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MODERN MATERIALS AND TECHNOLOGIES OF INDUSTRIAL WASTEWATER TREATMENT

Abstract: The article substantiates the necessity of using modern materials and technologies for purifying industrial wastewater, because the problem of processing waste products of galvanic production of machine-building enterprises is very important. The current situation in this area leads to environmental pollution by hazardous substances (CN^-, Cr^{6+}, F^-, Cd^{2+}), irrational use of raw materials and significant economic losses. Investigation of ways out of it is an urgent task. The results of a study of water supply and wastewater treatment problems are analyzed, i.e. the authors analyze the processing of technological solutions and wastewater, emphasizing the possibility of extracting valuable components and returning purified water to production. The authors propose to use hydrogen peroxide and hydrazine as a reagent for the extraction of metals at low salinity process water. An integrated approach to the analysis of the use of reagents, materials and technologies of wastewater treatment of industrial enterprises is proposed.

Keywords: wastewater, hazardous substances, precious metals, materials and innovative technologies, electroplating company.

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СОВРЕМЕННЫЕ МАТЕРИАЛЫ И ТЕХНОЛОГИИ ОЧИСТКИ ПРОМЫШЛЕННЫХ СТОЧНЫХ ВОД

Аннотация: В статье обосновывается необходимость использования современных материалов и технологий для очистки промышленных сточных вод, поскольку проблема переработки отходов гальванического производства машиностроительных предприятий является весьма актуальной. Сложившаяся ситуация в этой области приводит к загрязнению окружающей среды опасными веществами (CN^-, Cr^{6+}, F^-, Cd^{2+}), нерациональному использованию сырья и значительным экономическим потерям. Исследование путей выхода из этой ситуации является актуальной задачей. Проанализированы результаты исследования проблем водоснабжения и очистки сточных вод: авторы анализируют переработке технологических растворов и сточных вод, подчеркивая возможность извлечения ценных компонентов и возврата очищенной воды в производство. Авторы предлагают использовать перекись водорода и гидразин в качестве реагента для извлечения металлов при низкой солености воды. Комплексный подход к анализу использования реагентов, материалов и технологий очистки сточных вод промышленных предприятий предлагается.

Ключевые слова: сточные воды, опасные вещества, драгоценные металлы, материалы и инновационные технологии, гальваническое производство.

Introduction

Research in material science allow not only to develop new materials but discover new possibilities of using of already used materials.

These materials find application in various industries, including in engineering. In our opinion, the study of the properties and possibilities of application of these materials is highly important and may find applications in

various promising directions. Properties and characteristics of substances and the scope of their using in technological processes can be related to three major groups:

- characteristics and properties of materials and substances used in equipment and processes (including engineering work). It should be noted that the study of the characteristics of materials and substances necessary not only to analyze the operation of existing processes, but also for designing new equipment and processes;
- characteristics and properties of materials that are incidental in relation to the basic technological processes. These are materials whose properties and economic characteristics are of special value (e.g., precious metals).
- characteristics and properties of materials that are harmful and dangerous. Work with these substances requires the development of special equipment and technologies for their efficient utilization.

The results of studies of the properties of these substances must be taken into account at various stages of pre-production design.

The majority of enterprises in mechanical engineering are composed of either the electroplating workshop, or the workshops of metal preparation and application of various protective coatings (degreasing, pickling, galvanizing, etc.).

For coating on the surface being designed and implemented various innovative technologies. However, the electroplating technology is constantly improving and continues to occupy a leading position [1].

In the wastewater from electroplating plants contains several heavy metals and chemical contaminants which are dangerous for humans and for the natural environment. Especially dangerous are lead, cadmium, chromium, copper, zinc and nickel. The excess concentration above the minimum level leads to inhibition of growth and development of living organisms [2]. Heavy metals have carcinogenic, mutagenic, toxic and teratogenic properties. Normative documents relates these substances to elevated hazard classes and limit their concentration in water of objects of drinking and cultural-domestic of water using [3].

Relevance, scientific significance of the question

The relevance of the discussed questions is the possibility of using the obtained results for the solution of technical, environmental and economic problems. Comparative assessment of the strengths and weaknesses of various cleaning methods is an urgent task. The results of this analysis can be used to select promising methods and technologies improve wastewater treatment engineering companies.

Electroplating plants use water for a number of operations: for the preparation of technological baths, for cooling of equipment, for washing of parts. Washing of parts is an important link in the chain of technological operations in the electroplating process. Transferring parts from one bath to another during the stages of pickling, degreasing, coating, the washing reduces contamination of parts. Contaminated technological water before discharge into the city sewer system or to return to production must be cleaned. Brief analysis

shows that in practice a significant number of industrial wastewater treatment methods are used [4 - 10].

Unfortunately, the problems of development and implementation of the universal purification methods remain unresolved. This is due to the properties and the increasing amounts of pollutants in the aquatic environment. The most important tasks are: neutralization and disposal of harmful and dangerous contaminants and separation from the solution of valuable substances such as gold, silver, and some heavy metals [11]. In connection with the above reasons, it can be argued that the study the properties of material and development of technologies for wastewater treatment of engineering enterprises is the important and promising direction, because it has the great national economic significance.

Statement of the problem

The main objective of this study is to analyze the current status of wastewater technologies of machine-building enterprises and identify promising directions of technological application of materials on the example of the electroplating.

The novelty of the proposed solution consists: in integrated approach to the analysis of the use of reagents, materials and technologies of wastewater treatment engineering companies; in proposal to use reagents that enable to extract the metals at low salinity process water.

Theoretical part

Research, design and implementation of systems of sewage treatment engineering enterprises is a challenging task. Achieving this goal requires the implementation of a large number of organizational and technological measures and understanding of the fundamental theoretical principles of chemical water treatment.

It should be noted that the majority of surveyed enterprises do not pay due attention to scientific approach. *Scientific methods* are very important for development of technological processes of water treatment.

The technology used, the reagents and materials often lag behind the advanced trends and do not meet modern requirements. From a theoretical point of view the most promising way to solve the problem of reducing consumption of the production of fresh water, prevention of environmental pollution and utilization of valuable components is creating the closed cycle systems of industrial water supply [12].

Mixing of spent technological solutions with wash water leads, to significant losses of metals. The resulting mixture of hydroxides of iron, chromium (3+), copper, Nickel, zinc and other components to be badly subjected to further processing (dehydration, drying) and is not suitable for recycling. Usually these sediments, deposited on the dumps and landfills, that are not designed for the safe storage of hazardous materials. This kind of waste leads to re-contamination of the environment [13].

The preferred option for the treatment of spent technological solutions is their regeneration in the plating shop. The first stage is the removal from

solution of unwanted impurities. Then the solution is filtered, adjusted, and can be used for its original purpose. It is the task of technologists of the galvanic plant.

However, the number of regeneration cycles cannot be infinite. Emergencies may arise, requiring the withdrawal of waste technological solutions from production. In this case, it is necessary to apply technologies and methods that allow to identify the most valuable components (chromium, copper, nickel, zinc).

The resulting substance should be prepared for further use, for example, in metallurgical production. Such methods should have the property of selectivity to individual components of process solutions.

Ideally, the addition of reagents should result in the formation of water and easily removable gases (CO_2, N_2, etc.).

At most of the enterprises surveyed, the treatment of chromium-containing effluents is carried out by reagent methods, which leads to the formation of non-recyclable mixtures of salts. For example, in the reduction of Cr (6+) to Cr (3+), ferrous sulphate ($FeSO_4$), sodium sulfite ($NaSO_3$), sodium bisulfite ($NaHSO_3$), sodium hydrogen sulfite ($Na_2S_2O_4$) are used.

The application of these reagents leads to a substantial cost overrun compared to the stoichiometric amount [14].

Large consumption of alkaline reagents (for example, $Ca(OH)_2$) is also required to precipitate a mixture of metal hydroxides. The result is a highly saline drain that is unsuitable for reuse and is discharged into the sewers. The mixed precipitate obtained by this treatment, are taken to the dump. This situation is unacceptable from an economic and environmental point of view.

On the basis of the analysis identified new reagents which provide the selection of metals with minimal the injection of excess reagent and a slight increase in the salinity of the purified solution.

For this purpose, the process of neutralizing chromium (6+) in sewage waters of galvanic production using H_2O_2 (hydrogen peroxide), N_2H_4 (hydrazine) as reducing agents was investigated.

We studied the application of these reagents in neutralization as wash water and waste solutions, for example a solution clarification of cadmium.

It has been established that hydrogen peroxide most efficiently reduces Cr^{6+} to Cr^{3+} in an acidic medium by the following equation:

$$H_2Cr_2O_7 + 3H_2O_2 + 3H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 7H_2O + 3O_2\uparrow$$

For the most efficient recovery of chromium is necessary to maintain the pH of the solution within the range of 1.5 – 1.6 in the slow injection of hydrogen peroxide with an excess of not more than 10 % of the stoichiometric amount.

Before deposition of chromium (3+) from the solution should be removed hydrogen peroxide, as it can lead to oxidation of chromium and formation of complex compounds.

The literature describes the possible use of hydrazine for recovery of chromium (6+) in neutral and alkaline medium according to the equation [15]:

$$4K_2CrO_4 + 3N_2H_4 + 4H_2O \rightarrow 4Cr(OH)_3\downarrow + 8KOH + 3N_2\uparrow$$

Studies found that the recovery of chromium (6+) is more efficient in acidic medium according to the equation:

$$2H_2Cr_2O_7 + 3N_2H_4 + 6H_2SO_4 \rightarrow 2Cr_2(SO_4)_3 + 14H_2O + 3N_2\uparrow$$

Both suggested reagent can provide post-treated chromium recovery, and can allocate the hydroxides of chromium and cadmium. Such operations can be carried out on existing plants.

We believe that we need to make the separation of waste streams in the electroplating shop. This operation will lead to sewage treatment processes with high efficiency and will create opportunities for utilization of the most valuable components. In practice, sewage with hazardous components (CN^-, Cr^{6+}, F^-) is fed to a sewage treatment plant through separate pipelines. After separate neutralization effluents are combined into a single stream. Further processing of this stream in the surveyed companies anticipates his discharge in municipal sewers. The negative results of such technology are described in the literature [16].

Effective extraction of heavy metals can be obtained from the use of complex schemes of cleaning. In this case, it may be arranged to return the rinsing water, the purified ion exchange, electrodialysis, membrane, flotation techniques or by evaporation [17-19].

It should be noted there is the significant progress in the technology of membrane separation. Reverse osmosis systems make a more effective extraction of the salts at a much lower than earlier operating pressure. Accordingly, it requires a much lower cost. Synthesized a significant number of new ion-exchange resins, is far more efficient than traditional ion exchangers [20].

New ion exchange resins allow to selectively extract the metals from the wash wastewater. On the basis of membranous and ion-exchange technology has created a local installation for the treatment of wastewater from electroplating facilities [21]. Local installations allow you to return the water to production. It should be noted that local units have limited performance. However, some companies use such methods and technologies in production.

The disadvantages of ion exchange and membrane techniques include the formation of eluates and concentrates, which require separate processing. Treatment of concentrates is a necessary and complex process. The methods used depend on the requirements for recycling the components to be isolated.

Purification methods using various nanomaterials [22, 23] refer to new technological solutions. Unfortunately, these methods have not yet received wide practical application.

Upon appropriate technological design, these materials can provide a breakthrough in the field of wastewater treatment.

Practical part

The results of the research are formulated the following practical suggestions:

- the use of advanced materials and technologies in wastewater treatment engineering enterprises requires the implementation of certain organizational principles. These principles should provide the optimum combination of environmental, economic and technical indicators;
- to clean chrome-containing waste technological solutions and wastewater, it is advisable to use hydrogen peroxide and hydrazine, which provide a minimal increase in salinity of the treated wastewater.

The concept of technological development of systems of water supply and wastewater treatment in machine-building enterprises are offered the following directions:

- development and implementation of waterless technology of application of protective coatings;
- accommodation-premises installations for the regeneration of process solutions and wash water (ion-exchange, membrane, electrochemical, evaporation) in the process lines electroplating;
- separation of waste streams according to the types of contaminants when discharged to the common sewage treatment plant;
- development and implementation of non-toxic (low toxicity) technological solutions;
- the prospective use of reagent-free technology with return of purified water in the production processes of wastewater treatment at treatment facility.
- development of low-waste processing of waste technological solutions for the purpose of extraction of valuable components and reducing the salinity of sewage;

Summary

The obtained results can be used in the design, construction, modernization and reconstruction of machine-building enterprises.

A new construction project or a reconstruction project should include new technological solutions for wastewater treatment.

These decisions must take into account the promising technologies of the main production.

In this regard, existing and reconstructed galvanic plants must provide:

- maximum service life of solutions of electrolytes, which is achieved through preventive and corrective actions;
- reduction of the diversity of electrolyte solutions;
- replacement of solutions of electrolytes with toxic components (cyanides, cadmium, chromium (6+)) for less toxic;
- application of non-reagent purification methods that provide the prerequisites for the introduction of drainless technologies.

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