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# TREATMENT OF THE PROCESSING WASTEWATERS CONTAINING HEAVY METALS WITH THE METHOD BASED ON FLOTATION

## OCZYSZCZANIE ŚCIEKÓW TECHNOLOGICZNYCH Z METALI CIĘŻKICH METODĄ WYKORZYSTUJĄCĄ FLOTACJĘ

**Abstract:** The aim of the studies carried out at full technological scale was to indicate optimal systems of the two-stage precipitation and coagulation (PIX 113 - SAX 18, PAX XL1 - SAX 18, ALCAT 102 - lime milk and SAX 18 - PAX 16) in the process of eliminating heavy metals from wastewaters made in the processing plant producing sub-systems for domestic appliances. Precipitated pollutions were thickened by flocculation and separated by hydrogen peroxide enhanced pressure flotation. The experimental installation of maximal flow capacity: 10.0 $m^3$/d consisted of: the storage-equalization tank, the processing pipe reactor, the pressure flotation station, and the reagent preparation and dosing station. Optimal doses of reagents and a flocculent as well as pressure and saturation time were defined for which maximal reductions in the load of heavy metals were achieved. The usefulness of hydrogen peroxide as a means of enhancing flotation was tested. The use of two-stage precipitation permitted the reduction in heavy metals (Cd, Cu, Cr, Ni, Sn, Zn), eg by applying ALCAT 102 - lime milk at the level exceeding 80%.

**Keywords:** wastewaters containing heavy metals, wastewater treatment, chemical precipitation, flotation

Considering widely documented toxicity, heavy metals belong to a category of troublesome components existing in the amounts of typical anthropogenic pollutants discharged with industrial sewage [1, 2]. Difficulty in pretreating and treating such wastewaters is usually connected with the level of concentrations and speciation forms of metals in wastewaters [3-6]. Several processes using different physico-chemical or mechanical methods of treatment of metal parts are related with the use of water and producing industrial effluents [7-9]. The load of heavy metals in such sewages reaches different levels of concentration and is mostly affected by the processes of covering, detox bath residues, cleaning metal surfaces or washing production areas [7, 8, 10]. In processing effluents, heavy metals are found in different physicochemical forms: ionic, ionic-coordinative, emulsive (eg water-oily and suspensive) [3, 8, 9]. The treatment of such wastewaters is practically conducted by using different physicochemical methods [3, 8, 9, 11]. The stage of basic, chemical treatment is mostly preceded by applying the systems of

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physicochemical removal of water-dispersed pollutant loads [2, 3, 9]. The flocculation, sedimentation and flotation methods are used in the first place at the wastewater pretreatment stage [8-10]. The essential stage of pretreatment is often held with the use of preliminary oxidation or reduction and then with chemical precipitation with flocculation to thicken the pollutants before their final physical separation [2, 3, 8-10]. The separation of the aggregated pollutants from the pretreated water is often carried out by flotation methods in different technical versions [12-15].

The study presents the results of tests conducted in full technological scale in order to compare systems of the two-stage precipitation and coagulation to eliminate heavy metals from the effluents formed during the production of metal parts for domestic appliances. The aim of the research was also to test the usability of hydrogen peroxide to support the flotating way of separating the precipitated and thickened solid pollutants.

## Materials and methods

The industrial wastewaters originated from the processes of chemical cleaning of metal surfaces, chemical covering with metal coats (galvanizing, chromium plating and coppering) as well as from physical treatment and linking of metal parts. The processing system of the treatment plant (Fig. 1) consisted of the storage-equalization tank (1) (volume 15.0 m$^3$) for raw wastewaters, equipped with the circulating pressure pump (2), the pipe reactor (3), and the flotation chamber (4) (volume 1.0 m$^3$) with the pretreated water saturation set (5). Precipitation reagents (ALCAT 102, PIX 113, PAX 16, PAX XL1, SAX 18 (Kemipol Police [16]) or lime milk) prepared at stations (6) - (8) in combinations acc. to the test requirements were dosed into the pipe reactor (3). The 0.5% aqueous solution of the flocculent (Praestol 8292 BC (Stockhausen)) was introduced into the pressure pipeline at the flotator expansion chamber (5) inlet, from station (9) (in the amount of 30.0÷40.0 g/m$^3$ of wastewater), and then the 30% solution of hydrogen peroxide from the dosing stage (10) was also introduced. The total time of the wastewater retention in the flotation chamber (4) was 60.0 minutes. Maximal, day amount of the wastewaters was 10.0 m$^3$.

The concentrations of heavy metals (Cd, Cr, Cu, Ni, Sn, Zn) in raw wastewaters (point A - Figure 1) and the pretreated ones (point B - Fig. 1) were determined acc. to PN-EN ISO 15586:2004 and 2005 (mineralization was made acc. to PN-EN ISO 15587-1:2002 and 2005) by the method of *atomic absorption spectrometry* AAS with the use of the appliance Spectr AA Varian 220 SS. The other parameters were determined acc. to the following standards: the reaction (pH) - PN-90/C-04540/01, *total suspended solids* (TSS) - PN-EN 872:2005, *chemical oxygen demand* determined by dichromate method (COD) - PN-ISO 15705:2005, *biochemical oxygen demand* (BOD$_n$) - PN-EN 1899-1-2002. The COD parameter for the pretreated wastewater is presented after correction by subtracting the fraction of residual hydrogen peroxide on the basis of the following relation COD$_r$ = COD$_p$ - f×d (COD$_r$ - corrected after subtracting the fraction of residual hydrogen peroxide, the concentration of which (d) was determined iodometrically, $f$ = 0.25 - literature correction factor [17-19], COD$_p$ - determined experimentally). The parameters of the mixed raw and pretreated wastewaters with the use of the tested precipitating-coagulating systems are presented in Tables 1 and 2.
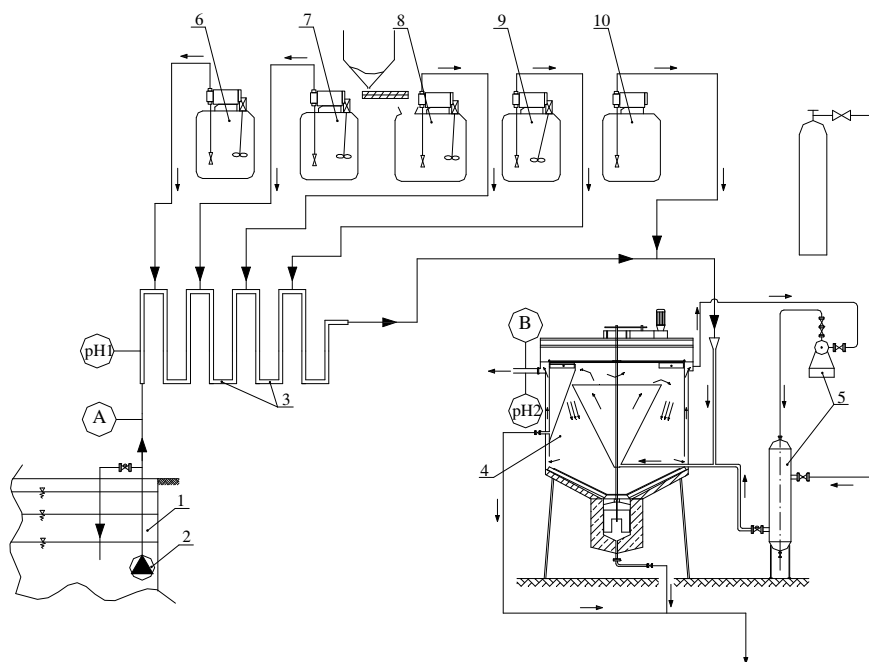
Fig. 1. The flow diagram of the experimental system; where: 1 - the ground storage-equalization tank, 2 - the circulation pump, 3 - the pipe reactor, 4 - the flotation chamber, 5 - the wastewater saturation set, 6 and 7 - the reagent preparation and dosing station, 8 - the lime milk preparation and dosing station, 9 - the flocculent preparation and dosing station, 10 - the perhydrol dosing station; A-B - points of taking samples for the analyses; pH1 and pH2 - the processing pH-meters

Table 1

Analytical values of the raw and pretreated (by precipitation with lime milk, flocculation and final pressure flotation) wastewaters from the production of metal parts for domestic appliances[*]

| Item | Parameter[a] | Unit | Raw wastewater[b] | Pretreated wastewater[c] |
|---|---|---|---|---|
| 1 | Reaction | [pH] | 5.2÷6.4 | 8.1÷8.9 |
| 2 | Total suspended solids TSS | [mg/dm$^3$] | 49.8÷204.8 | 2.7÷15.7 |
| 3 | Chemical oxygen demand COD$_r$ | [mgO$_2$/dm$^3$] | 287.9÷607.8 | 40.6÷103.5[d] |
| 4 | Biochemical oxygen demand BOD$_5$ | [mgO$_2$/dm$^3$] | 28.9÷70.2 | 11.6÷32.6 |
| 5 | Total chromium Cr | [mg/dm$^3$] | 2.67÷14.59 | 0.31÷3.95 |
| 7 | Tin Sn | [mg/dm$^3$] | 0.04÷0.16 | 0.00÷0.06 |
| 8 | Cadmium Cd | [mg/dm$^3$] | 0.00÷0.07 | 0.00÷0.2 |
| 8 | Copper Cu | [mg/dm$^3$] | 0.87÷8.76 | 0.06÷1.07 |
| 9 | Nickel Ni | [mg/dm$^3$] | 0.00÷0.21 | 0.06÷0.76 |

[*]flotation terms: saturation pressure - 400 kPa, time of saturation - 10.0 min, recirculation level - 15%, enhancing dose of H$_2$O$_2$ calculated in pure constituent 70.0 g/m$^3$ of the wastewater: [a] the determinations were made for samples taken from transportation pipeline (points A and B Fig. 1); [b] for 14 and [c] 13 measurement series; [d] for the pretreated wastewaters COD$_r$ = COD$_p$ – f×d (for f = 0.25 [17-19])

Table 2

Efficiency of the decrease in pollutants from wastewaters by using the systems with chemical precipitation (with coagulation) - flocculation with final pressure flotation[*]

| No. | Parameter[a)] | In %, the level of reduction by precipitation and coagulation with systems[**] PIX 113-SAX 18[a)] PAX XL1-SAX 18[b)] ALCAT 102-lime milk[c)] SAX 18-PAX 16[d)] |
|---|---|---|
| 1 | pH[f)] | 7.7 – 8.6  7.7 – 8.4  7.7 – 8.2  7.5 – 8.1 |
| 2 | TSS | 92.8 – 98.3  90.3 – 98.4  88.7 – 96.0  88.0 – 98.1 |
| 3 | COD | 33.1 – 60.7  30.9 – 56.9  46.4 – 66.2[e)]  28.4 – 48.9 |
| 4 | BOD$_5$ | 14.8 – 29.9  14.6 – 26.7  16.9 – 40.8  15.5 – 36.7 |
| 5 | Cr total | 52.1 – 67.0  49.2 – 68.5  80.5 – 88.6  51.2 – 60.1 |
| 6 | Zinc Zn | 71.7 – 84.7  60.3 – 71.4  90.2 – 98.7  61.3 – 76.4 |
| 7 | Tin Sn | 80.7 – 95.7  80.3 – 91.4  90.2 – 98.7  81.3 – 86.4 |
| 8 | Cadmium Cd | > 55.0  > 55.0  > 85.0  > 55.0 |
| 8 | Copper Cu | 69.6 – 84.6  73.6 – 84.9  90.5 – 99.1  60.7 – 69.2 |
| 9 | Nickel Ni | > 60.0  > 60.0  > 90.0  > 60.0 |

[*]the terms of flotation: saturation pressure - 450 kPa, saturation time - 10.0 min, the level of recirculation - 15%, enhancing dose of $H_2O_2$ calculated in pure constituent for the case: [a)] not used, [b)] 80.0, [c)] 50.0 and [d)] 60.0 g/m$^3$ of wastewaters; [**]List made basing on: [a)] 10, [b)] 13, [c)] 9 and [d)] 16 measurement series; [e)] for pretreated wastewaters $COD_r = COD_p – f \times d$ (for f = 0.25 [17-19]); [f)] values after 2nd stage of precipitation.

## Results and discussion

The processes of treating surfaces of metal parts for producing domestic appliances were mainly based on galvanizing, chromium plating and coppering. Heavy metals (M) in the treated wastewaters were found in different speciation forms, eg: $M^{n+}$(aq) or $[M(X)_x(H_2O)_y]^{x-n}$ (where: X - ions found in the wastewaters: $Cl^-$, $SO_4^{2-}$, $CO_3^{2-}$ and $NH_3$), which had a significant effect on eliminating by precipitation into sparingly soluble forms $M(OH)_{n(s)}$ [3, 5, 7, 8]. The treatment process by using the tested systems was based on applying the phenomenon of the precipitation of sparingly soluble hydroxide forms of type $M(OH)_{n(s)}$, eg, $Cr(OH)_{3(s)}$, $Cu(OH)_{2(s)}$, $Zn(OH)_{2(s)}$, $Ni(OH)_{2(s)}$, and $Cd(OH)_{2(s)}$, according to the simplified scheme of the reaction: $M^{n+}$(aq) + $nOH^- \rightarrow M(OH)_{n(s)}$. An essential problem to achieve maximal reductions was to define the optimal reaction providing the lowest solubility of the precipitated forms $M(OH)_{n(s)}$. Too high pH resulted in the increase in solubility of solid hydroxide forms acc. to the simplified reaction: $M(OH)_{n(s)} + mOH^- \rightarrow [M(OH)_{n+m}]^{-m}$. In the experimentally determined, slightly alkaline, final reaction (pH 7.5÷8.6) (Table 2), some amount of metals was found in soluble coordinative forms with prevailing monohydroxy ionic bonds, eg, $[CrOH]^{2+}$, $[CuOH]^+$, $[ZnOH]^+$, and $[CdOH]^+$ as well as $[NiOH]^+$ [8-10, 20, 21]. When the alkaline reaction decreased, the level of metal reduction was lowered, which was a result of dissolving hydroxide deposits and of forming coordinative forms by ligands $OH^-$, eg zinc to the forms of $[Zn(OH)_3]^-$ and $[Zn(OH)_4]^{2-}$, or copper and nickel: $[Cu(OH)_3]^-$, $[Cu(OH)_4]^{2-}$ and $[Ni(OH)_4]^{2-}$ [8-10, 20, 21]. The process of eliminating metals was also affected by sorption of the non-precipitated ones, eg $M^{n+}$(aq) on $Al(OH)_{3(s)}$ and $Fe(OH)_{3(s)}$, as a result of aluminum and iron hydrolysis introduced with reagents and on metal hydroxides precipitated from the wastewaters. The amount of sorbed metals occurred as ions: aqua-ions eg $Cu^{2+}$(aq), $Ni^{2+}$(aq), or $Cd^{2+}$(aq), or coordinative ions resulting from the presence of chlorides, carbonates or sulfates in the wastewaters, eg: $[ZnCO_{3(aq)}]^0$, and $[ZnSO_{4(aq)}]^0$, $[CuSO_{4(aq)}]^0$ and $[NiCO_{3(aq)}]^0$ [8, 9, 20]. Colloidal sols being

an effect of multi-stage hydrolysis might be found in significant concentrations in some phases of wastewater treatment. These forms may be eliminated by coagulation with $Al^{3+}$ and $Fe^{3+}$ ions and coprecipitation while forming floccules.

The use of two-stage precipitation of heavy metals elevated their reduction with reference to one-stage precipitation, eg with the use of lime milk (Table 1) and made it possible to establish precisely the reaction (pH) at which the reductions were maximal. The application of hydrogen peroxide increased the effectiveness of eliminating the precipitated and thickened pollutants from the pretreated wastewaters. This phenomenon was based on the use of the micro-bubble molecular oxygen produced from the decomposition of hydrogen peroxide acc. to the reaction: $H_2O_2 + 2OH^- \rightarrow O_{2(g)} + 2H_2O$ [22]. Enhancing flotation of the pollutants with hydrogen peroxide was possible for the systems: PAX XL1 - SAX 18, ALCAT 102 - lime milk and SAX 18 - PAX 16. For PIX 113 - SAX 18, the presence of $Fe^{3+}$ made hydrogen peroxide decompose instantly and clearly worsened the quality parameters of the treated wastewaters at the installation outlet.

## Conclusions

The application of the discussed method of pretreatment with the use of the two-stage precipitation of sparingly soluble forms permits the efficient elimination of heavy metals found in soluble forms of ionic systems, as well as in forms of colloids and suspensions in the total wastewaters from the production of domestic appliances. The most effective system (the reduction of 80.5÷99.1%) to eliminate heavy metals occurred to be the pretreatment system ALCAT 102 - lime milk - flocculation - pressure flotation with pH = 7.7÷8.2 and with an enhancing dose of hydrogen peroxide 50.0 $g/m^3$ of the wastewater.

## References

[1]   Kong IC, Bitton G, Koopman B, Jung KH. Heavy metal toxicity testing in environmental samples. Rev Environ Contam Toxicol. 1995;142(3):119-147.
[2]   Rüffer H, Rosenwinkel KH. Taschenbuch der Industrieabwasserreinigung. München Wien: Oldenbourg Verlag, 1991:503-530.
[3]   Tünay O, Kabdasli NI, Tasli R. Pretreatment of complexed metal wastewaters. Water Sci Technol. 1994;29(9):265-274.
[4]   Lesmana SO, Febriana N, Soetaredjo FE, Sunarso J, Ismadji S. Studies on potential applications of biomass for the separation of heavy metals from water and wastewater. Biochem Eng J. 2009;44(1):19-41.
[5]   Sud D, Mahajan G, Kaur M. Agricultural waste materials as potential adsorbent for sequestering heavy metal ions from aqueous solutions - A review. Biores Technol. 2008;99(14):6017-6027.
[6]   Ahluwalia SS, Goyal D. Microbial and plant derived biomass for removal of heavy metals from wastewater. Biores Technol. 2007;98(12):2243-2257.
[7]   Kiptoo JK, Ngila JC, Sawula GM. Speciation studies of nickel and chromium in wastewater from an electroplating plant. Talanta. 2004;64(1):54-59.
[8]   Barakat MA. New trends in removing heavy metals from industrial wastewater. Arab J Chem. 2011;4(4):361-377.
[9]   Fenglian F, Qi W. Removal of heavy metal ions from wastewaters: A review. J Environ Manage. 2011;92(3):407-418.
[10]  Kurniawan TA, Chan GYS, Lo WH, Babel S. Physico-chemical treatment techniques for wastewater laden with heavy metals. Chem Eng J. 2006;118(1-2):83-98.
[11]  Al Aji B, Yavuz Y, Koparal AS. Electrocoagulation of heavy metals containing model wastewater using monopolar iron electrodes. Sep Purif Technol. 2012;86:248-254.
[12]  Rubio J, Souza ML, Smith RW. Overview of flotation as a wastewater treatment technique. Mineral Eng. 2002;15(3):139-155.

[13] Peleka EN, Lazaridis NK, Matis KA. A hybrid flotation: Microfiltration cell for effluent treatment. Int J Environ Waste Manage. 2011;8(3-4):273-285.

[14] Zamboulis D, Pataroudi SI, Zouboulis AI, Matis KA. The application of sorptive flotation for the removal of metal ions. Desalination. 2004;162(1-3):159-168.

[15] Santander M, Valderrama L, Guevara M, Rubio J. Adsorbing colloidal flotation removing metals ions in a modified jet cell. Mineral Eng. 2011;24(9):1010-1015.

[16] http://www.kemipol.com.pl/products

[17] Kang YW, Cho MJ, Hwang KY. Correction of hydrogen peroxide interference on standard chemical oxygen demand test. Water Res. 1999;33(5):1247-1251.

[18] Żak S. Problem of correction of the chemical oxygen demand values determined in wastewaters treated by methods with hydrogen peroxide. Proc ECOpole. 2008;2(2):409-414.

[19] Talinli I, Anderson GK. Interference of hydrogen peroxide on the standard COD test. Water Res. 1992;26(1):107-110.

[20] Nurchi VM, Villaescusa I. Sorption of toxic metal ions by solid sorbents: a predictive speciation approach based on complex formation constants in aqueous solution. Coord Chem Rev. 2012;256(1-2):212-221.

[21] Charerntanyarak L. Heavy metals removal by chemical coagulation and precipitation. Water Sci Technol. 1999;39(10-11):135-138.

[22] http://h2o2.com/industrial/applications.aspx?pid=102&name=Iron-Metals-Removal-with-Hydrogen-Peroxide

# OCZYSZCZANIE ŚCIEKÓW TECHNOLOGICZNYCH Z METALI CIĘŻKICH METODĄ WYKORZYSTUJĄCĄ FLOTACJĘ

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**Abstrakt:** Przeprowadzono badania w pełnej skali technologicznej, mające na celu wytypowanie optymalnych układów dwustopniowego strącania i koagulacji (PIX 113 - SAX 18, PAX XL1 - SAX 18, ALCAT 102 - mleko wapienne i SAX 18 - PAX 16) w procesie usuwania metali ciężkich ze ścieków z linii wytwarzania podzespołów do sprzętu gospodarstwa domowego. Wytrącone zanieczyszczenia zagęszczano flokulacyjnie i wydzielano techniką flotacji ciśnieniowej wspomaganej nadtlenkiem wodoru. Instalacja doświadczalna o maksymalnej przepustowości 10,0 $m^3$/d składała się z ziemnego zbiornika magazynująco-uśredniającego, rurowego reaktora procesowego, stacji flotacji ciśnieniowej oraz stacji przygotowania i dozowania reagentów. Wyznaczono optymalne dawki reagentów oraz flokulantu, a także ciśnienia i czasu saturacji, dla których zachodziły maksymalne redukcje ładunku metali ciężkich. Sprawdzono przydatność nadtlenku wodoru w procesie wspomagania flotacji. Zastosowanie dwustopniowego strącania pozwoliło na uzyskanie redukcji metali ciężkich (Cd, Cu, Cr, Ni, Sn, Zn) np. za pomocą układu ALCAT 102 - mleko wapienne na poziomie przekraczającym 80%.

**Słowa kluczowe:** ścieki zawierające metale ciężkie, oczyszczanie ścieków, strącanie chemiczne, flotacja