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POSSIBILITIES OF PURIFICATION OF EFFLUENTS FROM PESTICIDE PRODUCTION USING MAGNETIC TREATMENT AND ELECTROCOAGULATION

The paper deals with the application of magnetic treatment and electrocoagulation in the treatment of industrial effluents from the production of the perocin pesticide. The use of magnetic treatment and electrocoagulation intensifies the process of coagulation and sedimentation. Different variants of a technological scheme for treatment of industrial effluents have been suggested, namely: mechanical sedimentation, filtration, magnetic treatment, electrocoagulation, and reagent removal of zinc.

1. INTRODUCTION

One of the trends in the technology of treatment of municipal and industrial effluents is application of electrocoagulation, electroflotation-coagulation, and treatment in a magnetic field [2]–[4]. In the present work, we have discussed the question concerning the application of the above methods to the purification of industrial effluents from pesticide production.

Industrial effluents were polluted with organic, inorganic, dissolved, and dispersed substances. The insoluble substances, i.e., kaolin (used as a filler in the finished product), geropon (suspension agent used to prevent sedimentation of suspended solids), and magnesite, are finely dispersed and form nonsettling suspension. The experiments carried out have shown that after mechanical sedimentation only the water quality does not meet the sanitary standards of 3rd category water with respect to suspended substances. Therefore, filtration of industrial effluents has to be included in the treatment process. Although the process of filtration is labour-consuming due to the cleaning of filter presses, it removes insoluble solids from

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industrial effluents. The effluents, however, contain a high concentration of dissolved substances (sulfate ions, zinc, etc.). The investigations have shown that the concentrations of these substances after filtration are too high to meet the required sanitary standards. The average zinc concentration amounted to 0.41 g/dm^3, thus being 400 times higher than the admissible in the case of 3rd category waters (1 mg/dm^3), and the concentration of sulfate ions being 23.5 g/dm^3 was 78 times higher than that admissible to sanitary standards for 3rd category waters (0.3 g/dm^3). Removal of zinc from industrial effluents can be done by treating them with NaOH, Na_2CO_3, and Na_2S, separately or jointly, or by ion exchange methods [5], [8]. PORUBAEV [6] has found that preliminary sedimentation of zinc with Na_2CO_3, followed by a magnetic treatment and, finally, by the addition of a coagulant (limewash), is a possible way of meeting sanitary standards.

2. EXPERIMENTAL RESULTS AND DISCUSSION

2.1. MAGNETIC TREATMENT OF EFFLUENTS

The studies on magnetic treatment of artificial wastewaters (perocin dissolved in water) by means of a magnetic apparatus at one-time interception of the magnetic flux have shown that intensification of the magnetic flux increases the efficiency of $FeCl_3$ coagulation up to 15.5% as compared to the conventional method. The increase of efficiency of the coagulation process by 25 and 30% was due to the reduction of the time elapsing from the coagulant addition to the gel particle sedimentation at magnetic induction $B = 7.02 \times 10^{-2}$ T and 11.04×10^{-2} T at water flow rate $w = 0.8$ m/s. The magnetic treatment method permits shortening of the flocculation and sedimentation time during chemical coagulation because of the formation of bigger and more readily sedimentating gel particles.

The experiments were performed on artificially prepared water as well as on industrial effluents from the horizontal sedimentation tanks in the factory. The process was carried out by means of a magnetic apparatus providing the possibility of twelve-times interception of the magnetic flux. The effectiveness of the magnetic treatment was registered by an optical method described by AHMEROV [1]. The light permeability of the treated and untreated waters in the sedimentation process was compared with the distilled water standard. The measurement was made using "Specol" (cup 10 mm). The highest treatment effectiveness, i.e., 3.6–5.5%, was achieved at magnetic induction $B = 2 \times 10^{-2}$ T and $B = 3 \times 10^{-2}$ T, and w ranging within 0.3–0.4 m/s. Under the conditions stated, the artificial and industrial effluents were treated with an optimum dose (280 mg/dm^3) of $FeCl_3$ coagulant. The same dose was added to the untreated water (control sample). The sedimentation kinetics data are shown in fig. 1. It can be seen that the $Fe(OH)_3$ gel particles in the treated

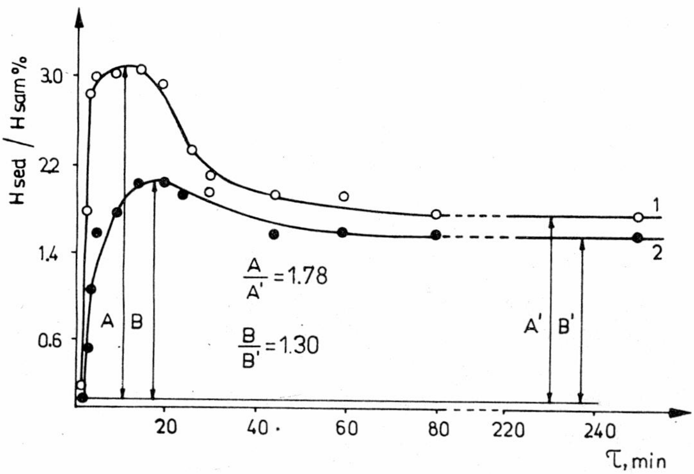

Fig. 1. Sedimentation kinetics of gel particles obtained after addition of the $FeCl_3$ coagulant
1 – treated water in the magnetic field, *2* – control sample, H_{sed} – height of $Fe(OH)_3$ sediment during sedimentation process in Imhoff cylinder (mm). H_{sam} – height of water sample taken for sedimentation in Imhoff cylinder (mm)

water (curve *1*) precipitate more quickly and the volume of the sludge in a given moment is higher than that in the control sample (curve *2*). It was established (according to SHAHOV [7]) that visible gel particles in the treated water appear in the 10th second and their agglomeration continues until the 55th second. In the control sample these effects occurred in the 20th and 100th second, respectively (intensification $\frac{10}{20}100 = 50\%$ and $\frac{55}{100}100 = 55\%$). At the end of the sedimentation process ($\tau = 250$ min) the light permeabilities of treated and untreated (control sample) waters were 92.5 and 89.2%, respectively (effectiveness of the magnetic treatment of water $\frac{89.2}{92.5}100 = 96.4\%$). The water subjected to magnetic treatment contained 28 mg of suspended solids per dm^3, and the untreated water, 54 mg of suspended solids per dm^3 after sedimentation. Figure 1 shows that the thickness of the sediment layer obtained at the constant $\tau = 220$ min after magnetic treatment is higher than that in the untreated water. For treated water at τ = const. = 220 min (from the 10th to the 230th min) the sediment is thickened by 1.78 times. The control sample, however, at const $\tau = 220$ min (from the 16.5th the 236.5th min) is thickened by 1.30 times. These investigations as well as the results obtained by PORUBAEV [6] suggest that after magnetic treatment of industrial effluents from pesticide production and a $FeCl_3$ coagulation process, the sedimentation of dispersed particles may be intensified and a more thorough zinc removal can be achieved by means of the reagent method with limewash. The magnetic apparatus can be installed after the horizontal sedimentation tanks or the filtration in the existing technological scheme.

2.2. ELECTROCOAGULATION TREATMENT OF INDUSTRIAL EFFLUENT

Electrocoagulation stimulates the flocculation of the insoluble solids which are in a dispersed state, thus leading to more efficient and quicker sedimentation of particles in the treated water as compared to the control sample. This results in a more intensive sedimentation, i.e., for the same sedimentation time the volume of sediment of the treated water is about 50% higher than that of the control sample. It has been established that during sedimentation the initial formation of the sediment in the treated water begins much earlier (as early as in the 5th min after the start). Sedimentation in the control sample begins in the 10th min after the start. Therefore, the treatment leads to intensification of the sedimentation process and in the case considered sedimentation begins in the 5th min after the start. Sedimentation in the treated water continues for 25 min; in the control sample it lasts 55 min. The treatment with electrocoagulation reduces the time of sedimentation to 30 min. At the end of the 25th min the volume of the sediment in the treated water is 1.87 times greater than that in the control sample due to the greater volume of the removed dispersed particles, which in the control sample remain in the water. Nevertheless, at the end of the 60th min the sediment in the treated water is thicker (46.5%) than that in the control sample (12.9%) for the same period of time.

After the treatment, at the end of the 25th min, perocine concentration in the sediment is the same as in the control sample sediment at the end of the 50th min (table). This allows its reuse for pesticide production (fig. 2, variant 1). Electrocoagulation decreases the content of insoluble substances in the effluents in the range from 0.1 to 8.15 g/dm^3 to the sanitary standard requirements for the 3rd category waters ($<$ 80 mg/dm^3). The same result cannot be obtained by mechanical sedimentation only in laboratory conditions for 2 h and in the existing industrial horizontal sedimentation tanks ($\tau = 16$ h). Some other parameters of treated water have also been improved, i.e., COD (by permanganate), BOD_5, perocine and zinc contents are lower by ca 1.05, 1.4, 1.15–2.18, 2.69 times, respectively, as compared to the control sample, mechanically sedimented for a period of 2 h only.

Table

Perocin content in the effluents, in the sediment of the control sample, and in the treated water sediment

Treatment regime		Perocin content		
Current intensity A	Current density A/m^2	Effluents weight %	Control sample sediment weight %	Treated water sediment weight %
2	375	74.1	70.5	69.5
8	1500	—	78.4	77.6
13	2440	—	78.4	76.4

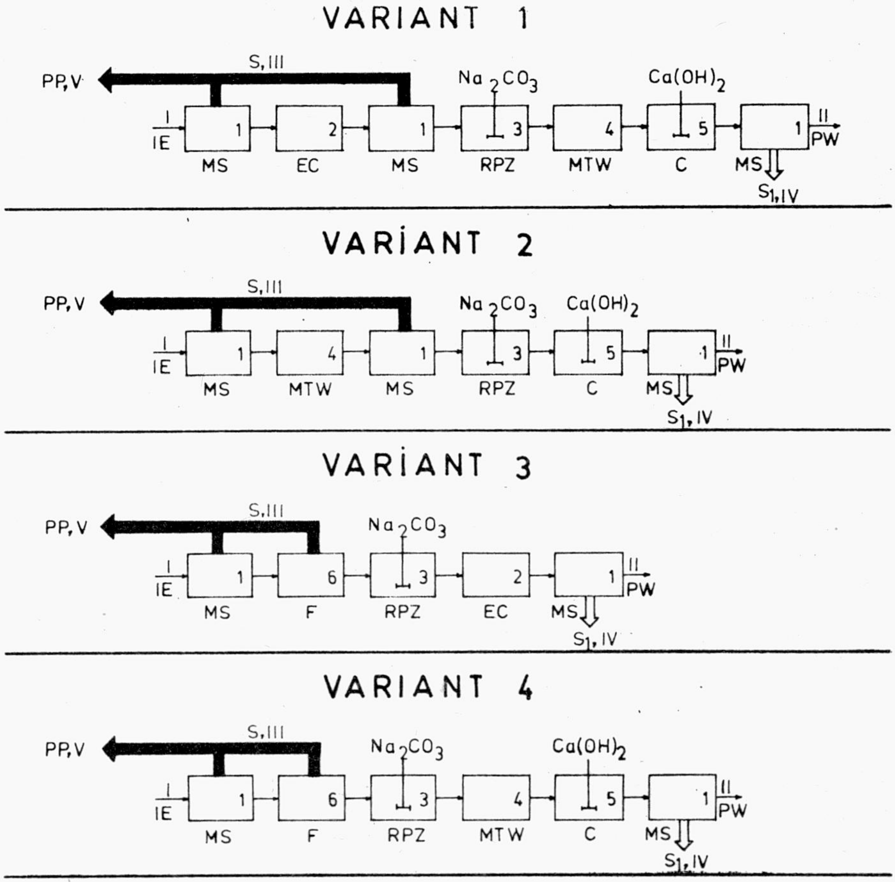

Fig. 2. Technological scheme for treatment of industrial effluents from perocin pesticide production

1 – mechanical sedimentation (MS), *2* – electrocoagulation (EC), *3* – reagent removal of zinc (RPZ), *4* – magnetic treatment of water (MTW), *5* – coagulation (C), *6* – filtration (F), I – industrial effluents (IE), II – purified water (PW), III – perocin containing sediment after MS of effluents treated by EC (S), IV – zinc containing sediment after MS of effluents treated with Na_2CO_3 (reagent), magnetic field and $Ca(OH)_2$ (coagulant), V – pesticide production (PP)

2.3. REAGENT AND ELECTROCOAGULATION REMOVAL OF ZINC

We have also investigated zinc removal from wastewater using Na_2CO_3. The zinc ions contained in the water form with the latter compound $Zn_3CO_3(OH)_4$, which is a poorly soluble compound [5]. According to FISHMANN [5] the following chemical reaction takes place

$$3Zn^{2+} + 5CO_3^{2-} + 4H_2O \leftrightarrows Zn_3CO_3(OH)_4 + 4HCO_3^- . \tag{1}$$

The optimum dose of the reagent ($Q_{NA_2CO_3}$) has been determined by the formula

$$Q_{Na_2CO_3} = 2.7 \cdot C_{Zn^{2+}} \tag{2}$$

where 2.7 is the quantity of Na_2CO_3 (mg) for the sedimentation of 1 mg Zn^{2+} according to chemical reaction (1), $C_{Zn^{2+}}$ – the concentration of zinc in the industrial effluents.

According to scientific data, in order to create optimum conditions for sedimentation of zinc by Na_2CO_3, it is necessary to have a considerable amount of the reagent [5].

Having in mind that electrocoagulation allows an increase of the purification degree when treating zinc containing industrial effluents (about 2.69 times more in comparison with the 2 hour mechanical sedimentation) and intensification of the sedimentation process, it is reasonable to carry out experiments for zinc removal by combining the reagent method with the electrochemical method of treatment.

The experiments were conducted using wash water prepared artificially by dissolving pure for analysis (pa) zinc sulfate ($ZnSO_4 \cdot 7H_2O$) in distilled water. The zinc concentration ranged from 87 to 107 mg/dm^3. After adding the required quantity of Na_2CO_3, determined by the formula (2), and stirring it, the water became turbid and small, fine particles of zinc carbonate were formed. Two samples were taken from the water thus treated: a control sample whose sedimentation lasted 2 h and a sample treated by electrocoagulation. The treatment was made at a current density i (i = 187.5, 375, 563, 1125 A/m^2) and water flow rate w (the rate interval 0.119–0.47 m/s). After the electrocoagulation, the treated water was retained for sedimentation for 2 h. Zinc was determined in the above two samples. Removal degree in the control sample amounted to 42% (52 mg/dm^3) and in the treated water it ranged from 94.8 to 99% (5.6 and 0.8 mg/dm^3). The highest removal efficiency was obtained at i = 563 A/m^2, w = 0.149 m/s, and electric treatment time τ_3 = 3.36 s. Electric energy consumption for the treatment of 1 m^3 of water ranged from 2.00 to 8.84 kWh/m^3. The volume of the sediment in the treated water was 1.7 times greater than that in the control sample. The application of electrocoagulation at a stoichiometric quantity of Na_2CO_3 allows the achievement of a high degree of purification and the respective sanitary standards (1 mg/dm^3) for 1st category water without an excess of reagent. Furthermore, the sedimentation of the particles of basic zinc carbonate was intensified, while sedimentation without electrocoagulation proceeded quite slowly and a large portion of the particles remained in the treated water. The sediment (S_1) obtained can be used in non-ferrous metallurgy for regeneration and production of zinc (fig. 2, variants 1–4).

3. TECHNOLOGICAL SCHEME OF PURIFICATION OF INDUSTRIAL EFFLUENTS FROM PEROCIN PRODUCTION

The studies carried out and the conclusions derived allow us to recommend a technological scheme for the treatment of industrial effluents from pesticide production. This scheme is made in four variants (fig. 2) and includes the following operations: mechanical sedimentation, filtration, magnetic treatment of effluents, electrocoagulation as well as reagent removal of zinc. The scheme will be tested in a pilot plant for purification of effluents from pesticide production.

4. CONCLUSIONS

The use of magnetic treatment and electrocoagulation allows intensification of the coagulation and sedimentation processes during the treatment of industrial effluents. The wastewater contains dispersed particles of the perocin pesticide. At the same time the following water parameters are improved: content of insoluble substances, perocin, zinc, COD (by permanganate), BOD_5, achieving the sanitary standards for 3rd category water (insoluble substances, zinc). For technological variants are given including mechanical sedimentation, filtration, magnetic treatment, electrocoagulation, and reagent purification of zinc.

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MOŻLIWOŚCI OCZYSZCZANIA ŚCIEKÓW Z PRODUKCJI PESTYCYDÓW W POLU MAGNETYCZNYM ORAZ W PROCESIE ELEKTROKOAGULACJI

Opisano wykorzystanie pola magnetycznego oraz procesu elektrokoagulacji w oczyszczaniu ścieków przemysłowych pochodzących z produkcji pestycydów. Stwierdzono, że obie metody zwiększają intensywność procesu koagulacji i sedymentacji. Zaproponowano różne schematy technologiczne oczyszczania ścieków przemysłowych obejmujące procesy mechanicznej sedymentacji, filtracji, oczyszczania w polu magnetycznym, elektrokoagulacji i usuwania cynku za pomocą chemicznego strącania.

ВОЗМОЖНОСТИ ОЧИСТКИ СТОЧНЫХ ВОД ИЗ ПРОИЗВОДСТВА ПЕСТИЦИДОВ В МАГНИТНОМ ПОЛЕ И В ПРОЦЕССЕ ЭЛЕКТРОКОАГУЛЯЦИИ

Описано использование магнитного поля и процесса электрокоагуляции в очистке промышленных сточных вод, происходящих из производства пестицидов. Было установлено, что оба метода увеличивают интенсивность процесса коагуляции и седиментации. Предложены разные технологические схемы очистки промышленных сточных вод, охватывающие процессы механической седиментации, фильтрации, очистки в магнитном поле, коагуляции и удаления цинка при помощи химического осаждения.