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THE SMALL-TONNAGE OLEO-CHEMICAL PLANT PROCESSING WASTEWATER TREATMENT AND AGRO-UTILIZATION

Slawomir Zak[1], Teresa Rauckyte[2]

[1, 2]*Department of Chemical Technology and Engineering, University of Technology and Life Sciences,3 Seminaryjna Street, 85-326 Bydgoszcz, Poland. E-mail: [1]zak@utp.edu.pl*

Abstract. The paper presents a developed method of pretreating wastewaters coming from small-tonnage oleo-chemical production and also the research results on variability of concentrations of nickel (Ni) 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 metal, were carried out according to Tessier's method for four years. Doses of wastewater directed on experimental plots were limited by total nitrogen concentration in final portions, not exceeding the maximal amount of 170 kgN/ha×year. The study revealed that total average concentration of metal did not significantly change during the experiment, including samples of soil treated with either the defatted raw wastewater or the pretreated wastewater. Analyzing the fractional content of individual metal in soil samples irrigated with the studied wastewater, a significant diversification of variabilities for individual fractional plots was found, which evidently justifies the necessity of two-stage physical-chemical pretreatment and further agro-utilization of wastewater from the oleo-chemical production with no risk of soil environment degradation.

Keywords: oleo-chemical plant processing wastewater, flotation, nickel, sequentially extraction.

1. Introduction

Small oleo-chemical plants deal generally 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.* 2004; Tashtoush *et al.* 2004; Ullmans Encyclopedia 1992; Haas *et al.* 2000; Angenent *et al.* 2004). Basic raw materials used for oleo-chemical production mostly come from postproduction animal fats (raw materials of 3rd 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; Dz.U.2003 Nr106, poz.1001; Żak 2005; Żak and Pawlak 2006). 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 and Pawlak 2006a). The production processes of fats of animal or vegetable origins 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 (Dz.U.2006 Nr 137, poz.984), as well as organic waste composes (Zuokaitė and Ščupakas 2007). Technological wastewaters from vegetable fat production are rich in phosphorus compounds and poor in nitrogen compounds (Rüffer and Rosenwinkel 1991; Chin and Wong 1981). The industrial wastewaters from animal fat production are rich in nitrogen compounds and potassium, and poor in forms of phosphorus (Rüffer and Rosenwinkel 1991; Industrieabawasserbehandlung 2007). Therefore it is possible to optimise and regulate the proportions N:P:K in the mixed wastewaters, pretreated or directed for watering and fertilization of soils. Due to significant contents of fats, suspensions and colloids generally found in a form of stable dispersions, it is necessary to use physico-chemical pretreatment (Niewiadomski and Szczepańska 1989; 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 and Rosenwinkel 1991; Chin and Wong 1981; Industrieabawasserbehandlung 2007; Ng *et al.* 1988; Mittal 2006; Żak and Zabłocki 2005; Rubio *et al.* 2002). One of the main parameters limiting the agro-utilization of the tested wastewaters is the content of heavy metals in soils where wastewaters are irrigated (Dz.U.2006 Nr 137, poz.984). The concentration level of wastewaters, including their volume, dosages and loads of pollutants

(Dz.U.2006 Nr 137, poz.984; Lepp 1981), 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 soil, undergo complex chemical and biochemical processes (Lepp 1981; Rattan *et al.* 2005). In literature, you can find various aspects of the agricultural use of wastewater from animal and plant fat production (Russel *et al.* 1993; Russel and Cooper 1987), 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. The problem may become important as regards cultivation technology and practical usability of plants cultivated on such irrigated arable grounds (Lepp 1981).

2. Experimental part

Figure 1 presents a simplified flowchart of physicochemical treatment system where the pretreatment of mixed wastewaters from the tested oleo-chemical production was carried out (Żak and Rauckyte 2008a). Post-processing wastewaters from the vegetable (CW1) and animal (CW2) fat plant were directed into a preliminary chamber of wastewater equalization, vol. 5.0 m^3, equipped with a bypass (1.1), and after that the averaged wastewater was pumped into an aerated chamber (1.3), vol. 50.0 m^3 (the 1st stage of pretreatment), equipped with fatty flotate skimmer (1.6).

Then, hydrogen peroxide was introduced from 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 a tank of additional 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).

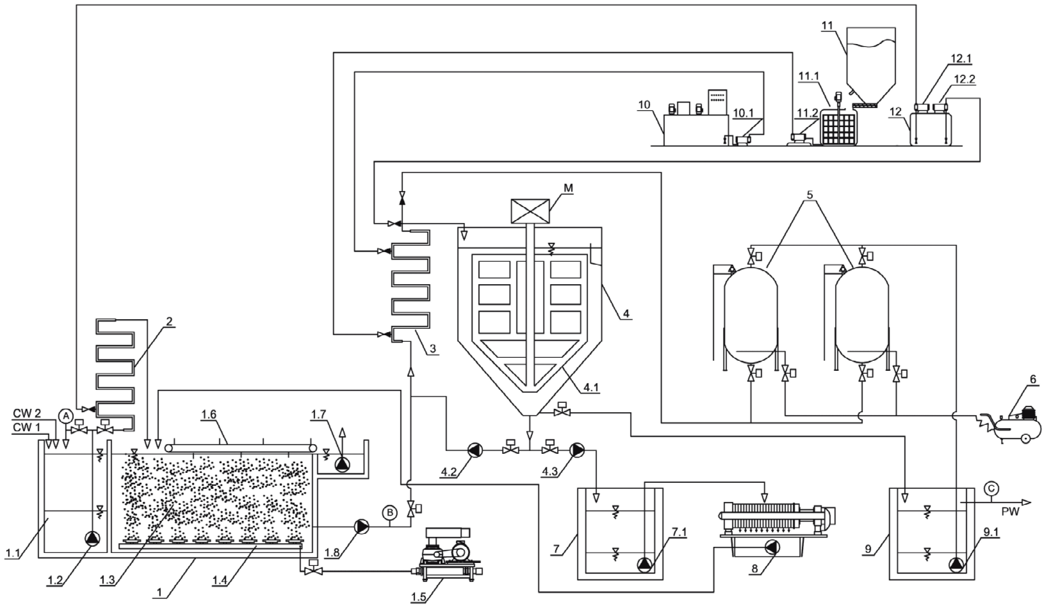


Fig 1. Flowchart of the experimental installation

Where: 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

Wastewater parameters were determined acc. 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, 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 the pretreated wastewaters was corrected by deducting the amount connected with hydrogen peroxide, acc. 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 2008), COD_p – measured).

The doses directed on experimental plots were limited by the total nitrogen concentration in all wastewater batches, not exceeding limiting amount of 170 kgN/ha×year. The following plants were sown on the experimental plots every year: oat, rape, triticale and mustard, which were introduced into soil in a 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, were taken acc. to Polish Standard PN-ISO 10381-2, from a surface soil layer of 0.0-20.0 cm. The reaction of soil samples was determined acc. to the procedure given in PN-ISO 10390:1997. Soil material for the analysis of the total content of nickel was sampled for 4 years, in equal every-month periods of time. Air died soil samples were mineralized and extracted with a mixture of acids (HCl, $\rho = 1.1830$ g/ml, and HNO_3, $\rho = 1.3410$ g/ml in volume ratio 3:1), acc. 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). Analytically determined average concentration of individual metal in the dried matter of the collected soil materials before the field experiment started are presented in the description of diagram 1.

Soil samples collected from the areas of experimental plots were also sequentially extracted acc. 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 acc. to the procedures given below.

I. Fraction I (exchangeable ions). In order to determine the 1st fraction metal contents, samples were treated with 20.0 ml (1.0 M) of $CaCl_2$ and, after mixing (with pH = 7.0), they were shaken for 1.0 hour at room temperature. After filtering solid parts, the filtrate was analyzed.

II. Fraction II (carbonate bounded forms). Soil samples remaining after implementing the procedure acc. to the point I, washed with water and dried, were submitted to extraction by adding 40.0 ml (1.0 M) of CH_3COONH_4 and acidifying with 80% CH_3COOH up to pH = 7.0. After mixing, the samples were shaken for 5.0 hours at room temperature. During this operation the pH was controlled: when pH > 7.0 – the sample was acidified. Filtrate was analyzed and the soil samples, washed with water and dried, were used at the 3rd stage of the extraction.

III. Fraction III. At this stage (determination of fraction connected with released Fe/Mn oxides), 40.0 ml (0.04 M) of the solution $NH_2OH{\bullet}HCl$ in 25% CH_3COOH was added to the dried solid state soil sample that remained after following the procedure acc. to point II. Samples (with pH = 2.0) were shaken for 5.0 hours at temperature $96\pm3^{o}C$. The filtrate was analyzed but the remaining solid material, washed and dried, was submitted to the 4th stage of the extraction.

IV. Fraction IV (forms connected with organic material). Solid material remaining from the stage described in point III was treated with 10.0 ml (0.02 M) of HNO_3 and 10.0 ml of 30% aqueous solution of H_2O_2, mixed (pH = 2.0) and shaken for 135.0 minutes at temperature 85 ± 2 ^{o}C. Then 10.0 ml of 30% H_2O_2 was added and shaken for 135.0 minutes. After that 20.0 ml (3.0 M) of CH_3COONH_4 in 20% HNO_3 (v/v) was added and shaken for 30.0 min at room temperature (pH = 2.0). The filtrate was analyzed and the washed and dried soil remains were used at the 5th stage of the extraction.

V. Fraction V (the residual forms). For the residue of the solid phase from point IV, 6.0 ml of HNO_3 and 4.0 ml of 30% H_2O_2 were added and mixed (pH = 2.0). The mixture was shaken for 1 hour at boiling point and at that time it was treated twice with HNO_3 and H_2O_2 up to the moment of releasing white fumes. Then 20.0 ml of 30% H_2O_2 was added and the sample was shaken for 30.0 minutes at boiling point. After cooling to the room temperature and separating from the solid residue, the filtrate was analyzed by using AAS. The results of the analyses for the contents of nickel in individual speciation fractions during four experimental years are presented in figure 2.

3. Results and discussion

The investigated production of technical fats of vegetable and animal origin was carried out by a small oleochemical factory in the countryside and the research results presented here are the continuation of the previous study (Żak and Rauckyte 2008a). The present study aimed to compare the level of the content and the changeability of heavy metal (Ni) 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.

To compare analytical results concerning the content of nickel, the area of the experiment plots was irrigated and fertilized separately by mixed raw wastewaters after their defatting and by pretreated ones. In 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; Russell and Cooper 1987; Żak and Rauckyte 2008; Lassat 2002; Żak and Rauckyte 2008a; Rauckyte *et al.* 2008; Manz *et al.* 1999; Paredes *et al.* 1986; Paredes *et al.* 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/d, and from the production of technical greases of animal origin by using the "wet method" – 7.5-12.0 m^3/d. Collecting raw wastewaters in the storage-equalizing tank aimed to stabilize the contents (1), to regulate the ratio of N:P:K, to cool (the temperature of raw wastewaters directly from the production was not less than 80^oC) and to defat by induced air flotation (IAF). During the experiment basic parameters for mixed raw wastewaters ranged as follows (Żak, Rauckyte 2008a): 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. Hydrogen peroxide added at this stage significantly stopped microbiological reduction processes, which stabilized substantially 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, carbon dioxide 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 ($H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$) improved considerably the process of impurities flotation by forming gaseous micro-bubbles that intensified the process of floating fatty contaminations. The phenomenon of micro-bubbles formation, advantageous for flotation, also results from decaying organic substrate, leading to the formation of carbon dioxide (www.h2o2.com; Steiner and Gec 1992). The applied oxidizer doses were similar to the examples described in literature (www.h2o2.com; Steiner and Gec 1992). The 2nd-stage installation worked at the maximum output of 20.0 m^3/d. During the experiment the pretreated wastewaters, after the 2nd physico-chemical stage achieved the following values of basic parameters (Żak and Rauckyte 2008a): 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 2008)) 809.6-4405.7 mgO_2/l, and biochemical oxygen demand (BOD_5) 467.9-2067.8 mgO_2/l. Transformations of the compounds contained in the pollution load, induced by hydrogen peroxide at the 2nd stage of pretreatment, can also provoke reactions between the organic protein substrate (B) and H_2O_2, such as: addition (e.g. $H_2O_2 + B \rightarrow B\bullet H_2O_2$), substitution (e.g. $H_2O_2 + 2BH \rightarrow BOOH + HB + 2H^+$ or $H_2O_2 + 2BX \rightarrow BOOB + 2HX$), and oxidation (e.g. $H_2O_2 + B \rightarrow BO + H_2O$) (Steiner and Gec 1992). The reactions carried out according to the outlines shown above lead mainly to a synthesis of more biodegradable forms or prone to biotransformation at the final stage of biological soil processes. 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 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 method AAS, and the parameter t means time of the experiment in month units) (Table 1). The registered content of total nickel, in the analyzed soil samples varied respectively: 9.2±1.3; mg/kg d.m., not exceeding the threshold values predicted for this type of soils (Dz.U.2006 Nr 137, poz.984).

Table 1. Equation of statistical distribution of nickel contents (C_M) in the soil layer irrigated and fertilized with defatted raw and pretreated mixed wastewaters from small-tonnage oleo-chemical production as a function of the four-year experimental period (t) [a, b)]

Metal (M)	Raw wastewaters $C_M(t)$	R^2 parameter	Pretreated wastewaters $C_M(t)$	R^2 parameter
Nickel (Ni)	$C_{Ni}(t) = 9E\text{-}05t^2 - 0.0036t + 8.7337$	0.0037	$C_{Ni}(t) = -5E\text{-}05t^2 + 0.003t + 8.6093$	0.0011

Where: [a)] in the equations: C_M – registered metal concentration (M) determined by method AAS, and parameter t – time in the experimental months; [b)] presented basing on the study (Żak and Rauckyte 2008a).

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. As a result, the content of fraction I for nickel registered during the experiment gradually decreased as far as samples of soils irrigated with the pretreated wastewaters were concerned (Fig 2). However, samples of soil treated with defatted raw wastewater were acidified from the initial level of $pH_0 \approx 6.7 \pm 0.3$ up to the final value $pH_K \approx 5.9 \pm 0.4$ (the plot was not limed, and the raw wastewaters, after their defatting, had the reaction pH ≈ 3.9 – 5.0). It induced an increase in the content of a exchangeable fraction for nickel (Fig 2).

This may be explained by appearing 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 together 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 and its organic ligand) and other organic, non-coordination soluble forms. The formation of metallo-organic bonds is also 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 depends on the reaction value (pH) of the tested soil environment (Lepp 1981; Rattan *et al.* 2005; Lassat 2002). For nickel (Fig 2), no significant changes were observed. But for samples irrigated with pretreated wastewaters, an obvious increase in the content of this fraction for metals was found (Fig 2). The solubility products for carbonates of the tested heavy metals ($MCO_{3(s)}$) were at low level (below 1.0 •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; Paredes *et al.* 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+}•aq, $CaOH^+$ or pairs of ions: Ca^{2+}•CO_3^{2-} and Ca^{2+}•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 2004; Rüffer and 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: $CO_{2(g)} \leftrightarrow CO_{2(aq)} + H_2O \leftrightarrow H_2CO_{3(aq)} \leftrightarrow H^+_{(aq)} + HCO_3^-{}_{(aq)} \leftrightarrow H^+_{(aq)} + CO_3^{2-}{}_{(aq)}$ essentially stabilises and prefers the type of transformations defined by energy (Russell and Cooper 1987; 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 distability 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; however, this factor has a significant effect on the dynamics of transformations and transport in soil, especially for outer substances introduced with pollution load (Chin and Wong 1981).

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 and pretreated processing wastewaters from oleo-chemical plant are free of heavy metals and 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 and Rosenwinkel 1991; Rack 2007).

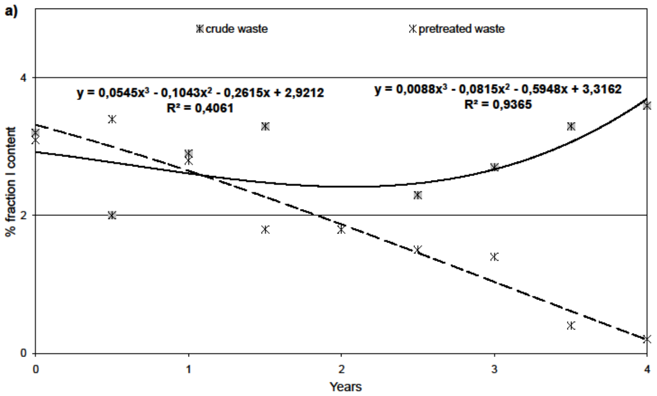
The obtained results suggest that the substances have no influence on the content of fraction III, which should be recognized as a desired effect of agro-utilization on soil quality. A clear increase in contents of fraction IV (the so called bonds with organic substances) for tested metal was found in the analyzed samples of soils irrigated with defatted raw wastewaters. The growth was registered at the ca 260% for the nickel (Ni) (Fig 2d). The increase in concentration of fraction IV varies for the individual metal 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 character of 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 nickel was observed (Fig 2). The results show a good efficiency of physico-chemical pretreatment which eliminates organic matter that can essentially modify a character of metallo-organic transformations, which is undoubtedly a desirable effect. Analyzing fractional contents in samples of soil irrigated with wastewaters, the definitely highest per cent fraction was registered for metal in the so called residual fraction (fraction V).

For samples of soil irrigated with pretreated wastewaters, the content of nickel - more than 85%. For fraction V, a residual of samples of soil irrigated defatted raw wastewaters, a decrease in the content of nickel was observed in time (Fig 2). The nickel decreased at 20-35% (Fig 2e).

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 samples 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 app. 0.3 of the unit). The parameter of pH is essential for almost all soil chemical and biological transformations.



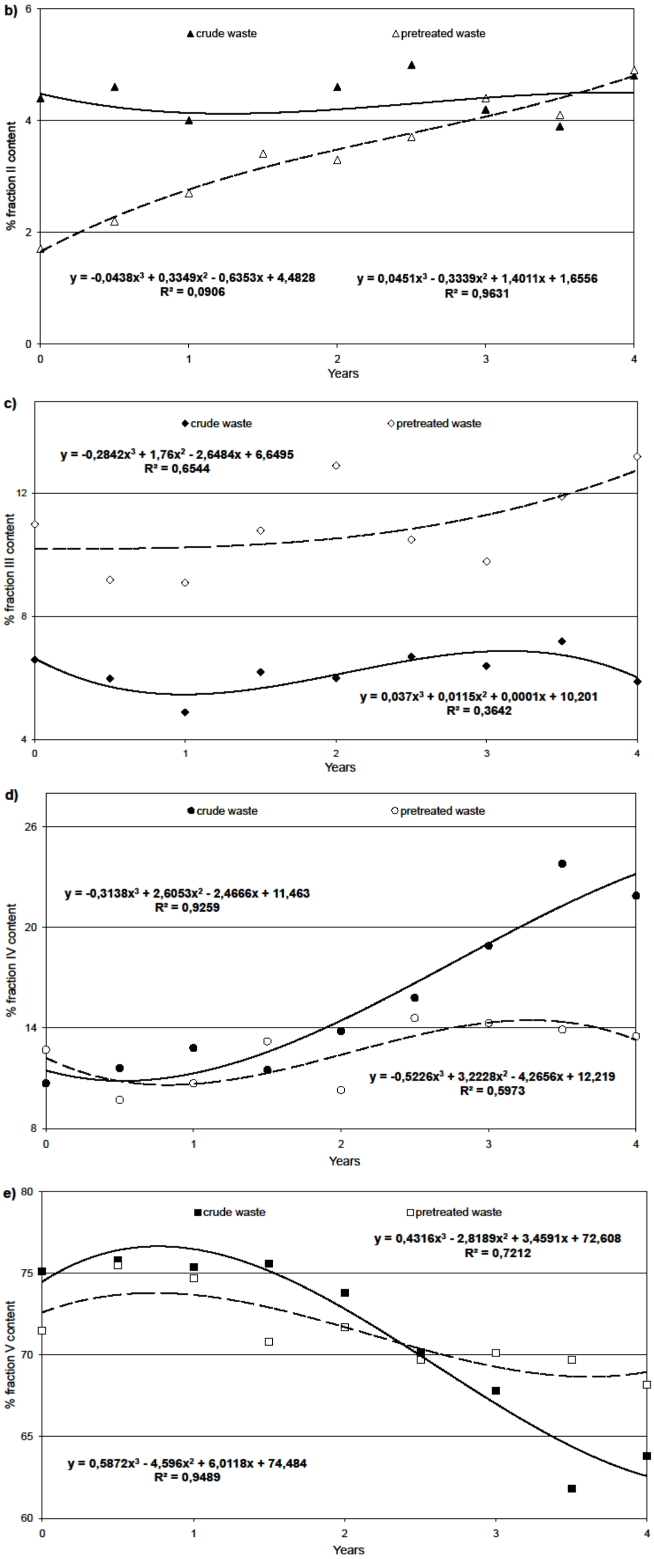


Fig 2. Changes in the fractional content of nickel (Ni) in the surface layer of soil from the experimental plots irrigated and fertilized with mixed wastewaters from an oleochemical factory: - defatted raw (solid line of the trend) and pretreated (broken line of the trend) ($C_{0(Ni)}$ – 9.3±0.6 mg/kg 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.

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 nickel in the irrigated and/or fertilized soils. The research carried out proved explicitly 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.

4. Conclusion

1. The pretreated mixed processing wastewaters from the production of technical fats of vegetable and animal origins made in low oleo-chemical plants show a more favorable ratio N:P:K for the needs of fertilization. In order to be used in agriculture, wastewaters should be effectively defatted and colloidal and suspension systems ought to be eliminated.
2. Analyzing, during the experiment, fractional content of the individual metal in samples of soil irrigated with pretreated wastewaters, a successive decrease in a exchangeable fraction and an increase in the fraction related to carbonate forms were found.
3. The stability of the fraction related to hydrated iron and manganese oxides as well as the fractions of the so called organic bonds was stated.
4. Further long-term irrigation and fertilization of the tested soil under the same agro-technical and technological conditions of the processing wastewater pretreatment will not cause any significant variations in the contents of individual speciation pools of nickel (Ni).

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