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The Use of Aluminum-Containing Waste Foraqueous Media Purification from the Compounds of Hexavalent Chromium

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Abstract: The necessity of wastewater treatment from hexavalent chromium compounds with mutagenic and carcinogenic properties is determined. There are given the known methods of sewage treatment from chromate ions and proved that the use of corundum crystals production waste as sorption material is promising. By XRD method the mineralogical composition of waste including oxides and hydroxides of aluminum in various versions is determined. XRF wave analysis has defined the component composition of waste, comprising over 97% of aluminum compounds in the form of oxides and hydroxides. The waste particles specific surface area was determined using a multipoint BET Method. Using a scanning electron microscope there were studied the morphological features of the waste particles and the complexity of their structure is revealed. There are constructed and analyzed the sorption and desorption isotherms of chromate ions on the waste components. A negative adsorption in the concentration range of chromate ions from 10-60 mg L^{-1} was revealed, the physical character of reversible chromate ions sorption processes was determined. The efficiency of the cleaning process modeling solutions up to 70% is shown.

Key words: Hexavalent chromium compounds, mutagen and carcinogen, wastewater treatment, waste production, aluminum oxides and hydroxides, sorption properties, cleaning efficiency

INTRODUCTION

The rapid growth of modern production leads to an increase of anthropogenic stress on the biosphere. The environment receives a huge amount of waste in different states of aggregation. Upon contact the waste with biologically active medium there migrate substances of different chemical nature-heavy metals, petroleum products, pesticides, synthetic surfactants, the elements of destruction of building materials, creating a real threat to the living components of the ecosystem including humans (Sverguzova *et al*., 2011). Thus, heavy metal ions, embedding into cell enzyme systems violate their functioning and cause severe disease (Moore and Ramamurthy, 1987).

There is a wide range of methods to treat waste water containing heavy metals (ATSDR, 2000). However, given the conditions of the waste water generation no method can be considered universal, so the development of effective and low-cost methods including those on the basis of industrial wastes is relevant.

METHODS

In the present studies for cleaning chromium containing modeling solutions there was used the waste generated during cutting and polishing corundum crystals grown by the Verneuil Method, on the product.

The X-ray analysis of the crushed in an agate mortar components of the waste was carried out on a diffractometer "DRON-2" with CuK α radiation and a nickel filter.

The component composition of waste was studied by X-ray fluorescence analysis of the wave spectrometer ARL 9900.

The study of the waste particle surface was performed by scanning electron microscope MIRA 3 TESCAN.

The specific surface area of the waste particles was determined using multipoint BET Method. The sorption capacity of waste particles was studied under static conditions by the limited volume of the solution at various initial concentrations of chromate ions. The sorption unit, i.e., the ratio of the volume of solution (mL) to weight (g) of the sorbent was 100. Exposure time with

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constant stirring was 24 h. Model solutions were prepared from a concentrated salt solution K_2CrO_4 mark "h". Absorbance of solutions was determined by KFK-2MP. Error does not exceed 5%. The concentration of chromate ions before and after the sorption equilibrium was determined by standard methods (Smirnov and Genkin, 1980).

The acidity of the environment model solutions was monitored at the beginning of the experiment and after the exposure time of the potentiometric method at pH meter pH 150 M pH to within ±0.05.

THE MAIN PART

Hexavalent chromium compounds pose a particular danger to biological ecosystems. They are more toxic than trivalent chromium compounds. Normative content of chromium (VI) in natural water in the territory of the Russian Federation corresponds to 0.05 mg L^{-1} and is limited by sanitary-toxicological endpoint. Content of chromium (VI) and chromium (III) in the composition of water entering water sources as a result of human activity, is 0.1 and 0.5 mg L^{-1}, respectively. The limiting, in this case is a sensory component (Smolenskaya *et al*., 2004). Many of hexavalent chromium compounds have high solubility and are not capable, like the compounds of trivalent chromium to form poorly soluble compounds in neutral and alkaline media.

Fomin (2000) notes that chromium and its compounds are mutagenic and carcinogenic in various stages of development of organisms. The intoxication of an organism with chromium and its compounds is accompanied by numerous pathological reactions of all organs and systems. Due to what is listed above, the delivery chromium compounds in the environment is unacceptable and the waste water containing chromium compounds must be subjected to a deep cleaning.

The basic techniques aimed to extract the chromium compounds from wastewater are the following:

- Biochemical, based on the ability of specific microorganism cultures to use the bound oxygen chromate in their living under anaerobic conditions
- Hyper filtration (reverse osmosis) based on the filtration of wastewater under pressure through a semi-permeable membrane, water-permeable but delaying the hydrated ions of dissolved salts
- Electrochemical, the essence of which is in the chemical reduction of dichromate and chromate ions by iron Ions (II) formed by electrolytic dissolution of steel anodes
- Pre-reduction reagent with the hexavalent chromium to trivalent chromium, such as salts of Iron (II)
- Sorption, consisting for example, chromium containing pre-filtration of acidified wastewater through activated carbon BAU

No less relevant are the methods which are actively being developed at present for recovering chromium compounds from the wastewater using waste industry and agriculture (Mamyrbayev, 2012). These wastes may have sorptive properties as well as used as the reagent.

In the practice of wastewater treatment there is known to use of artificial fibers and non-carbon materials of natural and artificial origin (metal oxides, clay rocks, zeolites, waste a number of industries). Natural zeolites, such as clinoptilolite and montmorillonite are recovered from industrial waste water of 90% or more, formed by chemical or electrochemical treatment of metals such as Pb^{2+}, Ba^{2+}, Sr^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}.

Lupandina considered the possibility of sorption removal of copper, cobalt, nickel, manganese, iron and chromium ions by the oxides of these metals at different pH values.

Sverguzova *et al.* (2011) analyzed in detail the various kinds of patterns of adsorption of anions (simple and complex, organic and inorganic) on the surface of iron, titanium, aluminum, chromium, zirconium and manganese oxyhydroxides.

Earlier the researchers (Smolenskaya *et al*., 2011) studied the mechanism of wastewater treatment from hexavalent chromium ions and copper ions and nickel single crystals of corundum waste product consisting of >95% of alumina and 40-50% humidity. In subsequent process steps, namely, cutting and polishing crystal grown products produced waste size from 0.05-1.4 mm and a moisture content of <5% which was used in these studies.

Model solutions was purified with a range of concentrations of chromate ion from 0.01-1.0 g L^{-1}. Reaction (pH) before entering a sorption material was 6.0±0.05. After 24 h after making the sorption material pH of the aqueous medium has reached 7.5±0.05 which suggests the presence of chromium ions in solution in the form of chromate.

The XRD data of waste (Fig. 1) showed that the most intense peaks correspond to partially amorphous aluminum oxides and hydroxides in various versions.

The X-ray fluorescence analysis of the composition revealed that aluminum compounds along with the waste also comprise other components shown in Table 1.

The 97.71% of the waste product consists of aluminum compounds, the share of other components amount to l<3%.

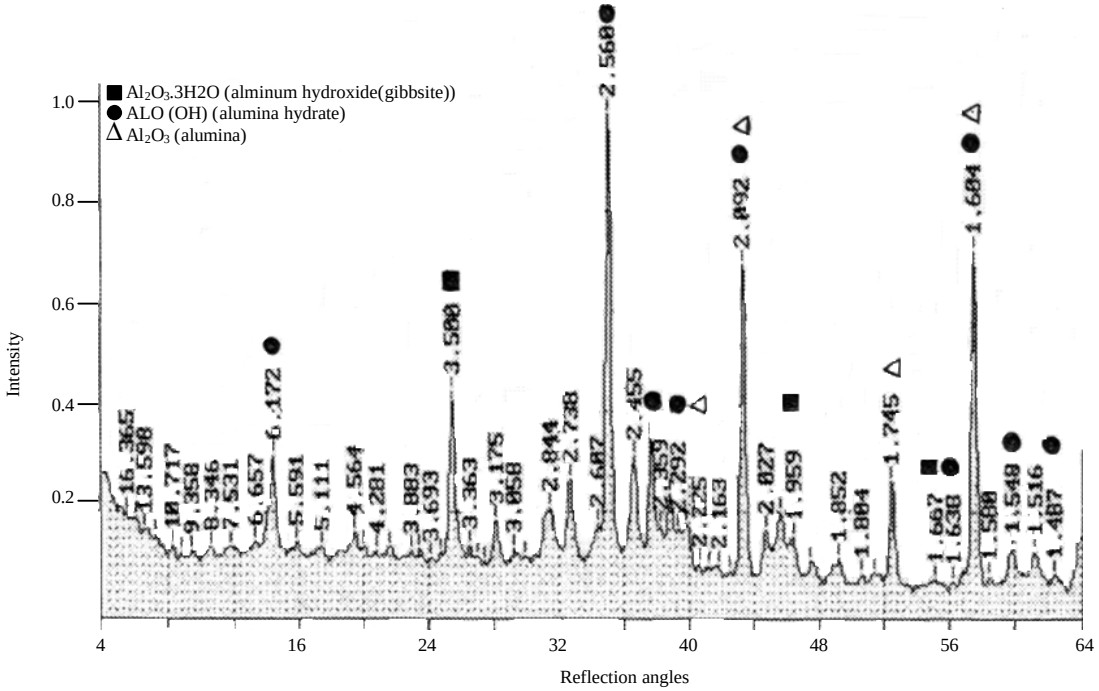

Fig. 1: The mineralogical composition of waste from cutting and grinding crystals

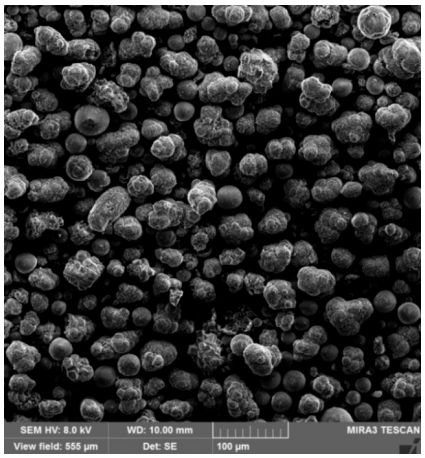

Fig. 2: A photomicrograph of the particles of waste from cutting and grinding product crystals

The micrographs clearly show that the waste particles have spheroidal structure with high surface area (Fig. 2). The size of the particles formed by cutting and grinding (10-75 microns) as well as chips, layering, deformation affects the formation of the specific surface.

The specific surface area of the waste particles is 64.6±4.5 m^2/g which suggests the presence of sorption activity of the test material. Sorption and desorption isotherms of chromate ions on the waste particles are shown in Fig. 3.

Table 1: The component composition of waste

Components	Content (%)	Components	Content (%)
Al2O3	97.71	SO3	0.0629
SiO2	0.983	K2O	0.0398
Na2O	0.288	Rh2O3	0.0286
Cl	0.268	Cr2O3	0.0204
Fe2O3	0.186	RuO4	0.0191
MgO	0.170	PdO	0.0112
CaO	0.144		

The plots located below the axis of $C_{equilibrium}$ characterize isotherms and indicate a negative adsorption on the initial stages of the process in a concentration range of chromate ions from 10-60 mg L^{-1}. Negative adsorption is observed in the case where the solvent, i.e., water is also adsorbed largely. The adsorption of water results in the increase of chromate ions concentration in the solution. On completion of the adsorption of water molecules there begins the sorption of chromate ions in a concentration range of 60-1000 mg L^{-1}.

According to the BET classification part of the adsorption isotherms in the range of 60-1000 mg L^{-1} refers to the type I, the convex portion of which indicates the presence of micropores sorbents (Kutsiy, 2004).

The location of the sorption and desorption isotherms in the coordinate system relative to each other indicates the mixed nature of the processes with a predominance of physical adsorption of chromate ions.

The physical sorption at the extraction of metals from solutions looks more preferable because it suggests the

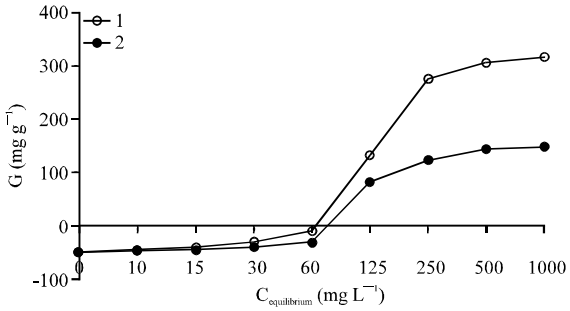

Fig. 3: 1) Sorption isotherms and 2) desorption of chromate ions on the particle surface

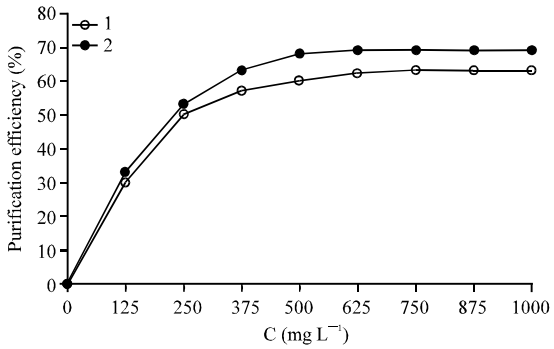

Fig. 4: The efficiency of cleaning model solutions from chromate ions with waste of corundum single crystals production; 1: waste humidity 40-50% and 2: waste from cutting and polishing crystals

possibility of regenerating the sorbent. Another no less important process is the concentration of solutions during washing sorbents which greatly facilitates the wastewater disposal process.

Treatment process efficiency under these conditions is 30-70% for the model solution in the concentration range from 0.125-1.0 g L^{-1} (Fig. 4, graphical depiction-2).

Line 1 shows the cleaning efficiency of model solutions from chromate ions by aluminum containing waste with a moisture content of 40-50%.

CONCLUSION

Thus, the findings of the research indicate the possibility of using aluminum-containing waste in the practice of cleaning solutions containing chromium compounds. This will partially solve the problem of creating low-waste technology systems within a particular economic area when the waste of one industry will serve as a raw material for another. It is necessary to know in detail the peculiarities of the formation of a waste, its properties as well as ways to improve efficiency, recycling and waste management in various technological purposes. This research is aimed at achieving these goals:

- By methods of XRD, wave fluorescence spectrometry, electron microscopy there were studied the qualitative composition and the main physical and chemical and surface characteristics of aluminum-containing waste products of corundum single crystals production
- By methods of isotherms construction there were studied the processes of sorption and desorption of chromate ions on the particles of waste. The mixed character of sorption processes with a predominance of physical interactions is determined
- The efficacy of the purification process of chromate-containing solutions is evaluated and it is established that cleaning is more effective for concentrated solutions with waste from cutting and grinding corundum crystals for product

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