Sorbents Obtained from Cellulose-Containing Waste for Water Purification

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Abstract. As a rule, ions of some heavy metals are always found in natural and waste waters. The purpose of this work was to study the sorption properties of carbon material obtained from secondary raw materials (hazelnut and walnut shells) according to the technology we have developed; determination of its applicability in the purification of drinking and waste water, in which ions of several heavy metals are simultaneously present. The salts of lead, cobalt, iron and cadmium, as the most important pollutants of the water basin, were the adsorbates.

Studies of solutions of various concentrations of metal ions showed that in the presence of all four ions, the maximum adsorption rate and the degree of extraction are achieved at a solution concentration of 0.0025 M Me^{+2} in 30 min, as for the effect of pH on the degree of sorption, the experimental results showed that the best values are achieved at pH 3 for cobalt ions and pH 3 ÷ 5 for copper, lead and iron ions.

It was found that the nature of sorption by these absorbers is the same: for a given metal, hydrated ions are adsorbed in the same way on different absorbers.

The larger the crystal radius of an ion with the same charge, the better it is adsorbed (sorption capacity for Pb^{++} ions is maximum, and minimum for Co^{++} ions).

Keywords: Adsorption · Heavy metals · Carbon · Waste water · Secondary raw materials

1 Introduction

Environmental pollution by industrial emissions is currently an acute environmental problem. A significant part of wastewater of various origins enters the environment without treatment, which negatively affects human health, the environment and the economy [1].

Among the most dangerous carcinogenic toxicants contained in industrial waste water are heavy metals belonging to I and II hazard classes. They rank second in terms of toxicological effects on the human body, behind pesticides.

Heavy metals include lead (Pb), cadmium (Cd), arsenic (As), chromium (Cr), copper (Cu), nickel (Ni), cobalt (Co), zinc (Zn) and others. It is necessary to constantly monitor

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their concentration in water to detect and assess contamination. Large amounts of heavy metals in wastewater can be caused by waste accumulation, increased human activity or industrial accidents. They accumulate in drinking water and can cause various diseases, as well as biological and genetic disorders [2].

To purify wastewater from water-soluble salts of heavy metals, chemical, physicochemical, biological and combined methods of water purification are applicable. However, these technologies are either often ineffective, produce secondary products, or are too expensive. In fact, when choosing a specific wastewater treatment technology, in addition to its effectiveness, environmental and economic aspects must be taken into account.

Among the physicochemical methods of detoxification of both gas and liquid media, adsorption stands out, as a universal process that allows you to almost complete removing of toxic impurities. The successful solution of many practical problems is determined by the choice of sorbents with optimal physicochemical properties and cost for these purposes [3].

Currently, the most versatile sorbents are materials made from chemically activated carbon [4]. These are materials with the best sorption properties, high porosity, developed surface area and mechanical strength.

2 Materials and Methods

At the Institute of Inorganic Chemistry and Electrochemistry of the Ivane Javakhishvili Tbilisi State University, a technology has been developed [5, 6] for obtaining carbon materials with a high surface area. This technology was used for many types of raw materials (used tires, hazelnut and walnut shells, nectarine kernel, sawdust, plastics, etc.).

The process is one-stage and does not require preliminary processing of raw materials. Carbon dioxide, water and various gases generated in the process are used as a reagents and energy sources. In this case, the reactor vessel (stainless steel) acts as a catalyst. Using this technology, carbon materials were obtained from recycled organic waste, which are cheap and efficient.

The physicochemical properties of the above materials were measured, namely, BET surfaces, areas and volumes of micropores (by capillary nitrogen condensation, on **Micromeritics**' GEMINI VII 2390T surface area analyzer), chemical composition (by a **Bruker's** QUANTAX energy dispersive X-ray spectrometry system (EDS) to **HITACHI** TM 3030 Plus scanning electron microscope (SEM)), ash content. For comparison, commercial activated carbon (BAU A) was used. The adsorption capabilities of these materials have been determined. The measurement results are published in works [7–9].

Studies have shown that these materials are characterized by a large specific surface area, porous structure, high adsorption capacity, and can be successfully used to extract various heavy metal ions from water separately. It was found that carbon materials obtained from hazelnut and walnut shells are characterized by the best adsorption properties with respect to ions of cobalt, lead, copper and iron. The maximum adsorption of ions such as cobalt, copper and iron, separately, is achieved in 30–45 min, and for lead ions, 5–10 min is enough.

As a rule, ions of some heavy metals are always found in natural and waste waters. The purpose of this work was to study the sorption properties of carbon material obtained from secondary raw materials (hazelnut and walnut shells) according to the technology we have developed; determination of its applicability in the purification of drinking and waste water, in which ions of several heavy metals are simultaneously present.

Studies of solutions of various concentrations of metal ions have shown that in the presence of all four ions, the maximum adsorption rate and the degree of extraction are achieved at a solution concentration of 0.0025 M Me^{+2} in 30 min. As for the effect of pH on the degree of sorption, the results of experiments have shown that the best values are achieved at pH 3 for cobalt ions and pH 3 ÷ 5 for copper, lead and iron ions. The adsorbates were aqueous solutions of nitrates of lead, cobalt, iron, and cadmium.

Table 1. The values of the sorption capacity (A, mg/g) and the degree of extraction (α, %) of metal ions (Pb^{++}, Cd^{++}, Co^{++}, Fe^{++} - 0,01 M), by sorbents obtained from various carbon materials (hazelnut and walnut shells) and factory activated carbon (fractional size 40 microns) after holding (stirring) in a solution (t = 25–270 C, T = 30 min. $V_{solution}$ = 100 ml)

Metal ions	Hazelnut shells		Walnut shells		Activated carbon BAU A	
	Sorption capacity (A, mg/g)	Degree of extraction (α, %)	Sorption capacity (A, mg/g)	Degree of extraction (α, %)	Sorption capacity (A, mg/g)	Degree of extraction (α, %)
pb^{++}	83,5	80,7	88,0	85,0	84,0	90,2
Cd^{++}	22,5	80,0	22,8	81,3	22,5	80,0
Fe^{++}	19,8	53,6	21,3	45,4	20,1	57,0
Co^{++}	13,2	89,5	12,6	85,6	12,2	83

The adsorption on various carbonaceous materials was studied in the joint presence of the indicated metal ions, in particular, from mixed model solutions containing equal amounts of lead (0.01 M), iron, cobalt and cadmium.

The carbon materials obtained by us in terms of sorption activity were compared with activated carbon of the BAU A brand. The results are presented in the Table 1.

3 Results and Discussion

As the results obtained show (Table 1), the parameters characterizing the sorption by these absorbers are approximately the same. This is due to the fact that the molecules of a substance, dissolving in water, decompose into ions, which are in a hydrated state. In this case, the solute is adsorbed on the surface of the adsorbent in the form of hydrated ions. Therefore, for a given metal, hydrated ions are adsorbed in the same way on different absorbers.

The sorption capacity in relation to Pb^{++} ions is maximum and minimum in relation to Co^{++} ions. In this case, the adsorption of metal ions is greatly influenced by the value of their ionic radius. The larger the radius of an ion with the same charge, the

better it is adsorbed, since with an increase in the radius, its polarizability increases, and, consequently, the ability to be attracted to the polar surface of the sorbents, i.e. its adsorbability, increases. At the same time, an increase in the ionic radius leads to a decrease in the hydration of the ion, which also contributes to an increase in the adsorption value.

Thus, the ions of heavy metals, which were used as adsorptives in our work, can be arranged in the following row in terms of increasing adsorption capacity, called the lyotropic series or the Hofmeister series:

$$A(Pb^{++}) > A(Cd^{++}) > A(Fe^{++}) > A(Co^{++}),$$

where, A is adsorption value.
Correspondingly [10],

$$r(Pb^{++})=1{,}21\ \text{À} > r(Cd^{++})=0{,}99\ \text{À} > r(Fe^{++})=0{,}8\ \text{À} > r(Co^{++})=0{,}78\ \text{À}$$

where, r is ionic radius of metal.

4 Conclusions

1. It was found that the nature of sorption by these absorbers is the same: for a given metal, hydrated
2. Ions are adsorbed in the same way on different absorbers.
3. The larger the crystal radius of an ion with the same charge, the better it is adsorbed (sorption capacity for Pb^{++} ions is maximum and minimum for Co^{++} ions).

Conflict of Interest. The authors declare that they have no conflict of interest.

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