INVESTIGATION OF THE METHOD OF CHEMICAL DESORPTION FOR EXTRACTION OF NIKEL IONS (II) FROM BENTONITE CLAYS

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Abstract. The problem of accumulation of spent sorbents is considered in the article; The main methods of desorption of pollutants and regeneration of sorbents are described; the effectiveness of the method of chemical desorption for extracting Nikel ions (II) from bentonite clays is investigated; the main ways of utilization of spent sorbents are considered.

Key words: bentonite clay, utilization, regeneration, chemical desorption.

Introduction

When using high-performance sorbents, water can be purified from pollutants to virtually zero residual concentrations. Significant advantages of the method are that sorbents can desorb substances from water at any concentration, including very small, when other methods of purification are ineffective. With the help of the sorption purification plant, up to 98 % of non–ferrous metals can be disposed from sewage of galvanic production [1].

The advantages of sorbents include low cost and affordability. There are over 110 deposits and manifestations of bentonites in Ukraine. The state balance of Ukraine's reserves includes 6 deposits (Gorbkivsk, Kudrinsk, Cherkasy, Kurtsivsk, Berezhansk, Pyzhivsk), whose stocks are classified by categories $A + B + C_1 - 2624$ thousand tons, $C_2 - 221$ thousand tons, balanced stocks by categories $B + C_1 + C_2$ is 1,415 thousand tons. Currently only three fields are developed: Gorbkivsk, Kudrynsk and Cherkasy, which makes up about 86 % of the country's reserves and gives the main percentage of extraction of bentonite raw materials. Kurchetsk, Berezhany and Pyzhivsk deposits are currently preserved [1].

Actuality, perspective and advantages of the use of natural mineral sorbents, in particular bentonite clays, in the processes of sewage treatment is substantiated in many scientific works. However, the question of the accumulation of sorbents that have used their sorption potential, regeneration or utilization remains relevant and requires the development of integrated waste–free technologies.

An analysis of recent studies and publications suggests that the problem of accumulation of spent sorbents is partly solved by restoring the sorption properties of the sorbent for reuse in the treatment processes.

Setting the task and its solution

Investigation of the adsorption process was carried out in an adsorption column with a stationary layer of the adsorbent.

Bentonite (type 2:1) of Cherkasy deposit of bentonite and paligorskite clays was used for research. The process of preparation of bentonite consisted of several steps: chopping into crumbs, drying at 120 °C for 45 minutes, grinding again into powder and sifting on sieves. The finished sorbent was loaded into a column with a diameter of 35 mm and a height of 20 mm [2].

To establish a number of regime parameters that require a detailed study of the adsorption processes, a number of previous experiments was carried out, which made it possible to draw the following conclusions:

1) temperature fluctuations from +10 to +30 °C do not detect a noticeable affect on the degree of adsorption of ions by Ni^{2+} bentonite;

2) the optimal ratio between the solid and liquid phases is 1:20; at higher dilution, the amount of adsorbed N^{2+} decreases, and the T : P ratio is lower, despite the improvement of the adsorption results, irrational, since already at T : P = 1: 7 there is a strong thickening of the pulp, which complicates further filtration processes;

3) the contact time of the adsorbent with the solution did not exceed 30–40 minutes, the total time of loading before the breakthrough of Nikel ions was about 2 h;

4) the range of investigated concentrations (0.5–1 g/l) of the adsorbent was selected based on practical considerations according to the possible content of the cation Ni^{2+} of actual effluents. The distribution coefficient (Kd) is calculated, which practically does not depend on the concentrations of ions in the solution, within the range of the selected interval;

5) Maximum absorption of Nikel ions (II) occurs within 3 hours. and is 2 %. Calculated values of the dynamic exchange capacity, which are in the range of 0.34 – 0.6, depending on the mass of the sorbent.

6) The adsorption efficiency was determined depending on the amount of sorbent in the stationary layer.

It is calculated that the effective volume when pumped through the model solution through the absorbent layer of 15 g is 3.47, and when passing the solution through 20 g of sorbent – 4.51.

The dynamic exchange capacity of the sorbent when pumped through the model solution through the mass of sorbent 15 g is 0.518 mg/g, and for 20 g of sorbent – 0.354 mg/g.

After saturation of the adsorbent with the absorbed substance, its desorption (regeneration) [1, 5, 8] is carried out, that is, the recovery of the adsorbate and recovery of the adsorbent. The process of desorption is considered to be one of the most important stages of the process of adsorption purification. First of all, it concerns the disposal of adsorbent wastes after their use in the process of wastewater treatment. After all, it is important not only to clear waste water from industrial plants and to obtain clean water, but also to ensure that utilized waste is a minimum amount so that they are non–toxic and harmless to the environment [3].

The authors [1, 58] among the main methods of conducting desorption during the purification of industrial gas and liquid streams include:

1) thermal (due to increase of temperature of the layer of adsorbent);

2) chemical;

3) Extruded (so-called cold);

4) extraction;

5) desorption by combined methods.

The application of a method of desorption depends on the adsorbent–adsorbate system, taking into account technical and economic indicators.

The choice of one or another method of regeneration is based on techno-economic and ecological foundation. Often in industrial practice, thermal methods of regeneration are used.

Thermal desorption, as the most commonly used method of regeneration of adsorbents, is carried out by heating the layer of an adsorbent by passing a desorbing agent through it (saturated or superheated water vapor, hot air, gas inert under these conditions), or by contact heating of the adsorbent (through the wall of the apparatus) with blowing a small amount of inert gas (for example, Nitrogen), which results in the release of the absorbed component from the adsorbent [1, 5, 7].

Depending on the adsorbent–adsorbate system, desorption in industrial conditions is usually carried out at moderate temperatures of 100–200 °C and at elevated temperatures of 200–400 °C [1]. Desorption at elevated temperatures in the range of 200–400 °C is usually carried out to isolate absorbed substances from zeolites (synthetic and natural), having a strictly ordered structure of pores and significant adsorption forces [1].

Extruding desorption is carried out by displacing from the adsorbent of the absorbed substance (adsorbate) by another component, which is an extruder (desorbent), to which the following requirements [8] apply:

- − good sorption ability;
- − ability to actively displace absorbed components from adsorbent;
- − fire and explosion protection;
- − ecological safety (non-toxicity);
- − low cost.

When choosing a desorbing agent, it must be taken into account that the adsorbent must not only effectively remove the adsorbate but also effectively remove it further.

Chemical regeneration involves the treatment of sorbent by liquid or gaseous organic or inorganic reagents at a temperature not higher than 110°C [1]. As a result of this treatment, sorbate is usually undergoing chemical transformation and is desorbed in the form of products of its interaction with the regenerating agent. Chemical regeneration often occurs directly in the adsorption apparatus. Most methods of chemical regeneration are highly specialized for sorbitans of a certain type.

The simplest method of regeneration of a sorbent is to heat it in some volume of water. This leads to an increase in the degree of dissociation and solubility of sorbate and, eventually, to the desorption of a part of the sorbate. Moreover, it is possible to heat not adsorbent, but water and filter it through a layer of the sorbent. The effect of such regeneration is small and is 10–40 % [1, 5, 8].

For the desorption of organic sorbate, extraction is often used [5]. For this purpose, low–boiling, easy to distill with steam organic solvents (alcohols, acetone, chloroform, dychloroethane, benzol, butyl acetate), followed by the separation of the spent solvent. It is important that [1]:

– the solubility of the sorbate in the solvent was higher than in water;

– the coefficient of distribution of sorbate in the extraction of its solvent from water was maximal; – the solvent is wetted well by the sorbent;

– had a low boiling point and viscosity;

– was non-combustible and explosive;

– desorbed easily from the sorbent after regeneration and accelerated to return it for the next processing cycle.

Also, the above methods combine with each other. For example, the extraction regeneration of sorbent from multicomponent sorbate is more effective when combined with chemical regeneration with successive treatment with several reagents under harsh conditions.

Although the methods vary, but the ultimate goal of processing the spent sorbent is to turn it into a harmless product that will not harm the environment and can be used for different economic needs [3–4].

Materials and methods

A study was conducted on the effectiveness of the method of chemical desorption for the extraction of Nikel ions (II) from bentonite clays.

The object of the study is spent bentonite clays from the Cherkasy deposit of bentonite and paligorskite clays, saturated with Nikel ions (II).

Investigation of the content of Nikel ions in the bentonite sample was conducted using a method based on extracting metal compounds from clay (converting them into a solution), obtaining a complex of Nikel with dimethylglyoxime (red–brown) and measuring the optical density of the solution. Nikel bound to a complex with dimethylglyoxime is pre–separated by extraction with chloroform, thus eliminating the influence of a number of interfering elements.

Preparation of the extractor. A pre–prepared sample of bentonite clay contained Nikel ions (II) of 0.354 mg/g. To remove available (acid soluble) forms of Nikel, 1M HCl was used. The ratio between bentonite and solution is 1:10, the extraction time is 1 hour when shaking on a magnetic stirrer. The resulting slurry was filtered through a folded filter, and the first portions of the filtrate were discarded.

Construction of gradation graph. In a volumetric flask of 25 cm^3, were added; 0; 1.0; 2.0; 3.0; 4.0; 5.0 cm^3 of standard Nikel solution at a concentration of 10.0 mg/cm^3, which corresponds to 0; 10.0; 20.0; 30.0; 40.0; 50.0 mg of Nikel, the solutions were brought to a volume of 10 cm^3 with distilled water, 2 cm^3 of bromine water, 2 cm^3 of a 4 % solution of ammonium persulfate and 2 cm^3 of 1 % dimethylglyoxime solution in 5 % potassium hydroxide solution were added. The contents of the flask were mixed, and after 10 minutes, a volume was brought to 25 cm^3 with distilled water and the optical density was measured at a wavelength of 450 nm (30 mm cuvette length).
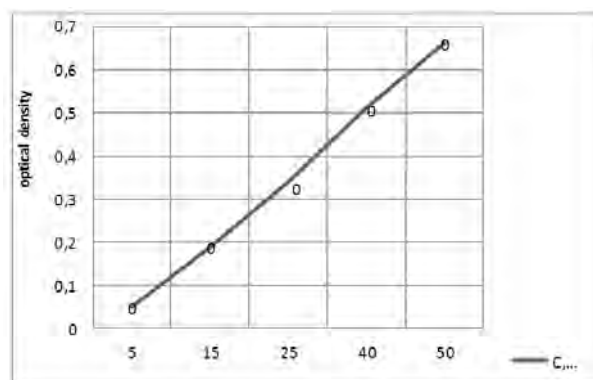
Received gradation graph (Fig. 1):

Fig. 1. Optical density dependence on the concentration of Nikel (II) ions in the solution

Progress. An aliquot of the analyzed solution of 5–50 cm^3 was placed in a separating funnel with a volume of 100 cm^3, arranged in a 10 % solution of ammonia to pH 5.5–6.0, 2 cm^3 of 1 % alcohol dimethylglyoxime solution was added and stirred. After 5 minutes, 5 cm^3 chloroform was added to the resulting solution and vigorously shaken. After separating the phases, the organic layer was transferred to a mixing cylinder of 100 cm^3. The residual aqueous solution was again poured into 5 cm^3 of chloroform and the extraction was repeated. To the combined organic extract, 5 cm^3 of a 0.5 M solution of hydrochloric acid was added and vigorously shaken. The aqueous phase was transferred to a volumetric flask of 25 cm^3. Re-extraction of Nikel in 5 cm^3 0.5 M solution of chloride acid was repeated in a mixing cylinder. The organic layer was discarded, and the aqueous solution was combined with the previous one. 2 cm^3 of bromine water, 2 cm^3 of 4 % ammonium persulfate solution and 2 cm^3 of 1 % solution of dimethylglyoxime in 5 % potassium hydroxide solution were added into the obtained re-extract. The contents of the flask was stirred and, after 10 minutes, brought to a volume of 25 cm^3. Measurements of optical density were carried out at a wavelength of 450 nm and a length of 30 mm cuvette.

For the reliability of the results, each experiment was repeated three times. All chemical reagents had the category "c.p." and "c.f.a".

The contents of Nikel in clay (X, g/kg) was calculated by the formula:

$$X = \frac{C \cdot V_0}{V_1 \cdot m},\qquad(1)$$

where C is the Nikel contents found on the graph, mg; V_0 – volume of output extractor, cm^3; V_1 – volume of extractor, taken for analysis, cm^3; m – clay marsh, g.

$$X = \frac{2{,}5 \cdot 31}{25 \cdot 10} = 0{,}31.$$

According to calculations, the bentonite sample contains Nikel ions (II) – 0.31 mg/g.

Comparing with the practical content of metal ions, the difference with the calculated values of Ni^{2+} in the sample of clay is – 0.044 mg/g or 12 %. This value is allowed within the experiment, taking into account the measurement error, due to losses of clay in the filters during drying and repeated extraction.

Consequently, the chemical method of desorption can be recommended for the removal of Nikel (II) ions from bentonite clays and conducting re-adsorption with spent adsorbents after preliminary removal of contaminants.

Purified bentonite clay and extracted metal ions can also be used in other sectors of the economy.

The strategy of disposal of spent sorbents after the treatment of wastewater from pollutants is to use them in various industries: as bedrock for the creation of anti–filter screens; as effective additives in the production of claydite; for the preparation of building mixtures based on plaster binder; addition of sludge to building plaster; use in building ceramics; like fertilizer, etc [4].

Also, according to the source [5], it was rational and economically advantageous to use the sorbent–saturated colored metal as a feed additive in the sulfide melt of the source Nikel–containing ore. Industrial testing of this recovery method has shown that the degree of Nikel extraction is 99.9 %, copper – 99.4 %, cobalt – 91 %.

Removed metal can also be used in other industries. After all, Nikel coatings have high corrosion resistance and good mechanical properties – hardness, durability. Nikel is one of the most important magnetic materials with a minimum coefficient of thermal expansion. These properties provide wide application of the Nikel process in many industries.

Nikel is used as a protective and decorative coating to protect products from corrosion in atmospheric conditions and alkaline media. In the open air at normal temperature, a thin passive film is formed on the surface of Nikel, which stops the process of further oxidation. A thin oxide film on the surface of coating does not change its outer appearance. The Nikel coating has a fine–crystalline structure and is perfectly polished. Due to this, Nikel coatings are used extensively for the finishing of products in various industries: in the manufacture of cars, bicycles, appliances, medical instruments and consumer goods.

Nikel coatings have high corrosion resistance, hardness and unique decorative characteristics. The gloss of Nikel coatings resembles a similar luster of chrome coatings.

Nikel coatings are applied to almost all ferrous and non–ferrous metals.

Today, there are no uniform requirements for the quality of raw materials regulated by state standards, with some exceptions. Due to the wide range of clay usage and the peculiarity of their processing, it is difficult to establish a clear relationship between the properties of raw materials and finished products. The suitability of raw materials is determined by the quality of finished products and the possibility of obtaining certain products and is regulated by technical requirements [8].

Utilization of spent sorbents helps not only to reduce the technogenic load on the environment, but also to improve the technology of creating alternative materials due to the use of high-quality clay material.

Conclusions

After saturation of the adsorbent with the absorbed substance it is possible to desorb it with chloride acid, and thus to restore the absorption capacity of the adsorbent.

The main methods of regeneration of adsorbents include: thermal, chemical, extruding, extraction, combined. The choice of one or another method of regeneration is based on feasibility studies.

We proposed to use a method of chemical extraction of Nikel ions (II) from the spent sorbent.

Purified bentonite clays can then be used in other sectors of the economy.

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