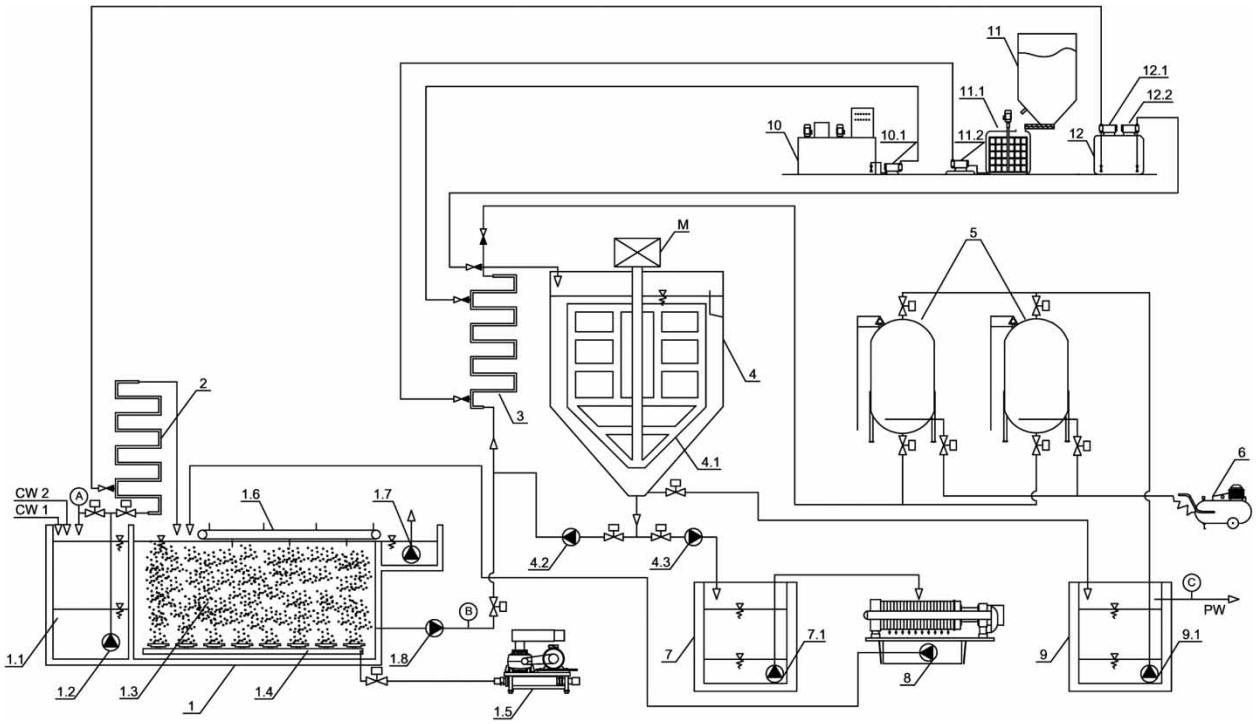

Fig. 1. Flowchart of the experimental installation; CW1 and CW2 – raw wastewaters from vegetable and animal fat production plants; PW – pretreated mixed wastewater; 1 – two-chamber storage-average tank for raw wastewater; 1.1 – preliminary averaging chamber with bypass; 1.2 – bypass pump; 1.3 – aerated preliminary chamber; 1.4 – set of aerating diffusers; 1.5 – compressor; 1.6 – flotate skimmer; 1.7 – pump for thickened fatty flotate; 2 – preliminary pipe reactor; 3 – 2nd stage pretreatment pipe reactor; 4 – batch process reactor; 4.1 – gate agitator; 4.2 – wastewater circulation pump; 4.3 – sludge pump; 5 – saturation station for pretreated wastewater; 6 – compressor; 7 – sludge thickening tank; 8 – frame filter press; 9 – pretreated wastewater tank; 9.1 – wastewater tank; 10 – flocculant preparation and metering unit; 10.1 – flocculant pump; 11 – CaO storage bunker; 11.1 – milk of lime preparation unit; 11.2 – pump for milk of lime; 12 – perhydrol unit; 12.1 and 12.2 – perhydrol pumps; M – mixer drive unit with gear-motor; A, B and C – wastewater sampling points for analyses

potassium (K) by using AAS (equipment: BUCK Scientific 210 VGP and Spectr AA Varian 220 SS) – PN-ISO 9964-1:1994, ether extract (EE) – PN-86/C-04573/01, total suspended solids (TSS) – PN-EN 872:2002, chemical oxygen demand determined by dichromate method (COD) – PN-ISO 15705:2005, biological oxygen demand (BOD_n) – PN-EN 1899-1-2002. The COD parameter concerning the pretreated wastewaters was corrected by deducting the amount connected with hydrogen peroxide, according to the relationship $COD_r = COD_p - f \times d$ (COD_r – corrected by subtracting the fraction of hydrogen peroxide, the concentration of which (d) was determined iodometrically, $f = 0.25$ – literature correction factor (Talinli, Anderson 1992; Żak 2008a), COD_p – measured).

During the experiment, basic parameters for mixed raw wastewaters ranged as follows (Żak, Rauckyte 2008b): reaction (pH) 3.9–5.0; total nitrogen (TN) 175.3–720.9 mg/l; total phosphorus (TP) 60.7–220.8 mg/l; potassium (K) 149.4–606.2 mg/l; ether extract (EE) 703.3–5999.0 mg/l; total suspended solids (TSS) 477.3–2530.0 mg/l; chemical oxygen demand (COD) 3348.9–10201.6 mgO_2/l; and biochemical oxygen demand (BOD_5) 905.8–4593.9 mgO_2/l.

During the experiment, after the second physico-chemical stage, the pretreated wastewaters, achieved the following values of basic parameters (Żak, Rauckyte 2008b): reaction (pH) 8.4–9.3; total nitrogen (TN) 88.8–170.7 mg/l; total phosphorus (TP) 11.3–40.8 mg/l; potassium (K) 66.9–483.7 mg/l; ether extract (EE) 3.7–27.3 mg/l; total suspended solids (TSS) 18.9–42.7 mg/l; chemical oxygen demand (corrected COD_r, for $f = 0.25$ (Talinli, Anderson 1992; Żak 2008a)) 809.6–4405.7 mgO_2/l, biochemical oxygen demand (BOD_5) 467.9–2067.8 mgO_2/l.

2. Results and discussion

To compare analytical results concerning the heavy metals content, the area of the experiment plots was irrigated and fertilized separately by mixed raw wastewaters after their defatting and by pretreated ones. In the literature, numerous reports can be found on agro-utilization of wastewaters from animal or vegetable fats production, including changes in the total content of heavy metals induced by agro-utilization (Lepp 1981; Rattan *et al.* 2005; Russell *et al.* 1993; Żak, Rauckyte 2008a, b; Lassat 2002; Rauckyte *et al.* 2008; Manz *et al.* 1999; Paredes *et al.* 1986, 1987; Tardioli *et al.* 1997).

However, there are no reports concerning changeability in the individual fractional fields during the multi-year research on fertilization and irrigation of soils with such wastewaters. This problem seems to be particularly interesting because the total content of heavy metals does not show transformations which take place with their participation or the components of wastewater load (or possible products of their metabolism in soil) during a multi-year supply of those substances into soil. In that case, mean daily volumes of wastewaters from individual processing lines were as follows: from the production of vegetable originated fatty acids, 5.5–10.0 m^3/day, and from the production of technical greases of animal origin by using the "wet method," 7.5–12.0 m^3/day (Rauckyte *et al.* 2008; Żak, Rauckyte 2008a). Collecting raw wastewaters in the storage-equalizing tank aimed at stabilizing the contents (1), regulating the ratio of N:P:K, cooling (the temperature of raw wastewaters directly from the production was not less than 80 °C) and defattening by induced air flotation (IAF).

Hydrogen peroxide added at this stage significantly stopped microbiological reduction processes, which substantially stabilized the process of fat separation. The oxidizer introduced in dosage 150.0–175.0 gH_2O_2/m^3 ceased the processes revealing characteristic thickening of waste volume, which was a result of biochemical transformations leading to evolving gaseous products, CO_2 in particular (Krause 1982). Hydrogen peroxide is characterized by well-known bactericidal and fungicidal properties, considerably limiting or eliminating undesirable biological processes and increasing biological stability of the pretreated wastewaters (Krause 1982).

An advantageous effect of hydrogen peroxide on the process of the destruction of protein-fats stable colloids was stated and, at the same time, elimination of fats by their flotating separation efficiently increased (efficiency 97–99%). Additionally, oxygen liberating during hydrogen peroxide auto-decomposition ($H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$) considerably improved the process of impurities flotation by forming gaseous micro-bubbles that intensified the process of floating fatty contaminations.

The second-stage installation worked at the maximum output of 20.0 m^3/day. The analyses of soil specimens showed that concentrations of individual metals were at the level of natural background of the tested soils. Slight fluctuations observed in metal concentrations in soil surfaces of the experimental plots were rather a result of vegetation processes of the sown plants. No effect of wastewater dosage on the level of the observed contents of heavy metals was found. The total content of metals did not vary during the experiment and was in accordance with a multinomial equation type $C_M(t) = at^2 + bt + c$ (where C_M – total concentration of analyzed metal, determined by the AAS method, and the parameter t means time of the experiment in monthly units) (Żak, Rauckyte 2008b).

The registered concentration of cadmium did not exceed 1.0 mg/kg d.m., ranging within the scope predicted for light soils, 1.0 mg/kg d.m. (Directive 76/464/EEC). Contents of total chromium, nickel, copper,

lead, and zinc in the analyzed soil specimens varied respectively: 13.0 ± 0.8, 9.2 ± 1.3, 11.6 ± 1.9, 10.9 ± 2.1, and 49.7 ± 2.7 mg/kg d.m., not exceeding the threshold values predicted for this type of soils (Directive 76/464/EEC).

Despite using pretreated wastewaters of pH = 7.8–8.8 in the four-year field experiment, no significant change was found in the experimental plots because the level of this parameter was within pH ≈ 6.7 ± 0.2 (pH_{KCl} = 3.7 ± 0.2). Thus, this is the reaction level at which ionic forms of metals (M), such as chromium, zinc, copper, lead, show natural preference to form sparingly soluble hydroxide forms of type $M(OH)_{n(s)}$. As a result, the content of fraction I for all metals registered during the experiment gradually decreased as far as specimens of soils irrigated with the pretreated wastewaters were concerned (Figs 2–7). Other ingredients (average concentrations of: humus, organic carbon, P_2O_5, K_2O, and magnesium) found in soil samples in that period showed no significant quantitative changes with reference to the values before starting the experiment. However, specimens of soil treated with defatted raw wastewater were acidified from the initial level of pH_0 ≈ 6.7 ± 0.3 (pH_{KCl} ≈3.7 ± 0.3) up to the final value pH_K ≈5.9 ± 0.4 (pH_{KCl} ≈ 3.1 ± 0.4) (the plot was not limed, and the raw wastewaters, after their defatting, had the reaction pH ≈ 3.9–5.0). Such soil components as P_2O_5, K_2O, and Mg did not reveal any significant quantitative changes during the experiment with reference to the values before the experiment. But in the case of humus, after the second year of the experiment a decreasing trend was observed (on average by 3.1% after the second year, 4.3% after the third year, and 4.9% after the fourth year). In the case of nitrogen, the increasing trend was noticed after one year in soil samples from the starting level ratio C:N – 10.9 to 9.8 after four years of the experiment.

It induced an increase in the content of an exchangeable fraction for each metal (Figs 2–4, 6 and 7), excluding copper (Fig. 5), for which no quantitative amounts were registered during the experiment (Fig. 5).

This may be explained by appearance of such conditions that enabled metals to release soluble forms, probably aquacomplexes: $[M(H_2O)]^{+m}$ as well as organic products of soil transformations, especially low-molecular weight acids during vegetation periods (e.g. from micro- and myco-logical soil transformations of poly- or oligosaccharides, e.g. glycogen supplied with wastewaters). This group may include both complex systems of type $[M(R)]^{+m+n}$ (where R – organic ligand, e.g. products of hydrolysis of polysaccharides: monoses or dextrins; products of soil metabolism: low-molecular weight acids, polyacids, low-molecular weight products of condensation, etc., both m and n – loads of metal, its organic ligand) and

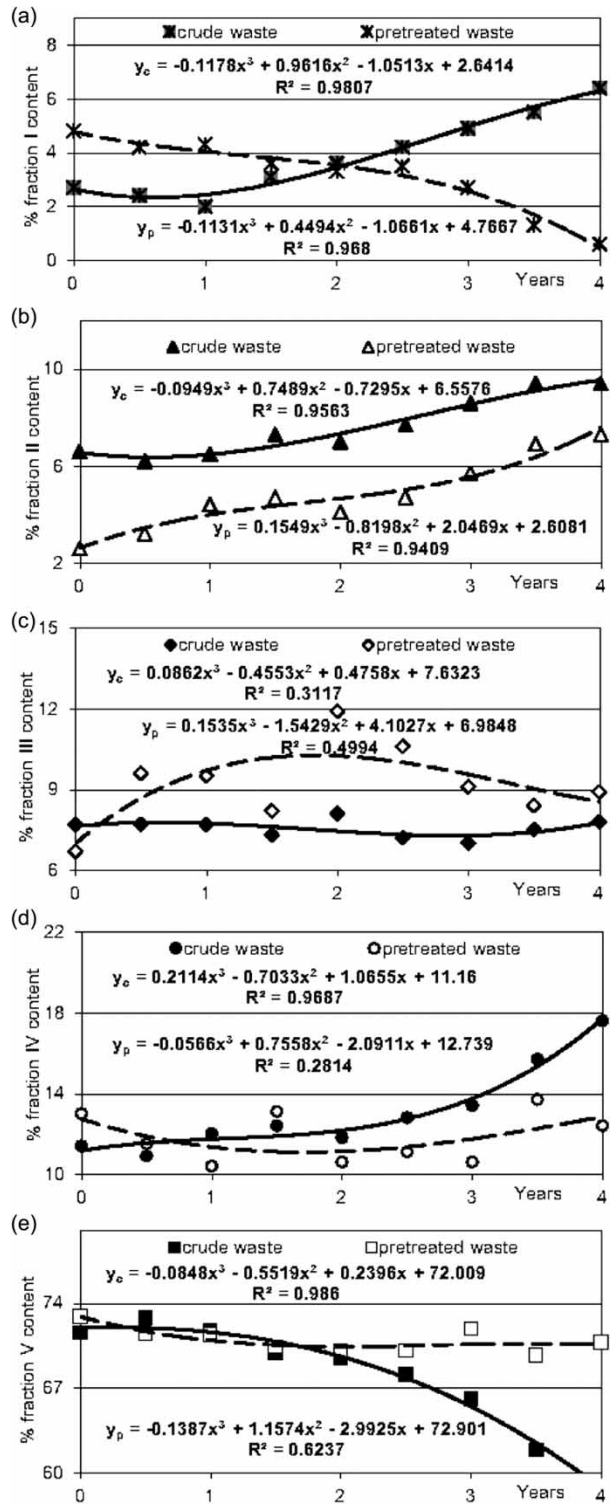

Fig. 2. Changes in the fractional content of cadmium (Cd) in the surface layer of soil from the experimental plots irrigated and fertilized with mixed wastewaters from an oleo-chemical factory – defatted raw (solid line of the trend – y_c) and pretreated (broken line of the trend – y_p) ($C_{0(Cd)}$ – 0.6 ± 0.2 mg/kg d.m.). Individual fractions are given in diagrams: (a) fraction I – exchanged, (b) fraction II – carbonate, (c) fraction III – connected with hydrated oxides of manganese and iron, (d) fraction IV – organic,e) fraction V – the residual

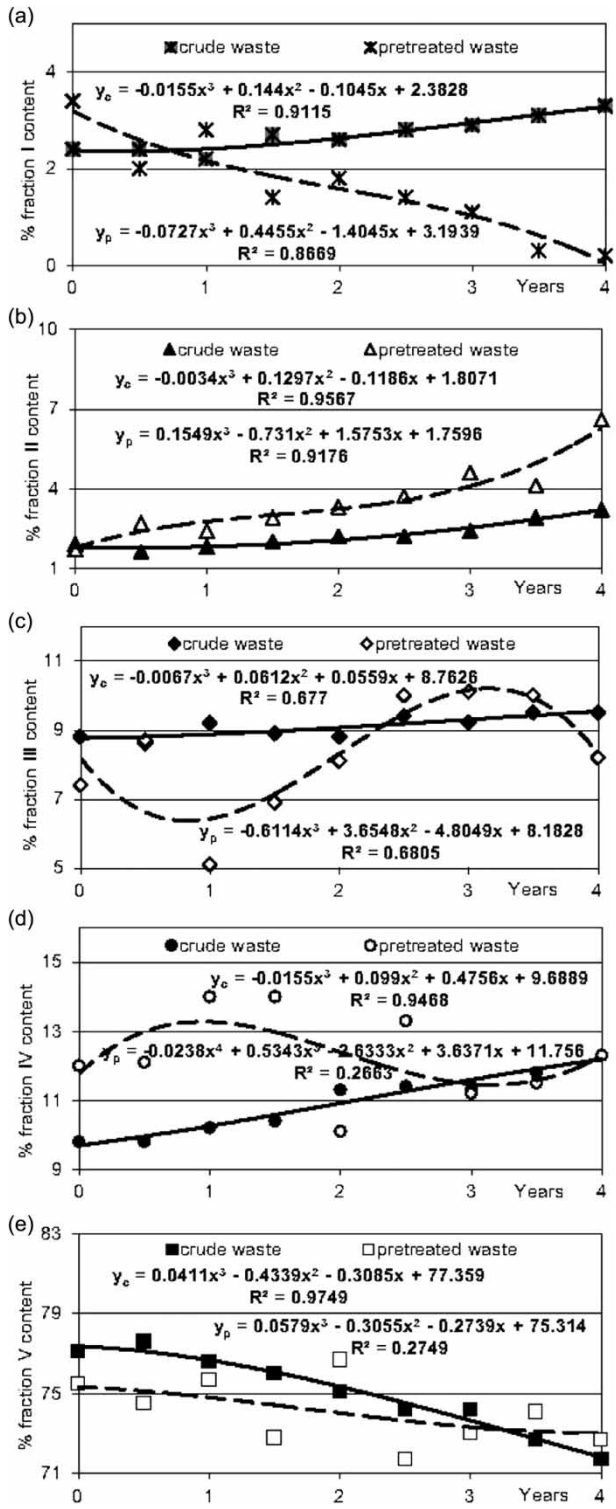

Fig. 3. Changes in the fractional content of chromium (Cr) in the surface layer of soil from the experimental plots irrigated and fertilized with mixed wastewaters from an oleo-chemical factory – defatted raw (solid line of the trend – y_c) and pretreated (broken line of the trend – y_p) ($C_{0(Cr)}$ – 13.0 $\pm$ 0.6 mg/kg d.m.). Individual fractions are given in diagrams: (a) fraction I – exchanged, (b) fraction II – carbonate, (c) fraction III – connected with hydrated oxides of manganese and iron, (d) fraction IV – organic, (e) fraction V – the residual

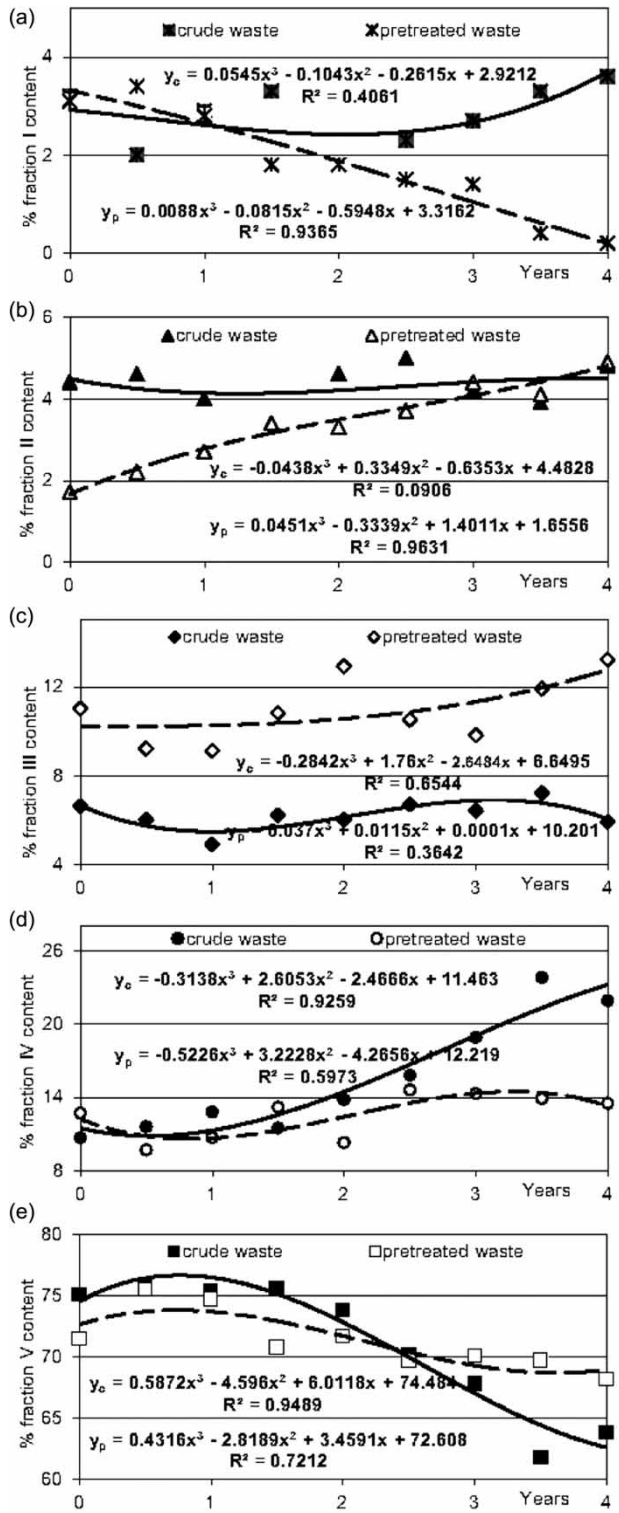

Fig. 4. Changes in the fractional content of nickel (Ni) in the surface layer of soil from the experimental plots irrigated and fertilized with mixed wastewaters from an oleo-chemical factory – defatted raw (solid line of the trend – y_c) and pretreated (broken line of the trend – y_p) ($C_{0(Ni)}$ – 9.3 $\pm$ 0.6 mg/kg d.m.). Individual fractions are given in diagrams: (a) fraction I – exchanged, (b) fraction II – carbonate, (c) fraction III – connected with hydrated oxides of manganese and iron, (d) fraction IV – organic, (e) fraction V – the residual

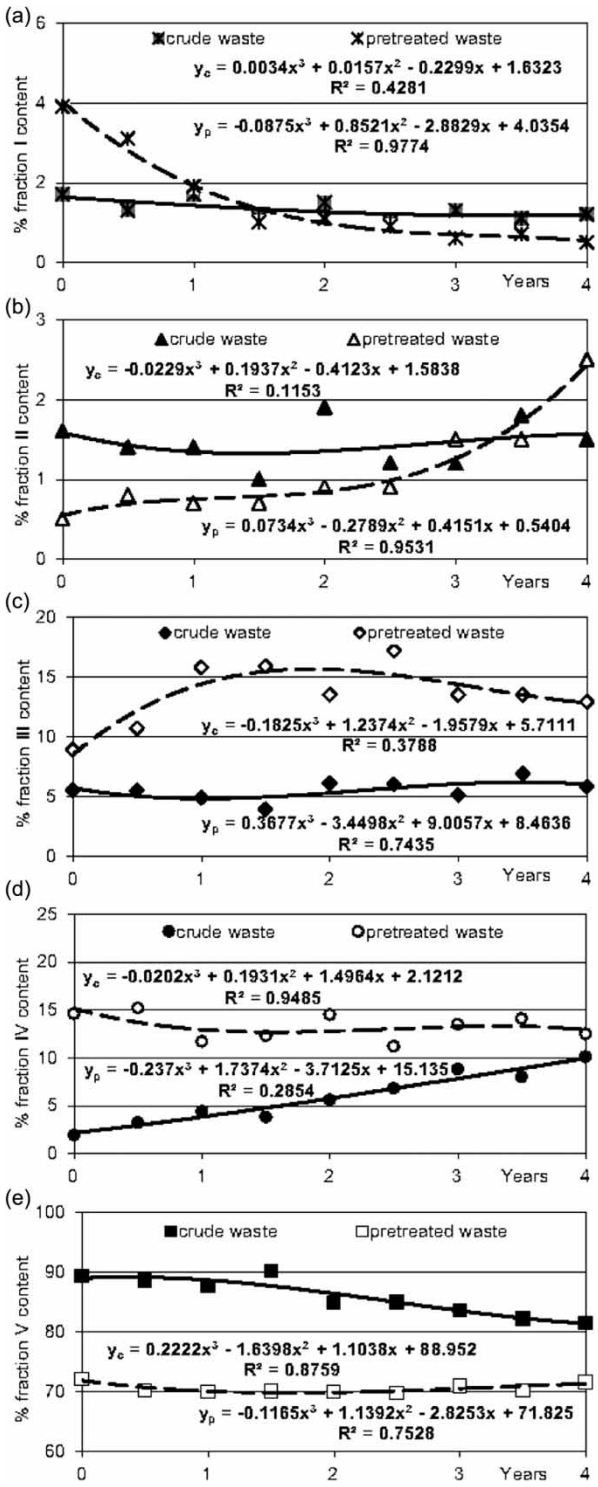

Fig. 5. Changes in the fractional content of copper (Cu) in the surface layer of soil from the experimental plots irrigated and fertilized with mixed wastewaters from an oleo-chemical factory – defatted raw (solid line of the trend – y_c) and pretreated (broken line of the trend – y_p) ($C_{0(Cu)}$ – 11.6 ± 0.8 mg/kg d.m.). Individual fractions are given in diagrams: (a) fraction I – exchanged, (b) fraction II – carbonate, (c) fraction III – connected with hydrated oxides of manganese and iron, (d) fraction IV – organic, (e) fraction V – the residual

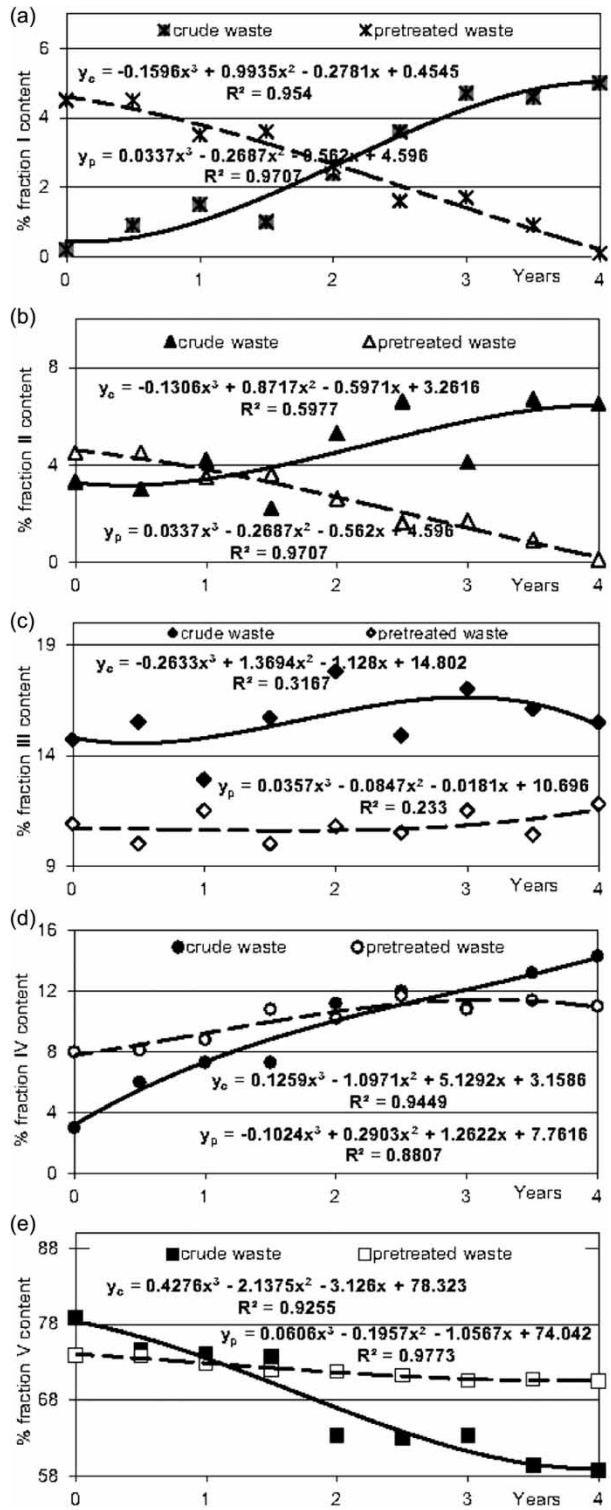

Fig. 6. Changes in the fractional content of lead (Pb) in the surface layer of soil from the experimental plots irrigated and fertilized with mixed wastewaters from an oleo-chemical factory – defatted raw (solid line of the trend – y_c) and pretreated (broken line of the trend – y_p) ($C_{0(Pb)}$ – 10.9 ± 1.2 mg/kg d.m.). Individual fractions are given in diagrams: (a) fraction I – exchanged, (b) fraction II – carbonate, (c) fraction III – connected with hydrated oxides of manganese and iron, (d) fraction IV – organic, (e) fraction V – the residual

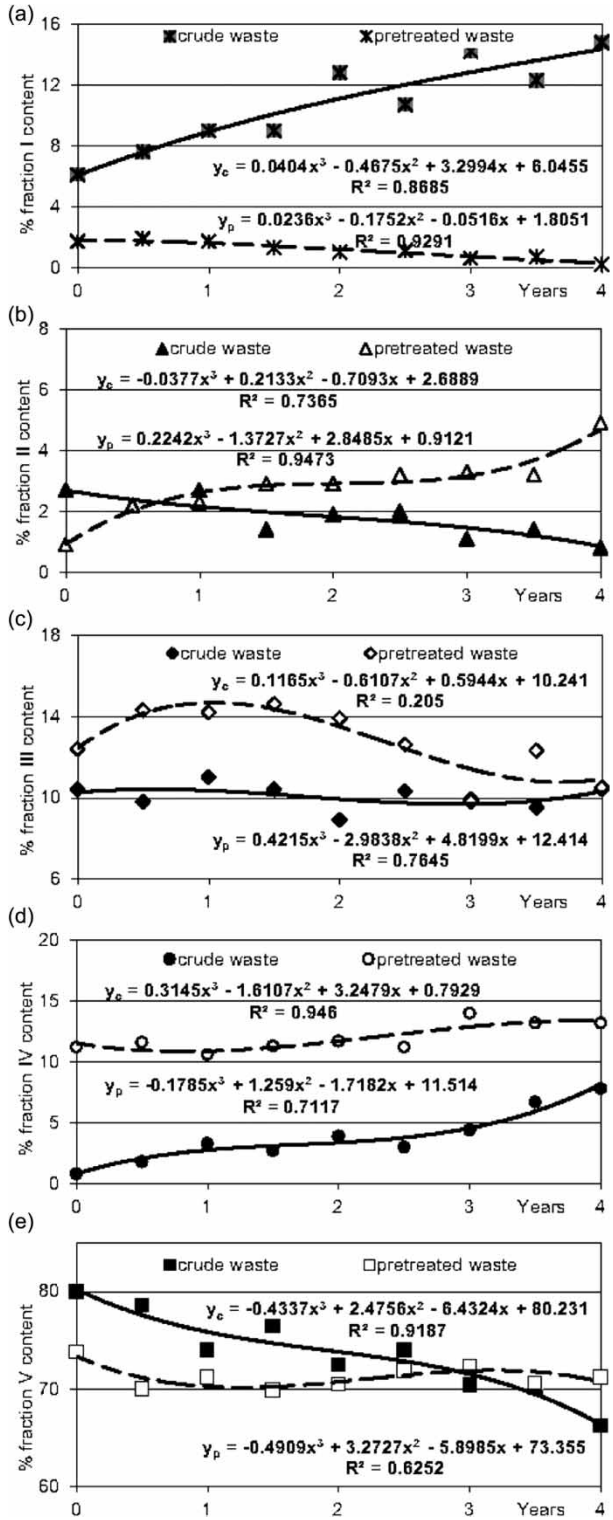

Fig. 7. Changes in the fractional content of zinc (Zn) in the surface layer of soil from the experimental plots irrigated and fertilized with mixed wastewaters from an oleo-chemical factory – defatted raw (solid line of the trend – y_c) and pretreated (broken line of the trend – y_p) ($C_{0(Zn)}$ – 49.7 ± 1.6 mg/kg d.m.). Individual fractions are given in diagrams: (a) fraction I – exchanged, (b) fraction II – carbonate, (c) fraction III – connected with hydrated oxides of manganese and iron, (d) fraction IV – organic, (e) fraction V – the residual

other organic, noncoordination soluble forms. The formation of metallo-organic bonds is justified by a permanent supply of organic substances to soil, inducing increased transformations of these substances and their products of decay, especially during vegetation. Thus, for soil treated with defatted raw wastewaters but not limed, an increase in cation-exchange capacity is observed.

This parameter and its unsteadiness strictly depend on the reaction value (pH) of the tested soil environment (Lepp 1981; Rattan *et al.* 2005; Lassat 2002). In the case of fraction II, connected with carbonate forms of metal compounds, an increase in concentrations of these forms of metals in specimens of soils treated with defatted raw wastewaters for cadmium, chromium, and lead was found (Figs 2, 3, and 6). For nickel and copper (Figs 4 and 5), no significant changes were observed and the zinc concentration decreased (Fig. 7). But for specimens irrigated with pretreated wastewaters, an obvious increase in the content of this fraction for metals was found (Figs 2–5 and 7), with the exception of lead (Fig. 6). The solubility products for carbonates of the tested heavy metals ($MCO_{3(s)}$) were at low level (below $1.0 \cdot 10^{-10}$), which means that such forms are naturally preferred under circumstances of the registered minimal variations in soil reaction (pH). With many diverse factors that affect the properties of a given type of soil, the introduction of the alien substances must result in essential changes in chemical, biochemical, and biological mechanisms (Lepp 1981; Manz *et al.* 1999). This also happens while introducing wastewaters from the tested oleo-chemical production or with a real structural probability of a new substrate to intensify established soil-forming processes (Paredes *et al.* 1986, 1987; Tardioli *et al.* 1997). Wastewaters, especially the pretreated ones, contain additionally mineral salts – ions of calcium (e.g. in a form of $Ca^{2+} \bullet aq$, $CaOH^+$ or pairs of ions: $Ca^{2+} \bullet CO_3^{2-}$ and $Ca^{2+} \bullet HCO_3^-$) which show a definite reactivity in relation to soil components by changing to some degree macroscopic properties and decide about buffer capacity (Tashtoush *et al.* 2004; Rüffer, Rosenwinkel 1991). With the significant participation of chemical and biological reactions which mineralise some organic wastes introduced to soil (where CO_2 is a final product of those transformations), the stability of soil reaction (pH) or its lack may also be a result of buffer capacity of the carbonate–hydrogencarbonate system. A system of equilibrium reactions: $CO_{2(g)} \leftrightarrow CO_{2(aq)} + H_2O \leftrightarrow H_2CO_{3(aq)} \leftrightarrow H^+_{(aq)} + HCO^-_{3\,(aq)} \leftrightarrow H^+_{(aq)} + CO^{2-}_{3(aq)}$ essentially stabilizes and prefers the type of transformations defined by energy (Lassat 2002).

In the case of fraction III (related to hydrated forms of manganese and iron oxides), a high stability was stated for soil specimens irrigated with the defatted raw wastewaters. It is understood as a permanent trend

to keep the content similar to the value of natural background for all metals tested during the experiment.

That means that the content of the substances in the wastewaters does not affect total changes in concentrations of this fractional group. As regards soil specimens irrigated with pretreated wastewaters, no statistical trends suggesting definite transformations were registered. It shows high contents instability of this fraction. It may be a result of content variability or the reaction courses of diverse vegetation processes of plants cultivated on the experimental plots. The participation of speciation forms of metals in soil as a multi-phase poly-dispersion system depends on several factors such as minerals forming a solid phase, the content and composition of organic matter, a volume of soil water, contents of soluble substances in soil water, a form and flow of soil water, local climate, diversity of microorganisms, the level of energy processes, etc. (Lepp 1981; Rattan *et al.* 2005; Manz *et al.* 1999). Legal environmental rules state that only toxic chemical components present in wastewaters are limited by norms, but the volume of water is not included into any legal restrictions; this factor has a significant effect on the dynamics of transformations and transport in soil, especially for outer substances introduced with pollution load. Introducing a new batch of organic-mineral substances with a considerable amount of water may lead to soil transformations and may change the content of speciation forms of metals, especially when wastewaters are used for a long time in agricultural production (Żak 2005). Defatted raw, pretreated processing wastewaters from oleochemical plant generally contain low-weight molecular substances of vegetable origin (e.g. lecithins, glicerols, proteins, aldehydes, ketones, lactones, sterols, tocopherols) or of animal origin (e.g. amino acids, products of protein degradation, mono- and oligosaccharides) (Rüffer, Rosenwinkel 1991; Rack 2007).

The obtained results suggest that the substances have no influence on the content of fraction III, which should be recognized as a desired effect of agro-utilization on soil quality. A clear increase in contents of fraction IV for each tested metal was found in the analyzed specimens of soils irrigated with defatted raw wastewaters.

The growth was registered at the following level for the individual metals: cadmium (Cd) ca 50%, chromium (Cr) ca 20%, nickel (Ni) ca 260%, copper (Cu) ca 500%, lead (Pb) ca 470%, and zinc (Zn) ca 350% (Figs 2–7). The increase in concentration of fraction IV varies for the individual metals and depends on a pure specificity of individual elements, on the properties of organic components introduced into soil with wastewaters (basic–acidic properties, condensation susceptibility, donor–acceptor properties, humification susceptibility, etc.) and also on the products of their bioconversions. Undoubtedly, the dynamics and characteristics of the humification processes with participation of outer organic substances introduced with the wastewaters affected such an essential change with reference to the initial conditions. However, the course of changes in concentration of this fraction for specimens of soil irrigated with the pretreated wastewaters shaped differently. No increase in the content of this fraction for cadmium, nickel, copper, and zinc was observed (Figs 2, 4, 5, and 7). For lead, the concentration of this fraction (IV) increased by 30–40% (Fig. 6) and for chromium the dispersion of the results was so large that it was impossible to interpret them explicitly and reliably (Fig. 3).

The results show good efficiency of physico-chemical pretreatment which eliminates organic matter that can essentially modify the character of metallo-organic transformations, which is undoubtedly a desirable effect. Analyzing fractional contents in specimens of soil irrigated with wastewaters, the definitely highest percent fraction was registered for each metal in the so-called residual fraction (fraction V). For specimens of soil irrigated with pretreated wastewaters, the content of cadmium and lead was at level of ca 70%, but for the rest of metals – more than 85%. For fraction V, a residual of specimens of soil irrigated with defatted raw wastewaters, a decrease in the content of each metal was observed in time (Figs 2–7). The lowest decrease was for chromium, copper, and zinc, approximately 10–15% (Figs 3–5), while for the other metals it shaped at 20–35% (Figs 2, 4, and 6). Fraction V is a group of compounds almost unrecognized both in content and structure, and its properties depend on local soil formation and environmental conditions, which makes a deeper interpretation difficult, basing only on quantitative transformations in time (Lepp 1981).

To sum up, we are able to suggest a thesis that, for specimens of soil irrigated with pretreated wastewaters, the lack of evidence to support a significant change in quantitative relations of the individual fractions resulted from the increase in buffer capacity of the investigated soil for which no significant variation in the reaction was found (excluding periodical minimal pH fluctuation approximately 0.3 of the unit). The parameter of pH is essential for almost all soil chemical and biological transformations. For cadmium, the fact of considerable diversity of the percent participation of fractions in time should also be assessed with respect to the dispersion of the achieved results, taking into account relatively low concentrations of this element in soil (for $Cd_{(0)} = 0.6\ (\pm 0.2)$ mg/kg d.m.), which affects statistical assessment of the obtained results. Basing on the studies carried out, it was found that the method of agro-utilization of the processing wastewaters from low tonnage oleo-chemical

production is an effective way of the tested wastes management, not resulting in significant changes in the contents of heavy metals in the irrigated and/or fertilized soils. The research carried out explicitly proved the necessity of pretreating mixed wastewaters from oleo-chemical production by using milk of lime, the application of which regulates advantageously the ratios N:P:K and eliminates poly- and oligostructural substances as well as excessive amounts of soluble forms of phosphorus.

Conclusions

1. The content of mixed effluents from oleo-chemical industry, both raw and defatted as well as the pretreated physico-chemically, used in the process of their agro-utilization in light soils, does not affect the total content of heavy metals (Cd, Cr, Cu, Ni, Pb, Zn) in the four-year period of irrigation and spreading with these wastewaters.

2. Mixed wastewaters from the oleo-chemical industry, pretreated in a two-stage physico-chemical process (the dispersed air flotation (DAF) and the coagulation combined with the precipitation with lime milk and final flotation enhanced additionally by the oxidation with hydrogen peroxide), disposed to light brown soils, do not induce any significant changes in basic chemical composition of the soils, however they affect the quantitative fluctuations in both elutable and carbonate fractions.

3. The mixed wastewaters from oleo-chemical industry, pretreated only by flotation defatting and directed to their agro-utilization in light Cambisols, induced small changes in chemical composition of these soils during the period of four-year agro-utilization, however, the significant quantitative changes were observed in fractional pools of metals, especially in interchangeable organic, carbonate fractions, and the so-called residuals.

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