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STUDIES OF ZINC AND LEAD REMOVAL FROM INDUSTRIAL WASTES BY ELECTROCOAGULATION

The results of laboratory-scale investigation on electrocoagulation process have been presented. Applicability of this process to treatment of industrial wastewater containing zinc and lead has been proved. It has been found that effectivity of the wastewater treatment depends on the following parameters: process duration, concentrations of these metals in the wastewater treated and its pH, as well as on the required degree of purification. The energy demand increases with the distance between electrodes.

1. INTRODUCTION

Among the latest methods used in water and sludge treatment the most interesting are those which do not require the use of reagents. They become more and more popular because of their practical applicabilities and possibility to avoid the equipment for receiving, storing, preparing, and dosing chemicals. Water and sludge treatment method by electrocoagulation applying an electrical field for electrolytic coagulation seems to be particularly attractive.

This method has found application in water treatment, in particular for improvement of its taste and smell. A much wider application is gained by electrocoagulation in the technology of industrial and municipal sludge treatment [1, 5, 7, 9]. This method has been successfully applied in treatment of industrial wastes from metallurgical, textile, chemical, wood, food, and farming industries. Ions of some metals were reported in [2–4, 6, 8] to have been effectively removed from the wastes. Positive results of these tests allowed to infer that electrocoagulation can be a useful method in zinc and lead removal from the industrial wastes.

METHODS

The investigations were performed on industrial wastes sampled from one of the zinc and lead mining and metallurgy complexes. At the moment of sampling the respective concentrations of zinc and lead ranged from 22.5 to 51.0 mg Zn^{++}/dm^3 and from 0.0 to

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53.0 mg Pb^{++}/dm^3. Since the process was to be conducted at constant zinc and lead concentrations in sludges, the latter were artificially enriched with $ZnCl_2$ and $Pb(NO_3)_2$ in cases when concentrations were lower than the estimated values. As a rule the sludge pH value was constant and equal to 7.5. In a few instances when pH was different, it was adjusted to this value. The process carried out in these conditions was close to the real one. To observe the waste treatment efficiency, concentrations of zinc and lead have to be controlled. They were determined by polarographic analysis using Czechoslovakian polarograph type LP7e and a recorder type TZ213 s.

The laboratory experiments on electrocoagulation were conducted under batch conditions applying the electrocoagulation unit consisting of a glass tank of a useful volume of 1.5 dm^3. Two electrodes, made of a steel sheet, were the basic element of the unit (dimensions: $0.16 \times 0.050 \times 0.001$ m, active surface 5×10^{-3} m^2). Both electrodes were interconnected by distance rods made of insulating material so that their spacing could be adjusted within 5×10^{-3}–5×10^{-2} m. To improve the efficiency of electrocoagulation during electrolysis the sludge was permanently stirred by means of a magnetic stirrer. Time of electrolysis ranged from 1 to 30 minutes.

A set of rectifiers RZ-24/10 was supplied with A.C., voltage of 220 V, through an autotransformer LA 2500. Such solution enabled to obtain current intensity of 2.2 A and a unit electrical charge of 2000 As/dm^3. After having performed several series of tests the technological scheme was completed with a chamber of free stirring. It comprised a tank with a useful volume of 1.5 dm^3 and a veritcal axis mixer. Free stirring time was 20 minutes; thereupon the separate sample was subject to 1 hour sedimentation. Zinc and lead were determined quantitatively, their values being a measure of the process efficiency.

3. EXPERIMENTAL

The wastes used and conditions applied were determined earlier.

First series of tests were made on the sludge in which the initial zinc concentration was equal to 22.5 mg/dm^3 and no trace of lead stated. The distance between the electrodes was 2 and 5×10^{-2} m. Electrolysis currents were: 0.42 A, 0.60 A, 0.75 A, and 1.10 A. In all the series the times used ranged from 1 to 25 min. The parameters applied enabled to obtain the unit electrical charge up 1200 As/dm^3.

After electrocoagulation and a 1.5 hour sedimentation zinc/lead concentrations in samples were determined. Similar current and time parameters were used in the series of the sludge in which zinc concentration was 29.0 mg/dm^3, and no lead was traced. The distance between the electrodes was 2.0×10^{-2} m and 3×510^{-2}m. Electrocoagulation of wastes in which zinc concentration was 3.5 mg/dm^3 was performed at electrolysis times ranging 1 within 30 minutes using different current intensities: 0.42 PA, 0.60 PA, 0.75 PA, 1.10 PA, and 2.2 PA. Such conditions made it possible to obtain an appropriate value of unit electrical charge. The distance between the electrodes was 5.0×10^{-3} and 3.5×10^{-2}m. Similarly, as in the previous series, the efficiency of electrocoagulation was controlled by determining zinc/lead concentrations in the effluent.

A series of tests performed at constant current/time parameters that characterize the process and at constant distances between the electrodes comprised the wastes in which zinc concentrations were 41.0 mg/dm³, 46.0 mg/dm³, and 51.0 mg/dm³; the corresponding concentrations of lead being 28.0 mg/dm³, 75.5 mg/dm³, and 35.0 mg/dm³, respectively.

The results of the series in which initial zinc concentration was 41.0 mg/dm³ and that of lead 28.0 mg/dm³ are presented in fig. 1. The influence of initial zinc concentration on

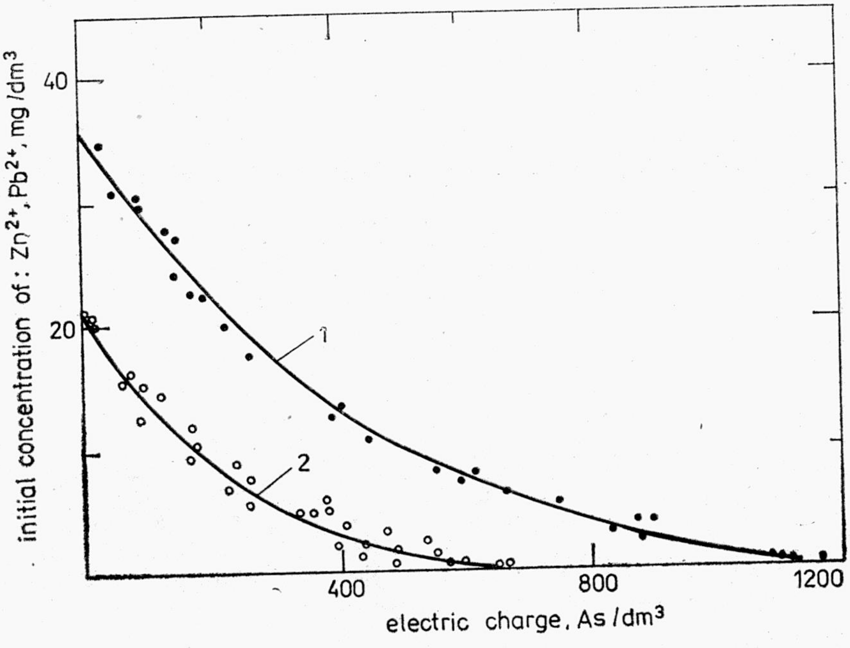

Fig. 1. Zinc removal by electrocoagulation performed on a laboratory scale in periodic conditions. Initial concentrations of lead and zinc 41.0 mg/dm³ and 28.0 mg/dm³, respectively

1 – zinc, *2* – lead

Rys. 1. Laboratoryjne usuwanie cynku przez elektrokoagulację w warunkach okresowych. Początkowe stężenia ołowiu i cynku 41,0 mg/dm³ i 28,0 mg/dm³

1 – cynk, *2* – ołów

its removal efficiency was determined from investigations performed for six initial concentrations of zinc. This dependence in the case of the three unit electrical charges 100 As/dm³, 300 As/dm³, and 500 As/dm³ is presented in fig. 2. A similar dependence in the case of lead is shown in fig. 3.

Laboratory-scale test performed in periodic conditions were to establish the effect of pH on the final effect of sludge treatment. A series of tests were made for zinc and lead concentrations equal to 41.0 mg/dm³ and 28.0 mg/dm³, respectively. The pH ranged within 5.1–9.5. Test results performed at 0.8 A and unit duration times of 5, 10, and 15 min/dm³ are presented in figs. 4 and 5.

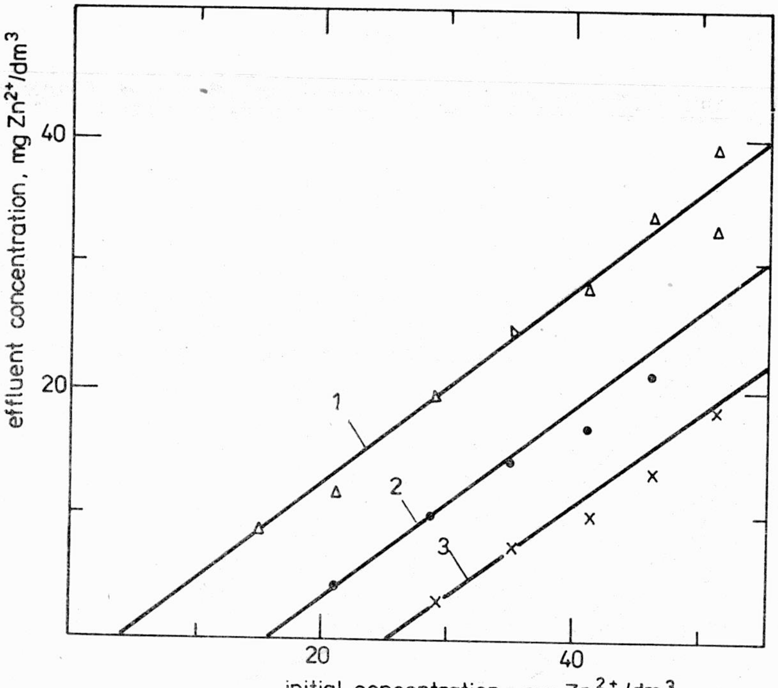

Fig. 2. The effect of initial concentration of zinc on the efficiency of its removal

Periodic conditions, sedimentation time 1.5 h, pH = 7.5, electric charge: *1* — 100 mg As/dm³, *2* — 300 mg As/dm³, *3* — 500 mg As/dm³

Rys. 2. Wpływ początkowych stężeń cynku na skuteczność jego usuwania

Warunki okresowe, czas sedymentacji 1,5 h, pH = 7,5, ładunek elektronowy: *1* — 100 mg As/dm³, *2* — 300 mg As/dm³, *3* — 500 mg As/dm³

4. DISCUSSION

Laboratory studies performed under periodic conditions allowed to state a number of relationships by which the usability of electrocoagulation in industrial wastes treatment could be characterized.

The results obtained on a laboratory scale for the wastes without lead in which initial zinc concentrations amounted to 22.5 mg/dm³ and 29.0 mg/dm³ have proved that zinc concentration can be reduced to 2 mg/dm³, thus according to the Government Circular from 29 XI 1975 to the level admissible for effluents discharged into the sewage system. The efficiency of this process depended on the magnitude of unit electric charge being the quantitative indicator of the iron introduced into the effluent. For wastes containing 22.5 mg of zinc/dm^3 the value of the electrical charge ensuring the required treatment degree was 370 As/dm^3, amounting to 610 As/dm^3 for zinc concentration of 29.0 mg/dm^3. Satisfactory results were also obtained in the remaining series of the tests. At initial zinc concentrations of

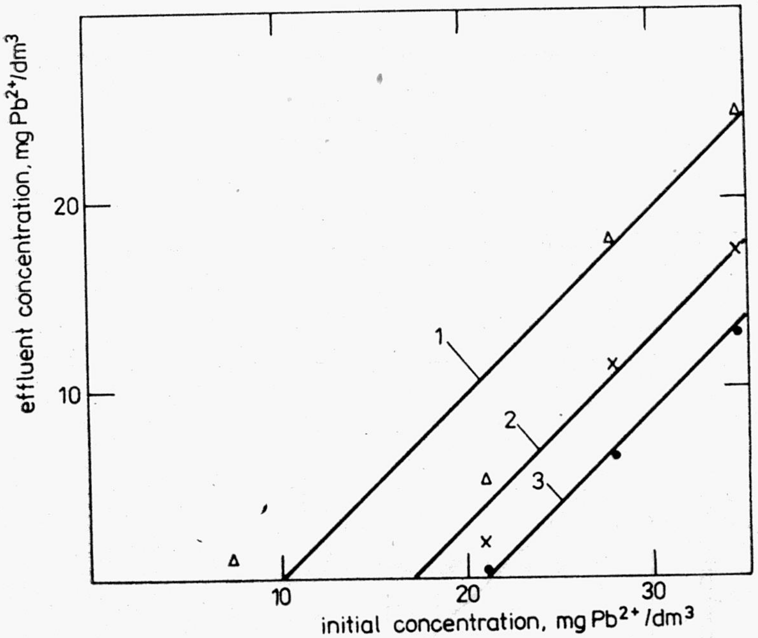

Fig. 3. The effect of initial lead concentration on the efficiency of its removal
Periodic conditions, sedimentation time 1.5 h, pH=7.5

Rys. 3. Wpływ początkowych stężeń ołowiu na skuteczność jego usuwania
Warunki okresowe, czas sedymentacji 1,5 h, pH = 7,5

35.0 mg/dm^3, 41.0 mg/dm^3, 46.0 mg/dm^3, and 51.0 mg/dm^3 the required values of unit electrical charges were 840 As/dm^3, 930 As/dm^3, and 1060 As/dm^3, respectively. Much lower values of the required electrical charges were stated at the removal of lead. At the initial lead concentrations of 7.5 mg/dm^3, 21.0 mg/dm^3, 28.0 mg/dm^3, and 35.0 mg/dm^3 the corresponding values of initial charge were 130 As/dm^3, 390 As/dm^3, 640 As/dm^3, and 840 As/dm^3, respectively. Such parameters quaranteed the required degree of treatment with respect to lead. The analysis of the results presented in fig. 1 allowed to state that at a constant initial concentration of zinc/lead the dependence of their removal on the unit electrical charge of electrocoagulation can be described with a chromographic curve.

When for instance initial zinc concentration is 41.0 mg/dm³, the equation takes the form:

$$C_{k_{Zn}} = \frac{q-1130}{-0.062-31.4},$$

where:

$C_{k_{Zn}}$ — final zinc concentration [mg/dm³],

q — unit electrical charge [As/dm³].

If the initial lead concentration is 28.0 mg/dm³, then the equation takes the form:

$$C_{k_{Pb}} = \frac{q-650}{-0.12q-31},$$

where:

$C_{k_{Pb}}$ — final lead concentration [mg/dm³].

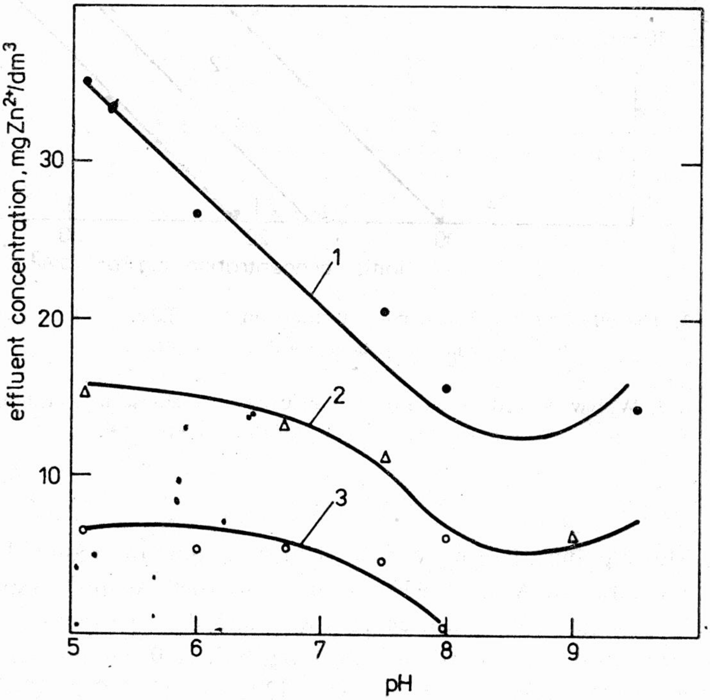

Fig. 4. The effect of pH on the efficiency of zinc removal

Periodic conditions, initial zinc concentration 41.0 mg/dm³, current intensity 0.8 A, sedimentation time 1.5 h

Rys. 4. Wpływ pH na skuteczność usuwania cynku

Warunki okresowe, początkowe stężenie cynku 41,0 mg/dm³, natężenie prądu 0,8 A, czas sedymentacji 1,5 h

A practical conclusion of the results obtained from investigations performed in periodic conditions are the relationships of technological parameters presented in figs. 2 and 3. From these relationships, the concentrations of lead and zinc in the untreated wastes and the required degree of treatment duration, time of electrolysis resulting from the amount of wastes and the capacity of equipment being known, it is possible to establish current conditions. The influence of the initial zinc/lead concentration in the wastes on the removal effect is shown in figs. 2 and 3 and can be described by simple equations, i.e.:

for zinc removal:

$$C_{k_{Zn}} = 0.8(C_{0_{Zn}} - a_{Zn}),$$

where:

$C_{k_{Zn}}$ — final zinc concentration [mg/dm³],

$C_{0_{Zn}}$ — initial zinc concentration [mg/dm³],

a_{Zn} — coefficient dependent on unit electrical charge and amounting to 5, 16, 27 for the electrical charges of 100 As/dm³, 300 As/dm³, and 500 As/dm³, respectively;

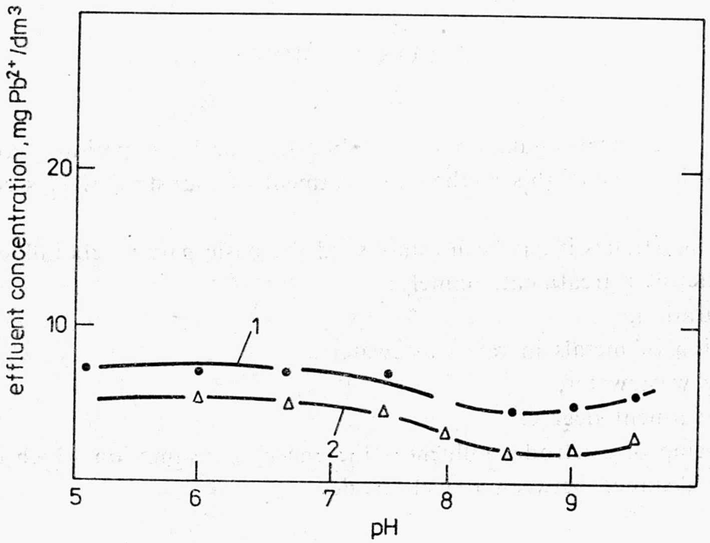

Fig. 5. The effect of pH on the efficiency of lead removal

Periodic conditions, initial lead concentration 28.0 mg/dm³, current intensity 0.8 A, sedimentation time 1.5 h

Rys. 5. Wpływ pH na skuteczność usuwania ołowiu

Warunki okresowe, początkowe stężenie ołowiu 28,0 mg/dm³, natężenie prądu 0,8 A, czas sedymentacji 1,5 h

for lead removal:

$$C_{k_{Pb}} = C_{0_{Pb}} - a_{Pb},$$

where:

$C_{k_{Pb}}$ — final lead concentration [mg/dm³],

$C_{0_{Pb}}$ — initial lead concentration [mg/dm³],

a_{Pb} — coefficient dependent on unit electrical charge and amounting to 10, 17, 21 for the charges of 50 As/dm³, 150 As/dm³, and 250 As/dm³, respectively.

The effect of the pH values on the efficiencies of zinc and lead removals are presented in figs. 4 and 5, respectively. From the results presented above it follows that pH has a considerable effect on the efficiency of treatment, especially on zinc removal. The best effects independently of the remaining parameters of the process were obtained at pH 8.5. It should be mentioned that all the investigations were carried at pH 7.5 of wastes, as this value occurs most frequently in wastewaters. The efficiency of the waste treatment by this method would be much improved by adjusting pH values. This problem should be analysed from economical view-point.

The energy consumption is a crucial factor as far as economics of wastewater treatment by electrocoagulation method is concerned. During investigations it has been established that at constant time of electrolysis and current intensity in each case an increase in spacing of electrodes increases the voltage drop on the electrodes, thus increasing the energy consumption. This is possible to use smaller distances between the electrodes.

5. CONCLUSIONS

1. Studies of electrocoagulation on a laboratory scale in periodic conditions have shown the applicability of this method in treatment of industrial wastes containing zinc and lead.

2. During the studies it has been established the basic parameters influencing the efficiency of wastewater treatment, namely:

process duration,
concentration of metals in raw wastewaters,
pH of raw wastewater,
required treatment degree.

3. The spacing of electrodes influences the energy consumption which increases with the increasing distance between the electrodes.

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BADANIA NAD USUWANIEM CYNKU I OŁOWIU ZE ŚCIEKÓW PRZEMYSŁOWYCH METODĄ ELEKTROKOAGULACJI

Przedstawiono w skali laboratoryjnej wyniki badań elektrokoagulacji. Wykazano przydatność tego procesu do oczyszczania ścieków przemysłowych zawierających cynk i ołów. Ustalono, że efektywność oczyszczania ścieków zależy od następujących parametrów: czasu trwania procesu, stężenia metali w ściekach, a także ich odczynu oraz od wymaganego stopnia oczyszczania. Odstęp między elektrodami wpływa na zapotrzebowanie energii elektrycznej; rośnie ono wraz ze wzrostem tego odstępu.

BESEITIGUNG VON ZINK UND BLEI AUS INDUSTRIEABWÄSSERN MITTELS ELEKTROKOAGULATION

Es wird nachgewiesen, daß die Elektrokoagulation sich zur Beseitigung von Zink und Blei aus industriellen Abwässern eignet. Die Leistung dieses Verfahrens hängt von der Zeit, von der Konzentration der Metalle im Abwasser, vom pH-Wert und vom Reinigungsgrad ab. Je größer der Elektrodenabstand, desto größer der Energieverbrauch.

ИССЛЕДОВАНИЯ ПО УДАЛЕНИЮ ЦИНКА И СВИНЦА ИЗ ПРОМЫШЛЕННЫХ СТОЧНЫХ ВОД МЕТОДОМ ЭЛЕКТРОКОАГУЛЯЦИИ

Представлены в лабораторном масштабе результаты испытаний электрокоагуляции. Доказана пригодность этого процесса для очистки промышленных сточных вод, содержащих цинк и свинец. Установлено, что эффективность очистки сточных вод зависит от следующих параметров: продолжительности процесса, концентрации металлов в сточных водах, их реакции, а также от тебуемой степени очистки. Расстояние между электродами влияет на величину потребности в электроэнергии; она возрастает с увеличением этого расстояния.