Recovery of Caprolactam Manufacture Solid Wastes

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Abstract

Basing on the results of experimental studies on equilibrium, kinetics and dynamics of adsorption process as well as mathematical modelling, a resource-saving and environmentally safe technology is developed for galvanic wastewater treatment from heavy metal ions. A schematic diagram is proposed for the unit of galvanic wastewater treatment.

Key words: heavy metals, spent active coal, adsorption, optimization, technology

INTRODUCTION

The manufacture of caprolactam represents one of large-scale manufactures with the use of great volumes of wastewater. At the stage of adsorption purification of low-concentration organomineral wastes from this manufacture a significant amount of spent adsorbent is formed which adsorbent is dumped to slag-heaps. Caprolactam contained in the sorbent enters into surface water reservoirs due to washout from the spent sorbent and by rains and thawed snow, which results in the destruction of natural ecosystems due to bioresistant and toxic properties of this substance. In this connection the recovery of the spent sorbent represents an important ecological problem.

This work presents the results of the investigation of potentialities for using a spent sorbent in the process of heavy metals adsorption as well as the results of the optimization of an adsorption filter and an adsorption technology for the extraction of heavy metal ions by a spent carbon sorbent.

EXPERIMENTAL

The subject of inquiry represented AG-OV-1 technical coal spent as a sorbent in the waste-water treatment process of caprolactam manufacture. After the saturation with caprolactam the samples were heated at the temperature of 250 °C for attaching the comprolactam molecules onto the surface of coal and thus obtained a modified kind of coal AG-OV-1cl. The investigations have demonstrated that after heating there are polymeric structures formed on the surface of coal those prevent caprolactam from washing away [1].

The IR spectroscopic analysis of samples modified with caprolactam has demonstrated that there is a considerable amount of the CN, CNO groups present on the surface of activated coal. Basing on these data it has been assumed that on the surface of activated coal, to all appearance, the formation of complex compounds with the ions of heavy metals might occur whereupon the spent sorbent could be used for heavy metals extraction.

The wastewaters containing ions of heavy metals (HM) also represent a source of environmental contaminations. The majority of HM ions are characterized by I–II hazard level, exhibiting carcinogenic and mutagenic properties with a cumulative effect. Currently available methods of wastewater purification from HM ions (ion exchange, electrocoagulation, electrodialysis, *etc.*) are labour-consuming and re-

quire for a high consumption of reagents, desalted water, high electric power inputs and frequently result in the formation of by-products.

Within the framework of the creation of an adsorption technology we have carried out studies on the statics, kinetics and dynamics of adsorption processes [2]. The comparative studies on the adsorption of metal ions onto technical and modified coals have demonstrated [3] that the adsorption capacity with respect to the extraction of Pb^{2+}, Cu^{2+}, Cd^{2+} ions from model solutions and industrial wastewaters with the use of a modified kind of coal is 14, 1.5, 1.8 times higher than the mentioned value for technical coal, respectively

The optimization of the parameters of the adsorption column filled with the AG-OV-1cl adsorbent as well as of the mode of continuous purification process was carried out using a mathematical modelling method based on theoretical relationships describing mass transfer. The application of mathematical modelling methods has allowed us to reduce the volume of experimental research to a considerable extent. The theoretical calculation is based on the fundamental equation of external diffusion adsorption dynamics in the case of a linear isotherm, with the use of adsorption constants of the Dubinin−Radushkevich equation and experimental data concerning the kinetics for heavy metal ions sorption from technological wastewaters onto carbon sorbents:

$$\sqrt{\tau} = \sqrt{\frac{a_0}{wC_0}}\sqrt{H} - b\sqrt{\frac{a_0}{\beta_n C_0}} \qquad (1)$$

Here τ is the operating time for layer with length H before the occurrence of a breakthrough sorbate concentration (C); C_0 is the initial concentration of a substance in the flow, mmol/dm³; a_0 is the content of a substance in the stationary phase being in equilibrium with C_0, mmol/kg; w is the average flow velocity, m/h; β_n is the external mass transfer coefficient.

In order to verify such an approach, experimental studies were performed concerning the adsorption of metal ions under dynamic conditions by the AG-OV-1cl modified carbon adsorbent from wastewater of galvanic manufacture and output curves were plotted. Figure 1 demonstrates theoretical and experimental output curves of adsorption dynamics for various HM ions.
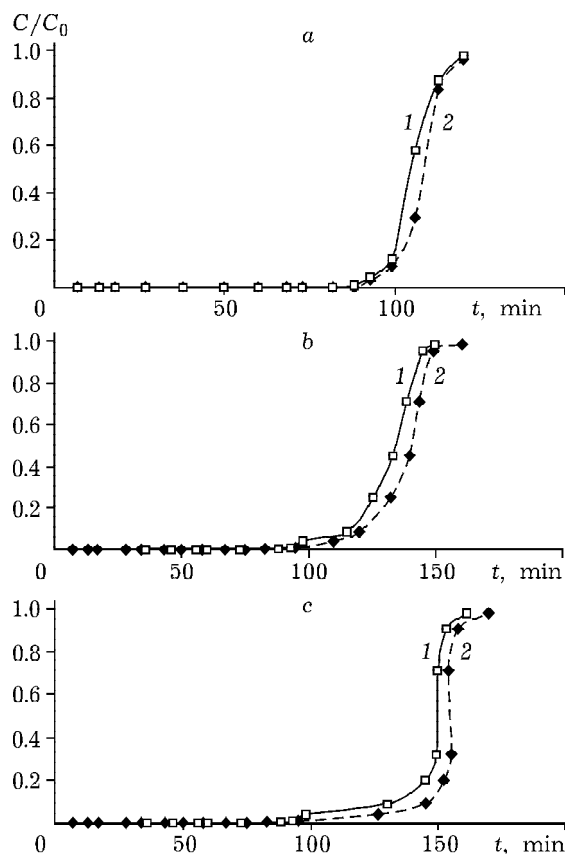

Fig. 1. Theoretical (*1*) and experimental (*2*) output curves for copper (*a*), cadmium (*b*) and lead (*c*) ion adsorption dynamics from aqueous solution for modified active coal AG-OV-1cl.

One can see that the results of experimental investigations and theoretical calculations are in a good agreement among each other, therefore equation (1) could be used for the calculation of adsorption columns.

The results of the studies on adsorption dynamics have demonstrated that the operating time of the column up to the breakthrough into the filtrate decreases according to the order Pb > Cd > Cu. In this connection calculation of an adsorption column for the galvanic manufacture has been carried out taking into account the adsorptivity of copper.

As the result of the calculation the following dynamic characteristics of the adsorption process were obtained: dynamic capacity, the velocity of operating zone movement, the operation time of a stationary layer, the length of operating layer, the amount of water purified before the breakthrough.

RESULTS AND DISCUSSION

The experimental and theoretical studies carried out have demonstrated that there is a potentiality of the adsorption extraction of heavy metal ions with the use of a spent adsorbent due to chemical interaction between nitrogen-containing surface groups of the adsorbent modified by caprolactam and heavy metal ions with the formation of complex compounds.

In order to solve the problems of environmental protection, resource saving and to prevent an enterprise from economic sanctions (penalties) for breaking the nature protection laws we have offered to include an adsorption purification stage in the existing technological process flowsheet of wastewater treatment (Fig. 2). The process of wastewater treatment with inclusion of the adsorption purification stage is realized as it follows.

Wastewater from washing baths after etching, degreasing and galvanic coating operations is dumped into neutralizer tanks 1. The neutralization of acidic wastewater and the sedimentation of heavy metals is performed up to pH 8–9 with the use of 5 % lime milk solution. The lime milk from a feed tank 2 is fed into neutralizer tanks 1 with the help of a dosing
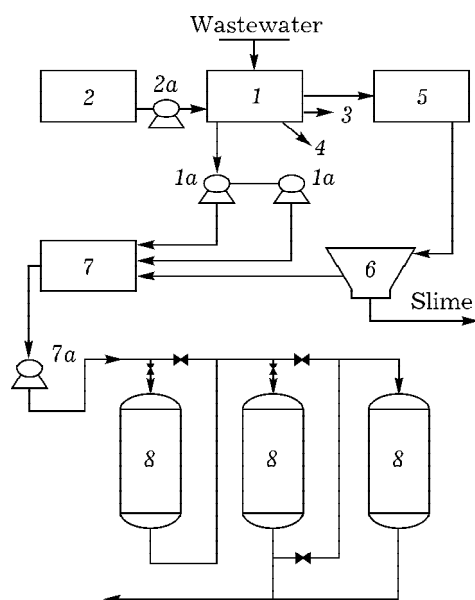

Fig. 2. Process flowsheet for purifying acidic wastewaters from galvanizing-bath room including the adsorption purification stage: 1 – neutralizer tank; 2 – feed tank; 3 – pH meter; 4 – automatic level meter; 5 – storage tank; 6 – centrifuge; 7 – sediment bowl; 8 – adsorbers; 1a, 2a, 7a – pumps.

pump 2a. Switching the dosing pump on and off is performed in an automatic mode depending on the indications of a pH meter 3 and a level meter 4 in the feed tanks.

The neutralization of acidic wastewater results in the formation of both dense precipitates (calcium sulphate, etc.) and loose precipitates such as metal hydroxides. The completion of the neutralization process is determined from the indications of an automatic pH meter. Two pumping-out pumps (1a) are installed in order to pump-out the neutralized wastewaters into a sediment bowl. The pumps are blocked together so that when one of them being out of operation the second pump could operate to provide any sucking away line. Switching the pumping-out pump on and off is performed either in an automatic mode depending on the indications of the pH meter or in a manual mode provided that the neutralizer tank volume is completely filled.

The sediment formed is pumped into a storage tank 5. The sediment (suspension) flows down through a pipeline from the storage tank to the bottom of the rotor of an operating centrifuge 6. Under the action of the centrifugal force the sediment is separated into the liquid and the solid phases. The particles of the solid are deposited onto the walls of the rotor, whereas the clarified liquid flows upwards and is vented into a sediment bowl through a pipeline 7. The suspension feeding is stopped when the solid phase fills more than 1/3 of the operation volume of the rotor. The rotor is manually (using a scraper) cleansed to remove the solid phase of the sediment. The slime is damped to a refuse heap, whereas partly cleared water is fed from the sediment bowl for the adsorption purification using a pump 7a. The content of Cu, Cd and Pb ions in the wastewater before the adsorption purification amounted to as much as $1.25 \cdot 10^{-5}$, $7.11 \cdot 10^{-8}$, $3.76 \cdot 10^{-6}$ mol/dm^3, respectively.

At the moment of the pollutant breakthrough into the filtrate not all the layer of the active coal in a column is saturated up to the equilibrium with the input substance concentration in the wastewater fed into the adsorber. The adsorbent does not reach the equilibrium saturation level in the mass transfer zone within the operating layer. In order to increase the efficiency level of active coal ad-

sorptive capacity it is appropriate to use chains consisting of three adsorbers *8* connected in series instead of separate columns connected in parallel. In this case water successively passes through two columns and for the replacement of an adsorbent only the first (with respect to water flow) column containing active coal completely saturated up to equilibrium is disconnected. Simultaneously with the detachment of the first column by means of switching valve gates in manifold pipelines, a column with new active coal is switched to the second column remaining in the chain, which provides the constancy of conditions for the adsorption of dissolved pollutants the flow of the liquid.

Thus, in the block there should be at least three adsorption columns installed, two of those operate in series in the mode of adsorption of dissolved substances from the flow, and one column is used in the mode of adsorbent replacement.

Figure 3 demonstrates a schematic operation diagram of such installation. One can see that water from sediment bowls is supplied into adsorbers. At the first stage the adsorption water treatment is carried out with the use of units A and B connected in series, whereas the replacement of spent active coal is performed using unit C (see Fig. 3, *a*). By the moment when the breakthrough pollutant concentration occurs behind the layer of the unit B, the active coal of the adsorber A is completely saturated which adsorber A is switched off for replacing the adsorbent. Instead of the unit A an adsorber C is connected in series to the adsorber B, and the operation of the installation proceeds till occurring the breakthrough in the filtrate, which is fixed behind the unit C (see Fig. 3, *b)*. Since this moment the adsorber B is replaced with the adsorbent, and a unit A refilled with new active coal is connected to the adsorber C instead of the adsorber B (see Fig. 3, *c).*

Owing to such operation of adsorption columns the volume of the solution under purification from an organic component within the first column of the block is 30 % higher than the volume of the solution purified using a single adsorption column. Adsorptionally purified water with the content of metal ions at a level of 10^{-8} mol/dm^3 returns into the technological system for salt dissolution stage, whereas the spent adsorbent is supplied for recovery. The calculations have demonstrated that at the present volume of wastewater flow rate (5 m^3/h) and quantitative composition of pollutants each column provides a high-quality wastewater purification from heavy metals during 9.5 months.

The technology developed for galvanic bath wastewater treatment with the use of a sorbent spent in the caprolactam manufacture could be realized on the basis of Russian domestic production run equipment. In order to determine the stability of chemical bonds of heavy metal ions on the surface of the adsorbent spent in purifying the wastewaters from galvanic manufacture the spent adsorbent was held within one year in HCl and NaOH solutions with the concentration of 2 mol/L which solutions were changed every month. It has been established that the adsorbed ions of HM are not washed away with both acidic and alkaline solutions. To all appearance, it is caused by the fact that the metals use to form strong bonds with the surface of an adsorbent. Basing on this fact, the spent sorbent would be appropriate for use as an asphalt additive.

CONCLUSION

Owing to the reuse of wastewater in the technological process, with use of the technology suggested one could efficiently solve the problems of resource saving as well as provide the ecological compatibility of caprolactam manufacture.
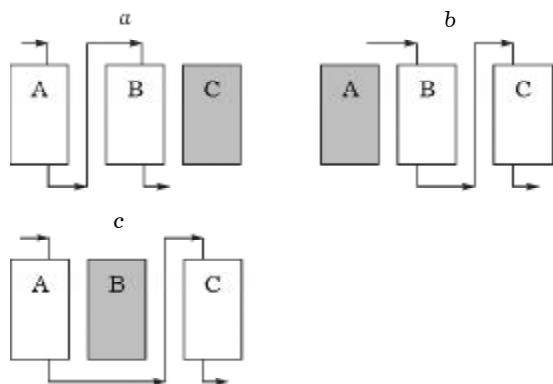

Fig. 3. Schematic operation diagram for an adsorbtion installation consisting of three units. See the text for designations.

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