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IMPROVEMENT OF THE FERRITISATION METHOD FOR REMOVAL OF NICKEL COMPOUNDS FROM WASTEWATER

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Abstract: A process for comprehensive treatment of wastewater flows of electroplating facilities was developed with ferritisation-based removal of nickel compounds. Effects of ratios of heavy metals concentrations and pulse electromagnetic discharges on ferritisation-based treatment of nickel-containing wastewater were studied. The treatment sediments were analysed by qualitative and quantitative phase analysis. Application of electromagnetic wastewater treatment for low-temperature ferritisation was proved to be economically viable.

Key words: water, treatment, electromagnetic treatment, ferritisation, nickel.

1. Introduction

Wastewater flows of electroplating facilities belong to the most hazardous industrial sources of environmental pollutants, as they contain ions of such heavy metals as iron, copper, zinc, chromium, nickel, etc. Discharges of such toxic wastewater flows into water bodies without a due treatment (including both diluted rinsing water and concentrated exhausted electrolytes, or eluates of regeneration of ion-exchange filters) disturb natural biological processes and reduce quality of natural water sources. In their turn, such adverse impacts affect sanitary living conditions of local residents and the national economy due to losses of valuable heavy metals. Now, more than 4000 electroplating facilities operate in Ukraine. Nationwide, these facilities generate more than 500 million m^3 of wastewater per annum. The rate of recuperation of heavy metals and duly treated wastewater reaches less than 10%, while in the Western Europe relevant figures are close to 97-98% (Hammer, 1996). Therefore, enhancement of environmental security by introduction of highly efficient wastewater treatment equipment, and by development of low-waste energy efficient technologies with closed resource cycles is now a priority sphere for development of the Ukrainian economy.

In recent years, electroplating facilities tried to enable comprehensive treatment of their wastewater flows by separation of particular electroplating operations (e.g. by establishing a separate nickel-plating unit). In such a case, efficient local wastewater treatment systems may be installed on-site.

In the majority of cases, Ukrainian electroplating facilities apply traditional reagent-based technologies to process wastewater flows with nickel compounds (Zapolsky, 2000). As a result, almost 2.4 thousand tons of highly toxic (and valuable) nickel are discharged annually into natural water bodies of Ukraine with inadequately treated wastewater discharges. Application of high doses of reagents for the wastewater treatment makes the water unsuitable for reuse in facility level closed water supply systems without its further purification. Reagent-based wastewater treatment technologies generate bulky sediments, poorly suitable for dehumidification. Their further utilisation is a difficult and expensive process. Therefore, development of a comprehensive, resource-efficient technology for treatment of nickel-containing wastewater is a promising option for improvement of environmental safety. Such a treatment presumes application of methods allowing to ensure the necessary level of wastewater purification with efficient removal of heavy metals in parallel with reduction of reagents dosage and amounts of sediments generated.

Accounting for the above considerations, the ferritisation method appears to be well suitable for treatment of wastewater flows of nickel-plating units that contain iron and nickel ions (Goldman, 2006; Tamaura et al. 1991; Mandaokar et al., 1994). The method allows to remove efficiently both heavy metal ions and organic compounds from the wastewater. Besides that, the method allows to remove chemically stable sediments easily from the cleaned water using magnetic field, as the sediments have ferromagnetic properties.

The range of key factors that regulate ferritisation treatment processes are known to include pH, temperature, concentrations of components and their ratios (Kochetov et al., 2010). It is worth to note that only

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*Corresponding Author, e-mail: gkochetov@gmail.com limited published information is available on how iron to nickel concentrations ratios influences the ferritisation process. Besides that, the ferritisation process is rather energy-intensive as it usually requires temperatures over 70ºC. As an alternative to thermal intensification of the process, medium amplitude pulse electromagnetic discharges may be applied (Kovaliova, 2012). However, such an option is also energy intensive.

Therefore, the aim of this study is associated with experimental research of influence of Fe^{2+} to Ni^{2+} concentrations ratios and application of pulse low amplitude electromagnetic discharges on the ferritisation-based comprehensive treatment of electroplating wastewater with removal of nickel compounds.

2. Experimental methods

Model solutions were used – in terms of concentrations and composition they were close to wastewater of nickel-plating units. Chemically pure $FeSO_4 \cdot 7H_2O$ and $NiSO_4 \cdot 7H_2O$ reagents were used. To adjust pH of the reaction mixture, 10% NaOH solution was added while stirring. See ferritisation parameters for 5 experimental series in table 1.

Two laboratory units were used for ferritisation process. The first unit operated with thermal treatment of model solutions (fig. 1a), while the second one used pulse electromagnetic treatment (fig. 1b), with magnetic flux amplitude of 0.23 to 0.43 T in the impact zone, operational frequency up to 0.9 kHz. Power capacity of this device is about 30 W.

Tab. 1. Ferritisation parameters at pH = 9.51.

Series #	Treatment		Ratio Z	T,ºC	Treatment time, min	Bubbling (O_2), m^3/hour
1	Thermal	with aeration	5:1	70	15	0.12
2			4:1			
3			2:1			
4		without aeration				-
5	Electromagnetic pulse			17	5	0.12

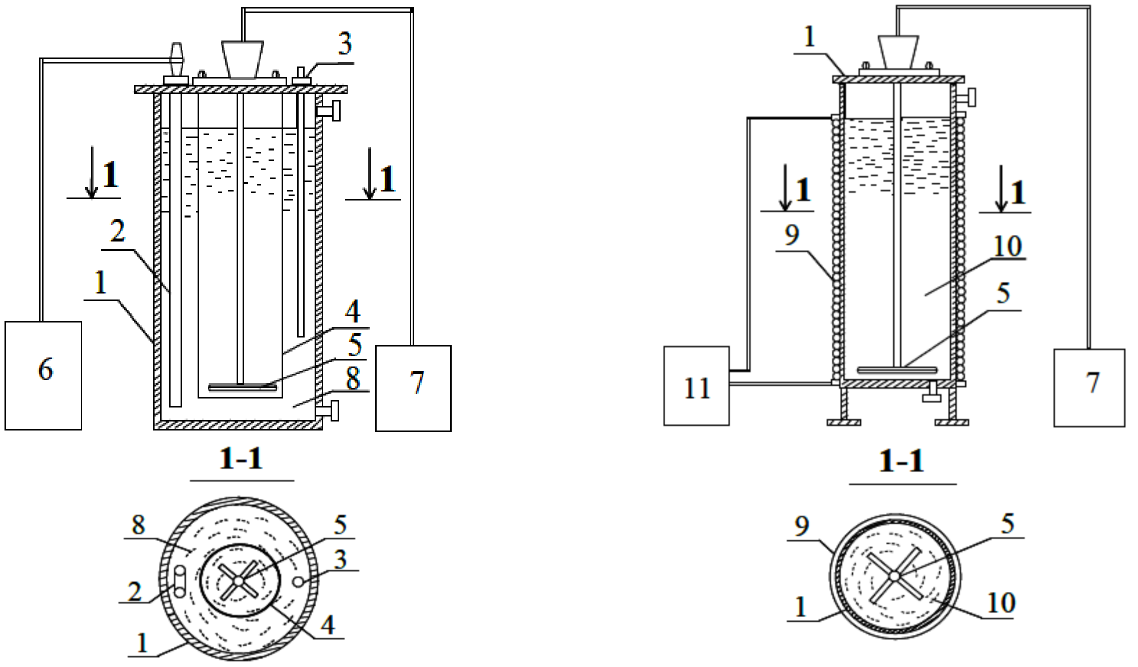


Fig. 1. Laboratory ferritisation units with thermal (a) and pulse electromagnetic (b) treatment of solutions: 1 – case, 2 – tubular electric heaters, 3 – thermometer, 4 – cylinder with treated solution, 5 – air distribution system, 6 – RPSh-5 voltage adjuster, 7 – compressor , 8 – water, 9 – aerial wire, 10 – treated solution, 11 – electronic unit.

The degree of water purification after ferritisation was estimated by equation:

$$a = \left(C_{in.} - C_{res.}\right) \cdot 100\,\% / C_{in.} \tag{1}$$

where: $C_{in.}$ is initial concentration of nickel ions in wastewater in mg/l and $C_{res.}$ is residual concentration of nickel ions in wastewater in mg/l.

Solution pH was controlled by pH-150 MA millivoltmeter. Residual concentrations of iron and nickel ions in purified water were measured by Saturn-2 flame atomic absorption spectrophotometer.

X-ray powder diffraction study of the sediments was carried out with application of Shimadzu XRD-6000 X-ray diffractometer in step mode (Cu - Kα radiation). XRD patterns were processed with application of Match V.1.9a software (Crystal Impact) and reference cards ICCD PDF2 + - 2003 (The International Centre for Diffraction Data).

In the case of thermal wastewater treatment, heat power consumption was estimated by equation:

$$W = C \cdot V \cdot \left(T_2 - T_1\right) \tag{2}$$

where: C is water specific heat capacity; V is volume of the wastewater heated in m^3 and T_1, T_2 initial and final temperatures of the wastewater in °C.

Estimates were made assuming efficiency of electric heating of 95%. In the case of pulse electromagnetic treatment, estimates were made accounting for output power of the unit, volumes of wastewater treated and duration of ferritisation process.

3. Results and discussion

In the course of ferritisation processes with application of different methods of wastewater treatment, black disperse suspensions initially formed and later transformed into crystalline sediments of lower volume and dense structure. Table 2 contains results of study of thermal wastewater treatment, showing how alteration of ratios of iron to nickel concentrations (Z) may affect volumes of sediments in the samples studied. As data of Table 2 suggest, at Z (2:1), (4:1), sufficiently dense sediments were produced. After drying they become dark brown in colour. It is worth to note that at higher Z values (5:1), volume of the sediments increases and dried sediments become light brown in colour. Data of Table 2 suggest that volumes of the crystalline sediments obtained are 1.5 to 2 times lower comparatively to sediments of reagent-based wastewater treatment (Zapolsky, 2000).

Results in table 2 also show that alteration of wastewater treatment methods also changes pH of treated water and volumes of the sediments obtained. As the Table data suggest, pH of treated water (except in the case of experimental series #4) allows to reuse it in electroplating facilities according to the due Ukrainian standards. Besides that, volumes of crystalline sediments in the case of pulse electromagnetic ferritisation treatment are lower by 30% and 14% comparatively to sediments in the case of thermal water treatment with aeration and without aeration, respectively.

Table 3 shows residual concentrations of iron and nickel ions in treated water depending on concentration ratios Z in initial solutions. As the ratios increase, residual concentrations of both iron and nickel decrease. Results of experimental series #1 suggest that wastewater after ferritisation treatment may be used in closed water supply systems of electroplating facilities only for rinsing purposes. But the water cannot be used for production of electrolyte solutions, as residual levels of iron ions in the water exceed relevant MACs. Accounting for these considerations, we propose to apply further treatment of the water to meet the required quality standards for this purpose.

Tab. 2. Sediments volumes and pH of treated water after ferritisation.

Exp. series #	Treatment methods		Ratio Z	pH		V sed. %
				Before treatment	After treatment	
1	Thermal	with aeration	5:1	9.5	8.72	71
2			4:1		8.31	49
3			2:1		6.96	52
4		without aeration			9.07	64
5	Pulse electromagnetic				7.87	45

Tab. 3. Results of treatment of model wastewater solutions with nickel ions, at different Z ratios.

Exp. series #	Ratios Z	Concentrations (mg/l)								Degree of purification, %	
		Before treatment		After treatment		MAC (category 1)		MAC (category 2)			
		Fe^{2+}	Ni^{2+}	Fe^{2+}	Ni^{2+}	Fe^{2+}	Ni^{2+}	Fe^{2+}	Ni^{2+}	Fe^{2+}	Ni^{2+}
1	5:1	8760	1752	0.23	0.26	0.3	5.0	0.1	1.0	99.9	99.8
2	4:1	7300	1825	1.92	1.94					99.7	98.8
3	2:1	3820	1910	4.13	2.12					98.7	98.7

Table 4 shows residual concentrations of iron and nickel ions in treated water for different methods of wastewater treatment. The Table data suggest that water after pulse electromagnetic treatment may be reused in water supply systems of electroplating facilities only for rinsing operations.

We also analysed efficiency of ferritisation-based removal of nickel compounds from wastewater of electroplating facilities in comparison to other methods (Hammer, 1996). As data of table 5 suggest, the ferritisation process ensures higher degrees of removal of heavy metals from electroplating wastewater (98.7-99.9%), its removal efficiency exceeds efficiency of other wastewater treatment methods.

Based on available information on mechanisms of ferritisation processes, we may expect that the sediments will demonstrate a rather diverse phase composition, as they may contain different modifications of iron oxides and oxyhydrates, as well as so called phase particles - i.e. genuine ferromagnetic particles that demonstrate paramagnetic properties due to their small sizes (Yund and Kullerd, 1964).

Structural analysis of the ferritisation sediments suggests that the samples are highly crystalline: their XRD graphs display intensive narrow peaks in the range of 2Θ from 30º to 45º (Fig. 2a). Phase identification analysis of the samples reveals presence of iron oxides: Fe_3O_4 and γ-Fe2O3, and nickel ferrite Fe_2NiO_4. The phases are ferromagnetic, they have spinel-type crystalline lattice and are practically insoluble in alkaline and slightly acidic water. Their crystalline lattice parameters were determined based on XRD peaks in the precision area (Tab. 6).

Results of the quantitative phase analysis are shown at figure 2b. The graphs suggest that increasing concentrations of iron ions in initial model solutions result in increase of levels of nickel ferrite phase in sediments.

Tab. 4. Results of treatment of model wastewater solutions with application of different treatment methods (Z = 2:1).

Heavy metals ions	$C_{in.}$, mg/l	Treatment methods						MAC (cat. 1)
		Thermal				Pulse electromagnetic		
		without aeration		with aeration				
		$C_{res.}$, mg/l	α, %	$C_{res.}$, mg/l	α, %	$C_{res.}$, mg/l	α, %	
Fe^{2+}	3820	0.21	99.9	4.13	98.7	0.26	99.9	0.3
Ni^{2+}	1910	7.56	95.5	2.21	98.7	3.9	97.6	5.0

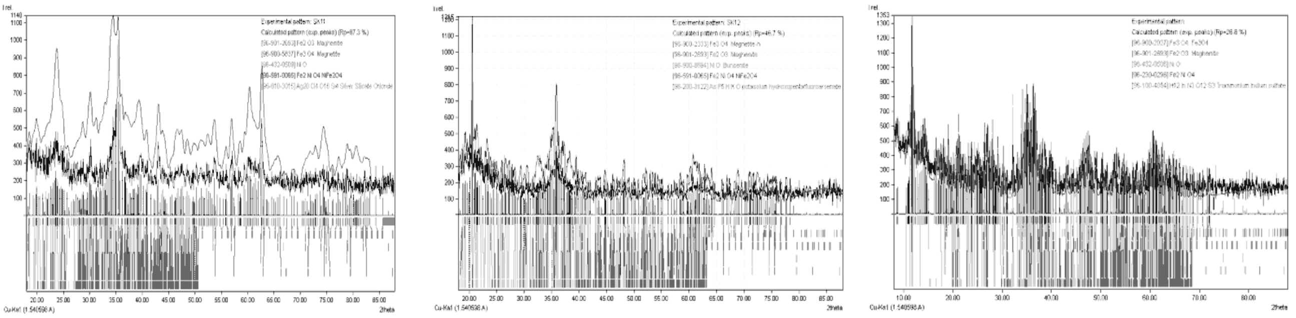
Tab. 5. Comparative analysis of different wastewater treatment methods in terms of nickel removal.

#	Methods	Purification degree, %	
		Fe^{2+}	Ni^{2+}
1	Reagent-based (milk of lime)	94 - 96	96
2	Electroflotation	98 - 99.3	98
3	Galvanic coagulation	96 - 98	99
4	Adsorbtion - on antracite(A-1) - on charcoal(BAU)	 - 70	 65 96 -98
5	Biological	90	50 - 90
6	Ferritisation	98.7 - 99.9	98.7 - 99.8

Tab. 6. Crystalline lattice parameters (a, nm) in sediment samples.

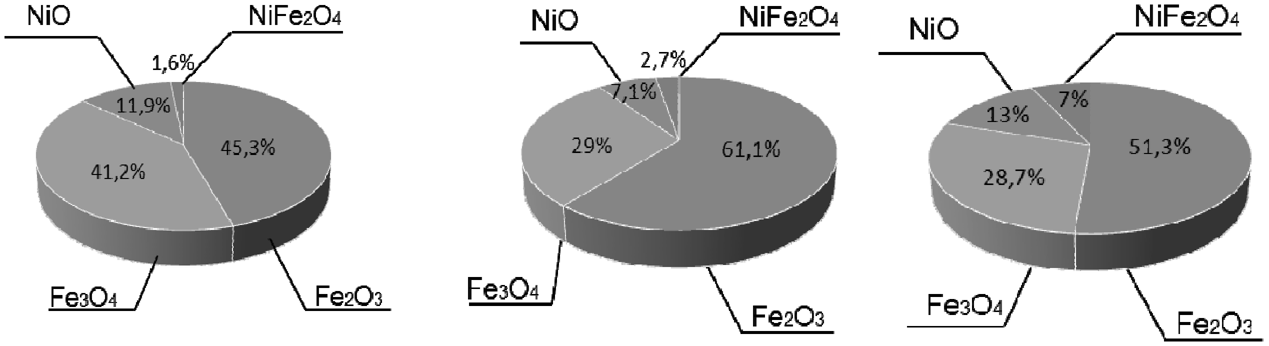
Sample #	Ferrite phases		
	Fe_3O_4	γ-Fe_2O_3	Fe_2NiO_4
1	0.83949	0.83386	0.83400
2	0.83960	0.83386	0.83400
3	0.83953	0.83386	0.83409

a)



Sample # 1 Sample # 2 Sample # 3

b)



Sample # 1 Sample # 2 Sample # 3

Fig. 2. XRD graphs (a) and phase composition (b) of sediments obtained at initial Fe^{2+}/Ni^{2+} ratios of: #1 – 2:1; #2 – 4:1; #3 – 5:1.

XRD graph of the sediment sample obtained by thermal wastewater treatment without aeration reveals highly disperse phases of Fe and Fe_3O_4. In the case of samples obtained with aeration and with application of thermal and pulse electromagnetic treatment, relevant XRD graphs contained peaks corresponding to interplanar spacings of crystalline oxygen-containing iron and nickel compounds. XRD graph of the sediment sample obtained with aeration reveals most clearly identifiable phases with cubic lattice: magnetite Fe_3O_4 with lattice parameter a = 8.396 Å and ferromagnetic iron oxide γ-Fe_2O_3 (a = 8.339 Å). Besides that, we also identified peaks of nickel ferrite $NiFe_2O_4$ and nickel oxide NiO phases.

In the case of pulse electromagnetic treatment, peaks of nickel ferrite $NiFe_2O_4$ phase (with inverse spinel cubic lattice and a = 8.339 Å), as well as peaks of nickel oxide NiO and nickel hydroxide $Ni(OH)_2$ were observed in the obtained sediment samples. Therefore, application of electromagnetic activation for ferritisation process promotes formation of crystalline phases with ferromagnetic properties.

Data of Table 7 allow to compare the power consumption of thermal and pulse electromagnetic methods of activation of ferritisation-based treatment of electroplating wastewater for removal of nickel compounds. The data analysis suggests that the pulse electromagnetic method allows to reduce electric energy consumption in 2 to 2.5 times comparatively to the thermal one.

Tab. 7. Power consumption of wastewater treatment methods.

Exp. series #	Treatment methods		Power consumption, kWh/m^3
3	Thermal	with aeration	67.2
4		without aeration	65.1
5	Pulse electromagnetic		26.9

Besides that, the ferritisation method is more advantageous in terms of environmental security and chemical stability of the sediments generated. We consider potential options for their utilisation: use in production of low-coercitivity ferrites or their application as raw materials for production of construction materials (bricks or ceramics).

4. Conclusions

Therefore, the analysis of studies in the sphere of ferritisation-based wastewater treatment methods for removal of heavy metals allows to evaluate the treatment as highly prospective one due to its clear technological, economic and environmental advantages comparatively to reagent-based treatment methods.

Influence of Fe^{2+} to Ni^{2+} ions concentration ratios on ferritisation treatment of electroplating wastewater was studied. Experimental results demonstrated that changes in Fe^{2+} to Ni^{2+} ions concentrations ratios in initial solutions affect both degrees of purification and quality of the sediments obtained. Experimental results of wastewater treatment with application of the proposed pulse electromagnetic activation suggest that the method ensures high degrees of wastewater purification (97.6-99.9%) allowing to reuse the treated water in closed water supply systems of electroplating facilities. Besides that, in comparison to the thermal activation option, power consumption was found to decrease substantially, making the technology cheaper and thus more attractive for investments of electroplating facilities. The wastewater treatment technology generates crystalline ferromagnetic sediments. Due to presence of oxides and ferrites, the sediments may be easily separated and are more chemically and thermodynamically stable (Zapolsky, 2000), allowing to find practical options for their utilisation in the marketable products, in contrast to sediments of reagent-based wastewater treatment technologies.

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