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REMOVAL OF HEAVY METALS FROM INDUSTRIAL EFFLUENTS IN THE PRESENCE OF AMMONIUM SALTS

It has been established that heavy metal ions cannot be precipitated by alkaline reagents in the presence of ammonium salts due to the formation of ammonia complexes. A method has been developed for removal of heavy metals from wastewaters in the presence of ammonium salts. The method is based on the precipitation of metal ions by phosphoric acid under specific conditions. The concentration of heavy metals in wastewaters after treatment is below the utmost permissible rates. An electronic system was devised for automatic operation and control of the technological process, which guaranteed a high purification effect at a minimum consumption of reagents.

1. INTRODUCTION

The effluents of many plants contain heavy metals — zinc, copper, lead, cadmium, etc. Their ions have a negative ecological effect on the flora and fauna. They penetrate indirectly into man's organism as well. Cadmium accumulates in the human body and causes heavy damages even after a short period of action [1]. It causes kidney and liver diseases and its increased level in blood leads to hypertonia. The inorganic compounds of lead cause metabolic disorder and appear to be ferment inhibitors. Lead compounds can replace calcium in the bones and become a source of poisoning for a long period of time [2]. The organic compounds of lead are even more toxic.

The other heavy metal ions, i.e., zinc and copper, are also dangerous for man when occurring in high concentrations. That is why, by virtue of a number of normative documents, the discharge of industrial effluents containing heavy metals above allowable concentrations into reservoirs is forbidden.

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The most often applied technique in heavy metal removal systems is the classical method of precipitation with alkaline reagents such as NaOH, Na₂CO₃, Ca(OH)₂, etc., [3]–[6]. Such a method of wastewater treatment has a number of disadvantages, i.e.:

1. The metal hydroxide floc is extremely difficult to settle and dewater.

2. The difficulty of settling and the fact that all metal hydroxides exhibit some solubility result in incomplete metal removal. In some cases, effluent requirements have been imposed which are below the solubility concentration of the various metal hydroxides. The problems are further complicated by the amphoteric nature of some metals as zinc, lead, etc., i.e., the tendency to redissolve at alkaline pH values.

Another technique for heavy metal removal is sulfide precipitation [7]–[8], utilizing inorganic sulfide, hydrogen sulfide or sulfide generated by anaerobic organic activity. This concept is based on the fact that virtually all metals exhibit low solubilities. Sulfide precipitation is often utilized for mercury and cadmium removal [9]–[10]. The major problem of this technique is the sulfide toxicity and therefore the reagent feed should be carefully controlled. When hydrogen sulfide in the form of gas is used as the precipitation agent, its toxicity and odour present problems. Often, the metal sulfides forming colloidal solutions are difficult to precipitate.

The disadvantages of the above-mentioned methods are decisive in searching for new and more effective ways of heavy metal removal from industrial effluents.

The technical-economic and ecological characteristics of removal methods includes the following obligatory indices: high removal effect, low cost of 1 m³ of treated effluent, and possibilities for automation of the technological process.

The removal effect, represented by the residual concentration, in precipitation methods depends first of all on the solubility of the compounds obtained and on the conditions under which the process is run, mostly on pH.

The presence of secondary salts leads to an increased solubility of the precipitate due to the higher ionic strength of the solution. Taking into account the fact that wastewaters contain other salts in large amounts and have not got a constant quantitative and qualitative composition, the optimum conditions of precipitation for each particular element must be experimentally determined.

The cost of 1 m³ of treated water depends on the amount, price, and availability of the reagents required for its treatment. A high removal effect and low cost require automation of the technological process.

2. EXPERIMENTAL

In the paper we give the results of a phosphate treatment method which has been developed and applied to effluents containing heavy metals (zinc, cadmium, lead, and manganese). The method is based on the precipitation of heavy metals in the form of not readily soluble phosphates under certain conditions.

The effect of treatment is calculated according to the following formula:

$$\alpha = \frac{C^0 - C}{C^0} \cdot 100$$

where:

C^0 – heavy metal concentration before precipitation, kg/m^3 ,

C – heavy metal concentration after precipitation, kg/m^3 .

The concentrations of Zn^{2+} , Cd^{2+} , Pb^{2+} and Mn^{2+} ions are determined by flame absorption spectrophotometer Perkin-Elmer 4000. The relative standard deviation of the analyses is 1.5%.

PO_4^{3-} concentration in the samples is determined spectrophotometrically. The method is based on the formation of a phosphorus–molybdenum complex and its subsequent reaction with ascorbic acid to a molybdenum blue. The absorption is measured by means of a KFO photocolormeter ($\lambda_{\text{max}} = 720 \text{ nm}$) against a blank. The relative standard deviation of the method is 1.65%.

From the results shown in tab. 1 it is evident that the highest value of α in the studied range is obtained at $7.5 \leq \text{pH} \leq 8.0$. Under these conditions, the residual

Table 1

α versus pH in precipitation process

pH	Cadmium		Lead		Zinc		Manganese	
	$C_{\text{Cd}^{2+}}$ kg/m^3	α %	$C_{\text{Pb}^{2+}}$ kg/m^3	α %	$C_{\text{Zn}^{2+}}$ kg/m^3	α %	$C_{\text{Mn}^{2+}}$ kg/m^3	α %
5.5	0.1290	87.10	0.5300	47.00	0.0240	83.00	0.0330	94.90
6.0	0.0390	96.10	0.0005	99.95	0.0080	96.00	0.0096	98.50
6.5	0.0120	98.80	0.0002	99.99	0.0060	99.46	0.0022	99.66
7.0	0.0069	99.40	0.0001	99.99	0.0003	99.95	0.0004	99.94
7.5	0.0012	99.90	0.0000	100.00	0.0002	99.97	0.0001	99.98
8.0	0.0009	99.90	0.0000	100.00	0.0002	99.97	0.0001	99.98
8.5	0.0020	99.80	0.0000	100.00	0.0006	99.89	0.0003	99.95

$$C_{\text{Cd}^{2+}}^0 = 1 \text{ kg/m}^3, C_{\text{Pb}^{2+}}^0 = 1 \text{ kg/m}^3, C_{\text{Zn}^{2+}}^0 = 0.560 \text{ kg/m}^3, C_{\text{Mn}^{2+}}^0 = 0.650 \text{ kg/m}^3.$$

concentrations of Zn^{2+} , Pb^{2+} , Cd^{2+} , and Mn^{2+} ions are lower than the allowable levels for town sewerage, which are 10 mg/dm^3 , 0.2 mg/dm^3 , 0.2 mg/dm^3 , and 0.8 mg/dm^3 , respectively.

Minimum solubilities of the phosphates examined range within $7.5 \leq \text{pH} \leq 8.0$. Therefore, they precipitate almost simultaneously. Under these conditions, the concentrations of Zn^{2+} , Cd^{2+} , Pb^{2+} , and Mn^{2+} ions in the treated effluents are lower than the theoretical ones, calculated on the basis of the solubility concent-

ration of phosphates. The mechanism of this phenomenon is not fully understood, but it appears to be the result of coprecipitation.

The investigations show that the optimum pH range for complete precipitation of Zn^{2+} , Cd^{2+} , Pb^{2+} , and Mn^{2+} ions does not depend on their initial concentrations if they change from 0.1 to 1 kg/m³ (tab. 2). This dependence enables the utilization of

Table 2

Precipitation of Zn^{2+} , Cd^{2+} , Pb^{2+} , Mn^{2+} ions at $7.5 \leq pH \leq 8.0$

Concentration before precipitation C_{Me}^0 , kg/m ³	Concentration after precipitation $C_{Cd^{2+}}$, kg/m ³	Concentration after precipitation $C_{Pb^{2+}}$, kg/m ³	Concentration after precipitation $C_{Zn^{2+}}$, kg/m ³	Concentration after precipitation $C_{Mn^{2+}}$, kg/m ³
1.0	0.0009	0.0000	0.0002	0.0001
0.5	0.0008	0.0000	0.0002	0.0002
0.3	0.0007	0.0000	0.0001	0.0001
0.2	0.0007	0.0000	0.0002	0.0001
0.1	0.0005	0.0000	0.0002	0.0001

an electronic system for automatic control of the process by one parameter (pH) only. The principle of the system for automatic control of the technological process is stabilization of preset pH values in the range of $7.5 \leq pH \leq 8.0$. Under these conditions the heavy metal concentrations are below the allowable levels.

The technology developed has been tested in a pilot installation (fig. 1). The experiments were carried out with wastewaters of the following physico-chemical characteristics: pH 5.0-5.5, C_{Me}^0 0.1-1.0 kg/m³.

The industrial pH-meter 7 operates as a basic link (regulator) in the automatic control system of the technological process (fig. 2). When it is used as a regulator, and not as a registering device, its electrodes must meet some definite requirements, namely: the reference electrode potential must not be affected by secondary oxidation-reduction processes, which are possible to occur during effluent treatment; the electromotive force by which pH is determined must not be dependent on the temperature, i.e., the isopotential point should be near the measured pH value.

The industrial pH-meter, type MERA No. 5130 (made by the Polish firm ELWRO), which we have used, satisfies the requirements pointed out. Its sensor includes a glass No. 5151, type ESH-1000, a reference electrode type AgCl/P-211 T, and a thermoregulator TR 202/Pt-100 A. An industrial pH-meter, type ZEIBOLD, has also been used for the automatic operation and control of the technological process in effluent treatment.

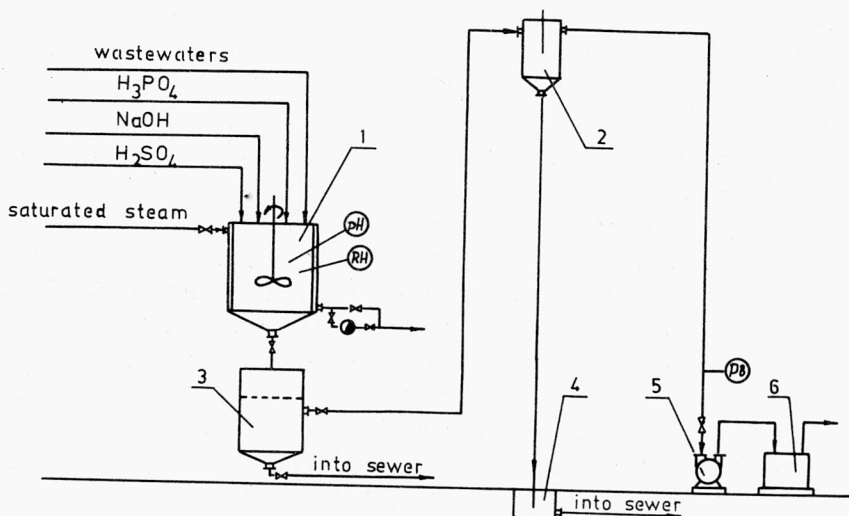


Fig. 1. Scheme of a pilot scale system for treatment of effluents containing heavy metals

1 - tank ($V = 2 \text{ m}^3$) with a propeller stirrer ($n = 150 \text{ rev/min}$) and electromotor, $N = 4 \text{ kW}$; 2 - dripp tray ($V = 0.5 \text{ m}^3$); 3 - nutsche filter ($V = 1.2 \text{ m}^3$); 4 - hydraulic valve; 5 - vacuum pump, type PMK-2; 6 - collector ($V = 0.2 \text{ m}^3$); 7 - pH-meter; 8 - RH-meter

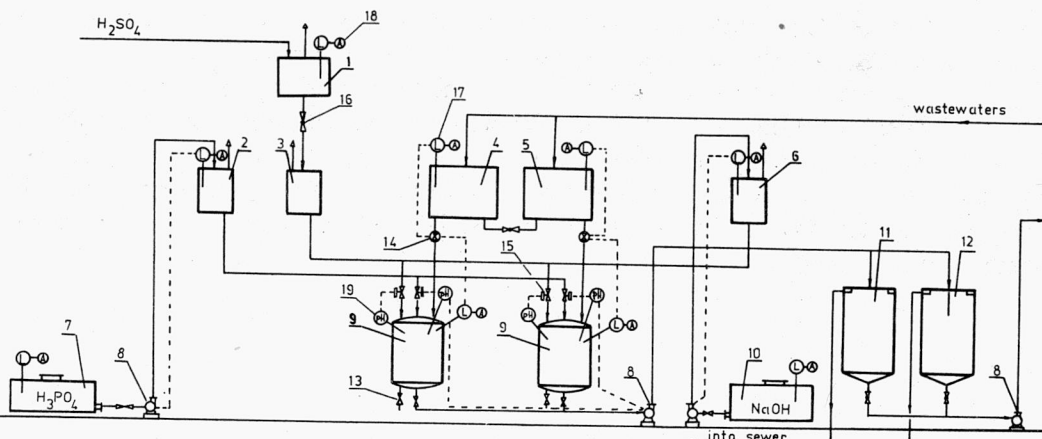


Fig. 2. Technological scheme for treatment of effluents containing heavy metals

1 - pressure vessel for H_2SO_4 ; 2 - dosing tank for H_3PO_4 ; 3 - dosing tank for H_2SO_4 ; 4 - WW reservoir; 5 - WW reservoir; 6 - dosing tank for NaOH ; 7 - precipitator tank; 8 - pump; 9 - toxic waste removal reactor; 10 - tank for NaOH ; 11 - clarifier; 12 - clarifier; 13 - valve; 14 - remote controlled valve; 15 - regulating pneumatic valve; 16 - plug valve; 17 - level-indicator; 18 - signalization; 19 - pH-meter

The results of the long studies in the pilot installation served as the basis of the project for designing an industrial system, the technological scheme of which is presented in fig. 2.

The technical and economic evaluation has shown a high economic efficiency of the developed technology that can be further multiplied by utilization of the sludge, containing non-ferrous heavy metals.

From fig. 2 it is evident that the electronic level-indicators and dosimeters play an important role in the automatic system. They are equally needed both in the automatic and in the manual remote control of the technological process of effluent treatment. The electronic level-indicators are of the electrode type.

The precipitation of heavy metals in the industrial system can be either a periodic or a continuous process. The choice of the way to run the technological process has its effect on the composition and properties of the precipitate obtained and also on the amount of water purified per hour; but it has no influence on the removal effect. The installation shown in fig. 2 has a capacity of 10 to 50 m³/h. The time needed for precipitation of the metal ions and sedimentation of precipitate is approximately 40 min.

3. CONCLUSIONS

A technological project for treatment of industrial effluents containing Zn²⁺, Cd²⁺, Pb²⁺, and Mn²⁺ has been presented. Its operation consists in the precipitation of these ions in the form of not easily soluble phosphates at $7.5 \leq \text{pH} \leq 8.0$. The concentration of the heavy metals is below the maximum allowable levels and pH values meet the requirements set by the normative documents.

The developed electronic system for automatic operation and control of the process ensures constant physico-chemical and technological conditions under which a high removal effect is achieved at minimum consumption of reagents and labour expenditure. This technique can be employed independently or in combination with ion-exchange techniques. The method is appropriate for heavy metal extraction from highly concentrated eluates.

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USUWANIE METALI CIĘŻKICH ZE ŚCIEKÓW PRZEMYSŁOWYCH W OBECNOŚCI SOLI AMONOWYCH

Wykazano, że jony metali ciężkich nie mogą być strącane w obecności soli amonowych przez odczynniki zasadowe, gdyż powstają wtedy kompleksy amonowe. Opisana metoda umożliwia usuwanie ze ścieków metali ciężkich w obecności soli amonowych. W swoistych warunkach jony metali są strącane przez kwas fosforowy. Stężenie metali ciężkich w oczyszczonych ściekach jest niższe od ich najwyższych stężeń dopuszczalnych. Aby proces był automatycznie kontrolowany, zaprojektowano system elektroniczny, który gwarantował efektywne oczyszczanie ścieków przy minimalnym zużyciu odczynników.

УДАЛЕНИЕ ТВЕРДЫХ МЕТАЛЛОВ ИЗ ПРОМЫШЛЕННЫХ СТОЧНЫХ ВОД В ПРИСУТСТВИИ АММОНИЙНЫХ СОЛЕЙ

Было обнаружено, что ионы тяжелых металлов могут осаждаться в присутствии аммонийных солей основными реагентами, так как образуются тогда аммониевые комплексы. Описанный метод дает возможность удалить из сточных вод тяжелые металлы в присутствии аммонийных солей. В специфических условиях ионы металлов осаждаются фосфорной кислотой. Концентрация тяжелых металлов в очищенных сточных водах ниже их допустимых концентраций. Для того, чтобы процесс был контролирован автоматически, была спроектирована электронная система, которая гарантировала эффективную очистку сточных вод при минимальном потреблении реагентов.