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Integrated treatment of chromium-containing wastewater with application of the improved ferritization method

Zintegrowane oczyszczanie ścieków zawierających chrom przy zastosowaniu ulepszonej metody ferrytyzacji

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Keywords: *ferritization, chromium ions, sediment, wastewater*

Abstract
Environmental protection problems are substantively associated with treatment of wastewater flows of industrial facilities. Therefore, it is advisable to improve and introduce resource efficient technologies allowing to remove toxic compounds from the wastewater and to utilize wastewater treatment residues. In this research study, ferritization-based wastewater treatment was studied to remove chromium (VI) compounds, that belong to the first hazards class chemicals. Comparative efficiency of application of thermal and electromagnetic pulse activation of the ferritization process was evaluated. Appropriate experimental installations were assembled and the main parameters of the treatment process were identified: the ratio of iron (II) and chromium (VI) ions, the amplitude of the magnetic field, the frequency of electromagnetic pulses, the duration of the ferritization process, the temperature and pH of the reaction mixture.
Expediency of using electromagnetic pulse activation of the reaction mixture has been studied and scientifically substantiated. Optimal values of the electromagnetic field amplitude for this activation method have been determined, that reach 0.01-0.09 T, as well as the ratio of concentrations of heavy metal ions Fe^{2+}/Cr^{6+} = 10/1 for wastewater from the chromium electroplating production line. The treated water was shown to meet requirements for its reuse in production processes.
The developed technology ensures introduction of a closed-circuit water supply at industrial facilities. High chemical stability of after-treatment sediments (residues) allows their safe disposal, in particular, their utilization in construction materials and paint coatings. Thus, this study contributes to improvement of environmental conditions at industrial facilities due to introduction of modern methods for processing toxic liquid waste flows, that also ensure rational use of water, reagents and energy at an industrial facility.

Słowa kluczowe: *ferrytyzacja, jony chromu, osad, ścieki*

Streszczenie
Problematyka ochrony środowiska jest merytorycznie związana z oczyszczaniem ścieków z obiektów przemysłowych. Dlatego wskazane jest doskonalenie i wprowadzanie zasobooszczędnych technologii pozwalających na usuwanie toksycznych związków ze ścieków i utylizację pozostałości po oczyszczeniu ścieków. W niniejszym badaniu badano oczyszczanie ścieków metodą ferrytyzacji w celu usunięcia związków chromu (VI), które należą do substancji chemicznych pierwszej klasy zagrożenia. Oceniono porównawczą efektywność zastosowania termicznej i elektromagnetycznej aktywacji impulsowej procesu ferrytyzacji. Zbudowano odpowiednie instalacje doświadczalne i zidentyfikowano główne parametry procesu oczyszczania: stosunek jonów żelaza (II) i chromu (VI), amplitudę pola magnetycznego, częstotliwość impulsów elektromagnetycznych, czas trwania procesu ferrytyzacji, temperaturę i pH mieszaniny reakcyjnej.
Celowość stosowania aktywacji mieszaniny reakcyjnej impulsem elektromagnetycznym została zbadana i potwierdzona naukowo. Wyznaczono optymalne wartości amplitudy pola elektromagnetycznego dla tej metody aktywacji, które sięgają 0,01-0,09 T, a także stosunek stężeń jonów metali ciężkich Fe2+/Cr6+ = 10/1 dla ścieków z linii produkcyjnej galwanizacji chromu. Wykazano, że uzdatniona woda spełnia wymagania dotyczące jej ponownego wykorzystania w procesach produkcyjnych.
Opracowana technologia zapewnia wprowadzenie wody o obiegu zamkniętym w obiektach przemysłowych. Wysoka stabilność chemiczna osadów (pozostałości) po oczyszczeniu pozwala na ich bezpieczną utylizację, w szczególności wykorzystanie w materiałach budowlanych i powłokach malarskich. Tym samym niniejsze opracowanie przyczynia się do poprawy warunków środowiskowych w obiektach przemysłowych poprzez wprowadzenie nowoczesnych metod przetwarzania strumieni toksycznych ścieków ciekłych, które zapewniają jednocześnie racjonalne wykorzystanie wody, odczynników i energii w obiekcie przemysłowym.

Introduction

In technological processes of electroplating production, a significant amount of exhausted electrolytes with a high concentration of heavy metals is formed. Application of the traditional reagent-based methods for treatment of these wastewater flows does not ensure a proper degree of removal of heavy metals and leads to formation of bulky and chemically unstable sediments [1]. Their disposal requires significant consumption of energy and chemical reagents [2,6]. In addition, application of these technologies entails significant economic losses due to losses of valuable non-ferrous metals [8]. Liquid electroplating waste cannot be discharged into centralized sewers due to associated environmental hazards, since chromium (III) and – especially – chromium (VI) compounds are extremely toxic to humans, as well as flora and fauna.

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As a rule, a reagent-based treatment of wastewater containing hexavalent chromium compounds is carried out in two stages. At the first one, a chemical reduction of the hexavalent form of chromium into its less toxic trivalent form takes place; and the second one included its sedimentation, as a rule, in the form of chromium (III) hydroxide.

The ferritization method is a promising one for industrial wastewater treatment. [2]. Analysis of prior studies [9] suggests that application of the thermal activation method of the ferritization process entails significant energy costs. Therefore, authors [4] proposed and scientifically substantiated feasibility of using electromagnetic pulse (EMI) activation of the reaction mixture. In paper [7], EMI activation was for the first time used to remove Cr^{6+} ions from wastewater. However, the technological factors of the ferritization process and its activation remained insufficiently studied.

The aim of this experimental study is – to identify the optimal values of the key technological parameters of the ferritization treatment with EMI activation of the process: the ratio of iron and chromium ions in the ferritization reaction mixture and the amplitude of the magnetic field of EMI activation. To reach the aim, the following research objectives were defined:

- to study influence of the magnetic field amplitude on the degree of chromium ions removal from the reaction mixture;
- to study quantitative and qualitative composition of the ferritization sediments at variable amplitudes of the magnetic field;
- to evaluate methods for safe disposal of the sediments obtained.

Experimental research methods

Exhausted electrolytes from the chromium electroplating line of a production facility were used to carry out ferritization studies on processing of concentrated chromium-containing wastewater. Activation of the reaction mixture was carried out in two ways: as thermal one [9] and EMI [7]. The process of ferritization with thermal activation was carried out at the installation, the basic technological scheme of which is shown at Fig. 1. It is known that the course of the ferritization process is mainly influenced by the following factors: the ratio of heavy metal concentrations, pH, temperature (T) of the reaction mixture, and time (τ) of the ferritization process [9]. Six series of experiments were performed, in which the concentration of Cr^{6+} was 1 g/dm^3, and the Fe^{2+}/Cr^{6+} ratio varied from 4/1 to 15/1 and at constant optimal values of pH = 10.5; T = 70°C and τ = 15 min, which were determined in [7]. The degree of Cr removal from chromium-containing wastewater was determined by the equation:

$$\alpha = (C_{ini.} - C_{res.}) \cdot 100\% / C_{ini.},$$

here C_{ini} and C_{res} refer to initial and residual concentrations of Cr ions in the wastewater.

In order to carry out research of ferritization with EMI activation, a laboratory unit was designed and assembled (Fig. 2), in which the reaction mixture was activated by alternating magnetic fields (Fig. 3) in a ferrite reactor. The concentration of the main component (Cr^{6+} ion) in these solutions reached 1 g/dm^3. The total concentration of heavy metal ions in the reaction mixture reached 10 g/dm^3. pH value of 10.5 was reached by addition of a caustic soda solution. The obtained suspension was placed into the reactor, and at room temperature it was treated with pulses of an alternating magnetic field and air was bubbled with a flow rate of 0.2 dm^3/min per 1.0 dm^3 of the reaction mixture. The amplitude of the magnetic field was changed in the range from 0.001 to 0.09 T using a developed computer program. Other parameters of the electromagnetic field remained unchanged. The composition of the sediment formed in the process of ferritization

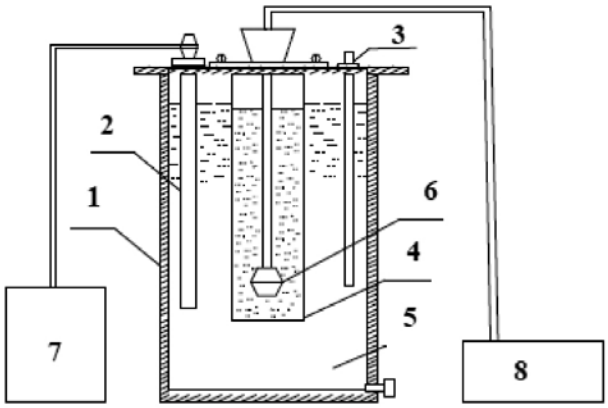

Fig. 1. Laboratory ferrite reactor. 1 – thermostat case; 2 – heating element; 3 – thermometer; 4 – cylinder with solution; 5 – water; 6 – aerator; 7 – rheostat; 8 – compressor

Rys. 1. Laboratoryjny reaktor ferrytowy. 1 - obudowa termostatu; 2 - element grzejny; 3 - termometr; 4 - cylinder z roztworem; 5 - woda; 6 - aerator; 7 - reostat; 8 – sprężarka

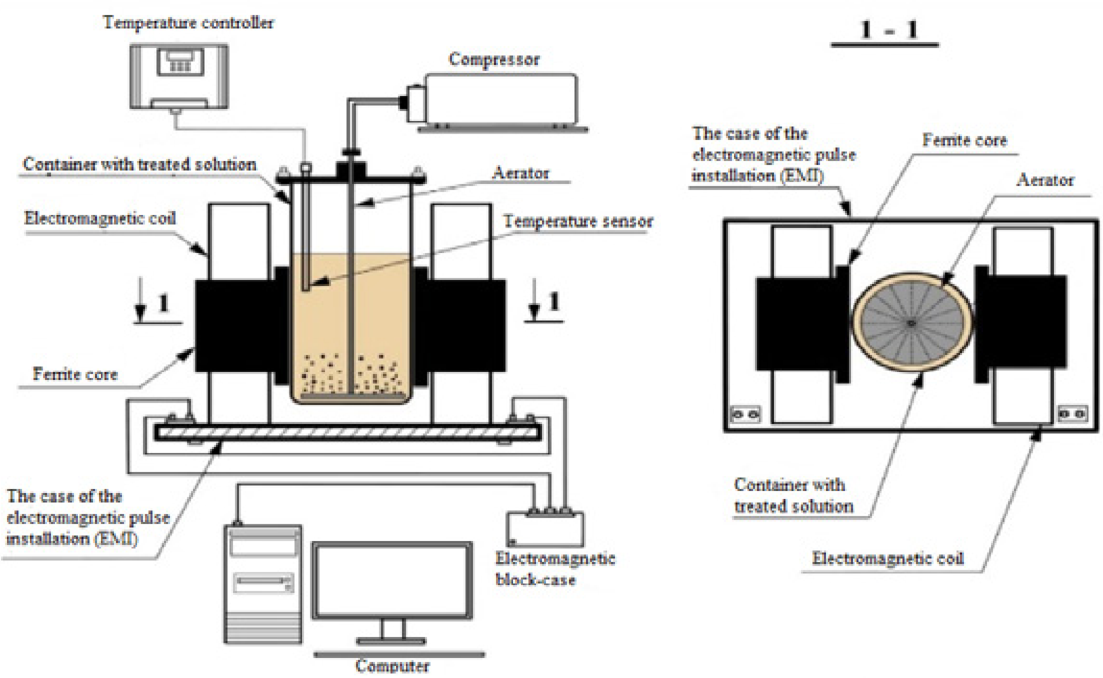

Fig.2. Schematic diagram of the laboratory installation for electroplating wastewater treatment by the ferritization method with electromagnetic pulse activation

Rys.2 Schemat ideowy instalacji laboratoryjnej do galwanicznego oczyszczania ścieków metodą ferrytyzacji z aktywacją impulsem elektromagnetycznym was assessed by X-ray diffractometry. Concentrations of chromium and iron in after-treatment water, after removal of sediment by filtration, were determined by the spectrophotometric method. The structural analysis of the obtained sediments was performed by the method of X-ray powder diffraction in Cu – Kα radiation. Powder diffractograms were deciphered using ICCD PDF2+ – 2003 reference cards (The International Center for Diffraction Data) and Match V.1.9a software (Crystal Impact).

Fig. 3. A view of the installation for EMI activation of the ferritization process: 1 – computer; 2 – electronic block-case; 3 – power supple; 4 – electromagnetic coll with steel core; 5 – container with processed solution

Rys.3 Widok instalacji do aktywacji procesu ferrytyzacji EMI: 1 – komputer; 2 – obudowa bloku elektroniki; 3 – zasilacz; 4 – kołnierz elektromagnetyczny z rdzeniem stalowym; 5 – pojemnik z przetworzonym roztworem

Table 1. Results of wastewater treatment (heavy metals removal) by thermal ferritization

Tabela 1. Wyniki oczyszczania ścieków (usuwania metali ciężkich) metodą ferrytyzacji termicznej

Experiment No	Ratio N	Concentrations mg/l					Removal degree [%]	
		Before treatment [g/l]		After treatment [mg/l]				
		Fe^{2+}	Cr^{6+}	Fe^{2+}	Cr^{3+}	Cr^{6+}	Fe^{2+}	Cr^{3+}
1	4:1	7,5	2,5	0,92	0,27	-	99,54	99,46
2	6:1	8,33	1,66	0,57	0,19	-	99,81	99,62
3	8:1	8,75	1,25	0,1	0,045	-	99,97	99,91
4	10:1	9	1	0,09	0,04	-	99,98	99,92
5	12:1	9,16	0,83	0,08	0,02	-	99,99	99,96
6	15:1	9,33	0,66	0,06	0,018	-	99,99	99,96

Results and discussion

Table 1 shows results of the studies on the influence of the ratio of concentrations of iron and chromium (N) ions in the initial solution on the residual concentration of these ions in the after-treatment water in the course of thermal ferritization. As can be seen from the data in this table, as the value of N increases, there is a gradual decrease in residual concentration of both iron and chromium in the after-treatment solutions. The obtained results of the degree of purification of wastewater in experiments No. 3 – 6 (Tab. 1) indicate that the wastewater treated by this method can be used in the close circuit water supply system of electroplating plants for operations of washing parts, as well as for preparation of new electrolyte solutions. We consider the optimal value of N to be the ratio of Fe^{2+} and Cr^{6+} in the reaction mixture as 10/1. Therefore, the determination of optimal values of the amplitude of the electromagnetic field for the ferritization activation was carried out precisely at this ratio of iron and chromium ions.

The results of experimental studies indicate that the degree of wastewater treatment efficiency increases with an increase in the amplitude of the electromagnetic field. As can be seen from the data given in Tab. 2, the best results were obtained with an electromagnetic field amplitude of 0.01 – 0.09 T. The degree of removal of chromium ions from wastewater under these conditions reaches 99.9%.

In the process of ferritization, a black dispersed suspension was formed in the solution, followed by formation of small volumes of crystalline precipitates with a dense structure. Structural studies of EMI ferritization sediments indicate that sample No. 4 has the highest content of the crystalline phase. It is this sample that has the narrowest diffraction maxima in the X-ray pattern. Identification of the phases showed that the sediment composition includes iron chromate ($FeCr_2O_4$) and magnetite (Fe_3O_4). The detected phases have ferromagnetic properties and spinel-type crystal lattice. The high chemical stability of the sediment is evidenced by the fact that it cannot be dissolved in water, in an alkaline and weakly acidic media [3].

Analysis of the data given in Tab. 2 indicates that the amplitude of the magnetic field affects both the residual concentration of heavy metals in the solution and the phase composition of the sediment. When the amplitude increases from 0.001 to 0.09 T, the amount of ferromagnetic phase $(Fe,Cr)_3O_4$, with a crystal lattice parameter of 8.39 Å, increases from 58 to 70%. The research results showed reliable immobilization of heavy metals in the sediment, which has ferromagnetic properties. Therefore, this sediment is easily separated from the liquid phase on magnetic filters. It should be noted that the absolute advantage of the ferritization technology of wastewater purification from chromium compounds using EMI activation of the reaction mixture is significantly lower energy consumption compared to the thermal method, which requires heating the reaction mixture to a temperature of more than 75^0C. The use of activation of the ferritization process by a variable magnetic field has a significant effect on the technical and economic parameters of obtaining ferromagnetic compounds due to the significant energy savings at the initiation of the

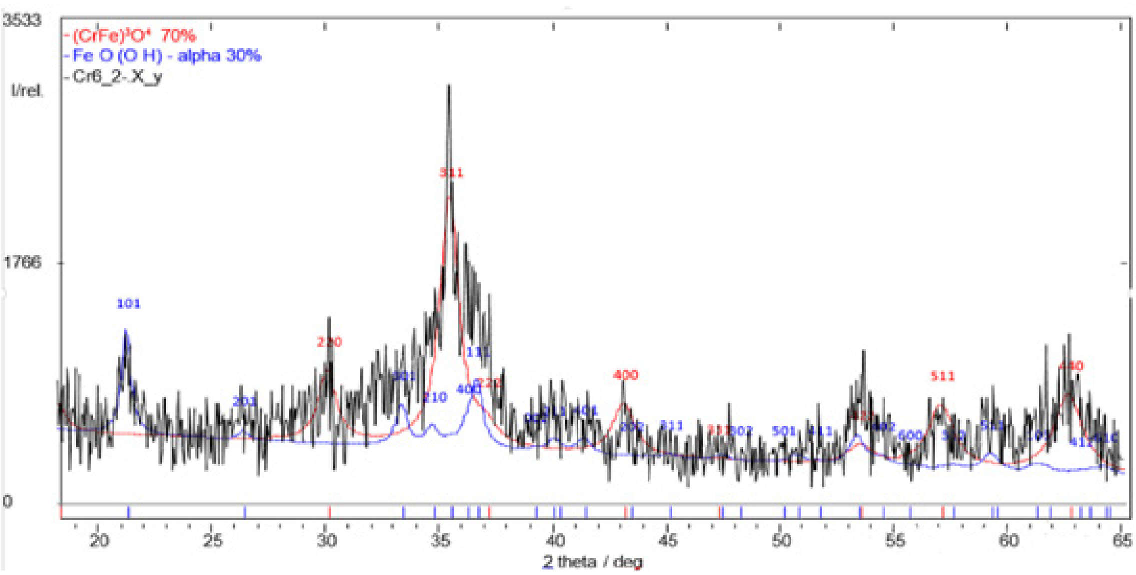

Fig. 4. Diffraction pattern of ferritization sediments with electromagnetic pulse activation

Rys.4 Obraz dyfrakcyjny osadów ferrytycznych z aktywacją impulsem elektromagnetycznym

Table. 2. Results of analyses for treated solutions of exhausted chromium electrolyte

Tabela 2. Wyniki analiz oczyszczonych roztworów wyczerpanego elektrolitu chromowego

No	Ratio Cr^{6+} /Fe^{2+}	The amplitude of the electromagnetic field [T]	Pulse frequency [Hz]	Duration of the process τ [min]	Temperature [C⁰]	pH	Residual concentration ±0.01[mg/l]		Degree of purification [%]	
							Cr^{3+}	Fe^{2+}	Cr^{3+}	Fe^{2+}
1	1:10	0.001	1	15	18	10.5	0.69	0.98	99.93	99.89
2		0.004					0.68	0.77	99.93	99.91
3		0.01					0.32	0.2	99.96	99.99
4		0.09					0.28	0.19	99.96	99.99

ferrite formation reaction. This method of activation makes it possible to reduce electric power consumption by more than 60% compared to the traditional thermal one, and – as a result – makes this technology attractive for investments. In addition, this energy-saving activation of the process is in compliance with certain technological parameters of ferritization and contributes to formation of a precipitate of mainly ferromagnetic phases of magnetite and iron chromate.

Utilization of production waste

The structure and chemical stability of the obtained sediments make it possible to carry out their environmentally safe disposal, using these electroplating production wastes in the initial kiln charge in production of alkaline cements [9]. In this study, test of the possibility of obtaining powder paint coatings with fillers, which are obtained from ferritization waste of processing exhausted electroplating electrolytes were carried out. (Fig. 5). In previous works, it was established that the use of iron-containing wastewater processing sediment as a filler in the amount of 10 to 15% of the total mass of the mixture leads to a significant (from 30 to 100%) increase in the main mechanical characteristics of the obtained coatings. In addition, this coating has increased corrosion resistance compared to traditional analogues. Development of such a technology will contribute to implementation of closed-cycle processes in conditions of electroplating production and to production of high-quality and environmentally safe coatings.

Fig. 5. Powder coatings with addition of 10 to 25% ferritization sediments from chromium-containing wastewater treatment.

Rys.5 Powłoki proszkowe z dodatkiem od 10 do 25% osadów ferrytycznych z oczyszczania ścieków zawierających chrom

Conclusions

Analysis and generalization of the data obtained confirm prospects of ferritization treatment of galvanic wastewater with application of energy-efficient EMI activation of the process. Studies were conducted to determine important parameters of the course of the process of ferritization of concentrated wastewater from the chromium electroplating line. In comparison with traditional thermal ferritization, the expediency of using energy-efficient EMI activation of the reaction mixture with the following parameters is shown: pH=10.5; pulse frequency of 1 Hz; the amplitude of the electromagnetic field of 0.09 T and the concentration ratio of iron and chromium ions of 10/1.

The results of the experiments demonstrate that treatment of chromium compounds containing wastewater by the method of ferritization with EMI activation provides a high degree of removal of heavy metal ions from the wastewater (up to 99.9%). Such after-treatment water meets requirements of the standards for its reuse in electroplating production processes. It is shown that when the amplitude of the EMI magnetic field for activation of the ferritization process increases, mainly stable ferromagnetic crystalline phases are formed. It is recommended to use this chromium-containing wastewater treatment residue as a component in construction materials for special purposes, in particular, in paint coatings capable of shielding electromagnetic radiation.

Further research efforts will be directed to development of studies on electromagnetic radiation shielding materials with application of chromium-containing waste from electroplating industries.

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