

Ecotoxicology of heavy metals: Liquid-phase extraction by nanosorbents

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Abstract. The paper considers the problem of extreme toxicity heavy metal compounds dissolved in wastewater and liquid emissions of industrial enterprises to living organisms and environment as a whole. The possibility of increasing extraction efficiency of heavy metal ions by sorption materials was demonstrated. The porous space of the latter was modified by carbon nanotubes (CNTs) during process of the chemical vapour deposition (CVD) of carbon on metal oxide catalysts. The increasing of the sorption capacity (10-30%) and the sorption rate of nanomodified activated carbons in comparison with standard materials in the example of absorption of Co^{2+} and Ni^{2+} ions from aqueous solutions was proven.

1. Introduction

Among all the known to humanity chronic poisoning the most significant place belongs to intoxication by heavy metal salts. They cause abnormalities, mutations and intoxication, reaching a certain concentration in the human body. In addition to their toxic impact, their ability to settle on the walls of the finest systems of the body and clog the channels of the liver and kidneys is not less dangerous, thus reducing their ability to filter. This inevitably leads to the accumulation of toxins and products of vital activity of various cells of the body, i.e., its self-poisoning [1-9].

One of the major anthropogenic source of heavy metal ions entering into the environment and, as a consequence, into the human body, is industrial wastewater enterprises of ferrous and non-ferrous metallurgy, mechanical engineering, petrochemical industry, thermal power stations, etc. Water is the host environment of heavy metals migration in the earth's crust. At an excessive density heavy metals begin to behave as toxicants and ecotoxicants. This has a devastating impact not only on biocenosis individual organisms, but also on the whole ecosystem. For example, the accumulation of heavy metals in plants leads to their accumulation in the food chain and can cause serious diseases of man and animals. Increasing of heavy metals concentrations in water, soil and plants cause specific toxicosis and various mutagenic effects to human beings. The result of such cell deviation of the human body can become imbalance regulation of their division, which usually leads to malignant disease: mutation, degeneration of peripheral nerves, liver cirrhosis and blindness [9, 10].

Thus, research in the creation and modification of new materials that effectively adsorbed heavy metals, and the search for ways of their key characteristics optimization are very relevant for the direction of environmental protection and human health in general. This is confirmed, in particular, by positive dynamics of the volume growth on industrial enterprises wastewater stream for cleanup from



heavy metal compounds, as well as the discrepancy between the existing materials with modern requirements [10-12].

Modern methods of aqueous solutions purification of heavy metals salts are not generalizing models and characteristic patterns. The ion exchange and complexation reactions due to the formation of hydroxides and physical adsorption, directly related to the specific surface of the adsorbents can be considered as a possible mechanism of ions sorption from solutions [2, 13].

One of the possible ways to intensify the liquid phase sorption processes of heavy metals is a modification of the sorbent using carbon nanostructures. The literary sources analysis shows that CNTs have unique absorption properties. Since the CNTs are surface structure, all of their mass is concentrated in the surface of layers. This defines an abnormally high specific surface of CNTs. This kind of characteristics allows us to consider the CNTs as a surface modifying material of the sorbent.

2. Experiment

The technology obtaining of modified materials experimental samples based on the CVD process [14, 15]. Nanomodified samples were synthesized in an industrial reactor of the synthesis CNTs (NanoTechCenter Ltd., Tambov, Russia). The porous material (a carrier (sorbent)) previously impregnated by a solution of a metal oxide catalyst obtained by the sol-gel method or by thermal decomposition of multicomponent systems (Fe, Co, Mo, Mg, Al). Impregnated sorbent was dried (80°-140°C) and annealed (500°-550°C). Technical grade propane-butane was used as a carbon gas mixture. The process of the CVD synthesis was conducted for 60 min at 650°C.

Complex studies of sorption inorganic substances (ions and hydroxide ions of toxic heavy metals) from aqueous solutions were made to determine the effectiveness of the obtained nanomodified sorbents.

The study of the adsorption of Co^{2+} and Ni^{2+} ions was performed on activated carbons AG-5, AG-5-N, NWC and NWC-N under static conditions. For carry out of investigation a seven tubes with 50 ml of the solutions and 1.75 g of the sorbent were taken. All samples were shaken during each 3 minutes, sorption time is 40 min (for the Co^{2+} ions) and 30 min (for ions Ni^{2+}). After that the solution was filtered, and the optical density was measured spectrophotometrically. Then the dependence of adsorption and the equilibrium concentration - adsorption isotherm, was constructed.

3. Results and discussion

The proposed technology allows to stably synthesize the CNTs with predetermined parameters (porosity and layer height, etc.) on the porous support surface (Figure 1). The structure of as-growing CNTs (Figure 2) was obtained by scanning electron microscopy (SEM) method (Carl Zeiss, Neon 40, Tambov, Russia).

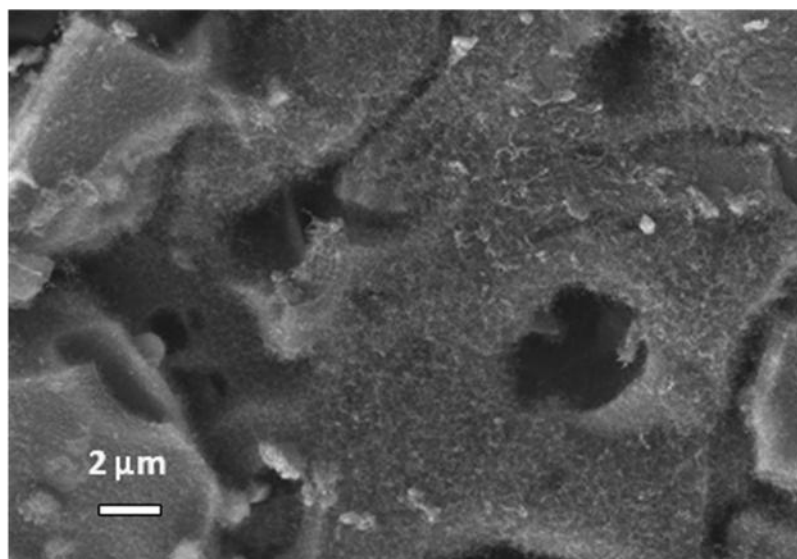


Figure 1. The granules surface of coconut activated carbon modified by the CNTs

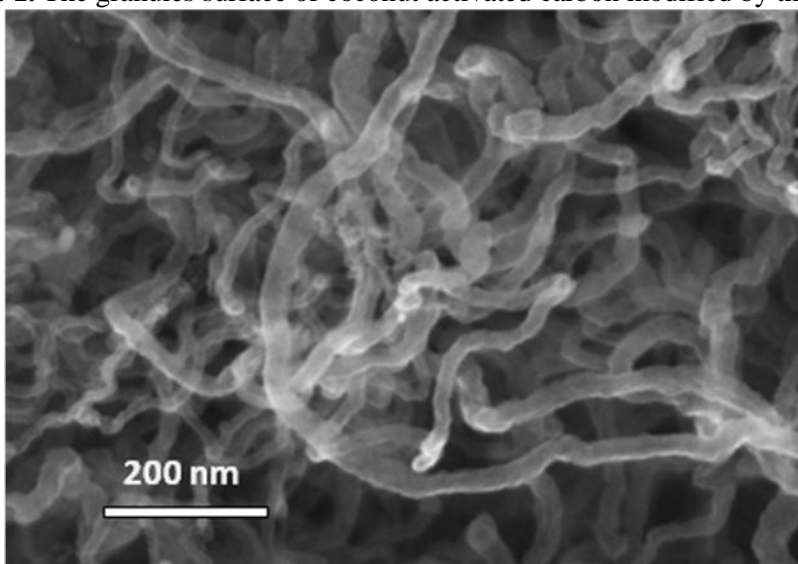


Figure 2. SEM-image of the CNTs structure

From the SEM images (Figures 1, 2), it can be seen that the products are nanotubes without visible admixture of other particles: CNTs diameter near 10-20 nm. There are small amount of catalyst nanoparticle with size about 25 nm.

After separating the adsorbent from the aqueous solution, the amount of adsorbed heavy metal ions can be evaluated according to the following equation:

$$Q = \frac{(C_0 - C_e) \cdot V}{m}$$

where Q is the equilibrium metal uptake (mol g^{-1}), C_0 is the initial metal concentration in the solution (mol L^{-1}), C_e is the equilibrium metal concentration in the solution (mol L^{-1}), V is the volume of the solution (mL), and m is the mass of the adsorbent (g).

Obtained comparative dependence - the adsorption isotherm of Co^{2+} and Ni^{2+} ions are shown in Figures 2 and 3, respectively.

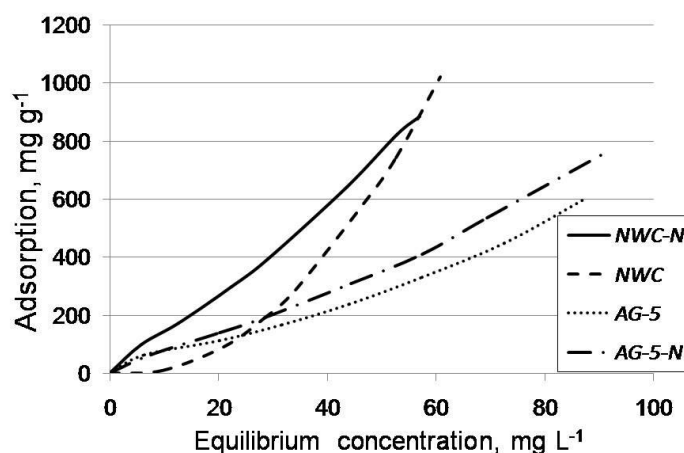


Figure 3. The adsorption isotherms of Co^{2+} ions at different types of adsorbents

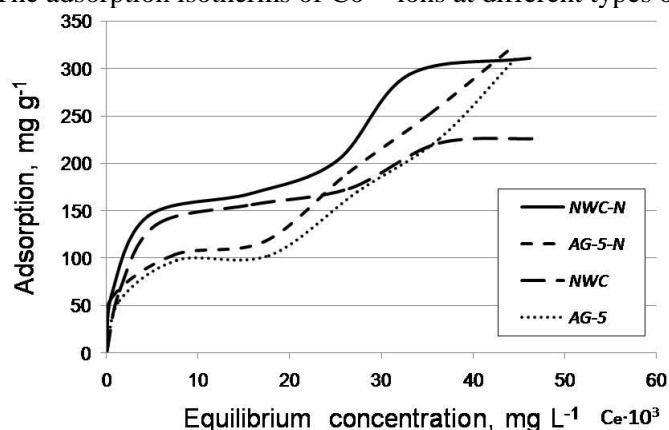


Figure 4. The adsorption isotherms of Ni^{2+} ions at different types of adsorbents

The effectiveness of the nanomodified materials in adsorption processes is confirmed, in particular, that nanomodified samples possess higher adsorption capacity at 30% of Co^{2+} and 10-15% for the Ni^{2+} in comparison with initial materials. These results also show that the nanomodified sorbents have higher adsorption rate.

The studies showed that there is a real possibility of applying the modification process on an industrial scale with an appropriate technical and economic effect due to a marked increase in indicators of quality cleaning.

4. Conclusion

The pollution of the biosphere by a group of contaminants, which has been generally termed "heavy metals", took the particular importance. Many heavy metals, when they come into a living organism, it leads to poisoning or death. These metals belong to the class of xenobiotics. Penetration toxicant in living organism occurs mainly through the water medium, so the waste water which is highly toxic, cannot be reset in open water without proper processing.

The experimental researches show that the complex sorbents based on activated carbons modified by carbon nanostructures are more effective in comparison with conventional counterparts and allow to deep treatment of aquatic environments.

The adsorption capacity of the nanomodified sorbent was shown that nanomodification of activated carbons increased the equilibrium adsorption of heavy metals (Ni^{2+} , Co^{2+}) by 10-30%. In addition, the developed technology of nanocarbon modification allows obtaining samples of sorbents based on carrier at different chemical nature with improved extraction of heavy metal ions from aqueous solutions.

Acknowledgments

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