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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Sorption of Heavy Metal Ions with Activated Carbons Obtained from Polyethylene Terephthalate Waste

N. V. Sych

Institute of Sorption and Endoecology Problems, National Academy of Sciences of Ukraine, Kyiv, Ukraine

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Abstract—The sorption capacity of activated carbons obtained from polyethylene terephthalate containers and packages with respect to heavy metal ions was examined. Based on the sorption capacities for Co^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}, the selectivity series were established for the samples prepared by conventional steam and gas activation and by the procedure involving pretreatment with sulfuric acid.

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As known, accumulation of heavy metal wastes resulted from technogenic pollution of the natural environment represents a severe environmental hazard. In this connection, high priority is attached now to improving technically simple and economically attractive methods for removing technogenic pollutants from process effluents and soils. Sorption technologies traditionally used for removing heavy metals from aqueous solution belong to fairly efficient options [1]. Their optimization lies above all in development of inexpensive sorbents selective to impurities to be removed. A suitable raw material can be found in spent polymer containers and packages accumulated in huge amounts as a household waste polluting the environment.

In this context, of much current interest is the application of spent polyethylene terephthalate (PET) containers and packages as precursors for development of an efficient sorbent for treating process effluents. This was the subject of much investigation by both Russian and foreign researchers [2–7]. The benefit from PET waste processing is dual. First, plastic containers and packages discarded annually in amounts of thousands of tons as undesired waste can be converted to a useful product, activated carbons. Second, the resulting sorption materials are suitable for wastewater treatment applications. This can contribute to finding solutions to many of the routine problems related to overcoming the environmental pollution.

Here, we examined the pore structure and sorption properties of the activated carbons obtained from spent PET containers and packages. Also, we analyzed the selectivity of these activated carbons with respect to heavy metal ions and assessed their suitability for removing technogenic pollutants in the form of heavy metal ions.

EXPERIMENTAL

Activated carbon samples for our studies were prepared from PET by pretreatment of a PET matrix (polymer flake) with sulfuric acid (sample I), followed by steam activation. For comparison, we used a sample prepared by direct carbonization of a PET matrix (sample II), followed by activation under similar conditions. We examined sorption of the Co^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} ions from individual solutions at the initial concentration of 50 mg l^{-1}, as well as from a model solution simulating a multicomponent system (Co^{2+}, Mn^{2+}, Ni^{2+}). Sorption tests were carried out at pH = 4 (sol : liq = 1 : 250) for 24 h under permanent shaking. After the sorption equilibrium was established, the mass was filtered. The content of the metals in the filtrate was determined by atomic-absorption method on an S-115M spectrometer. The experimental data were determined accurately to within 5%.

The sorption capacity was determined by the formula

$$A = \frac{(c_0 - c_{eq})V}{m},$$

where c_0 is the concentration of the initial solution, mg l^{-1}; c_{eq}, concentration of the equilibrium solution, mg l^{-1}; V, volume of the solution poured, ml; and m, mass of the weighed portion of the adsorbent, g.

The adsorption selectivity expressed as the distribution coefficient of the metal ion between the solid phase and solution was calculated by the formula

$$K_d = A/c_{eq}.$$

The pore structure of the resulting adsorbents was analyzed using the nitrogen adsorption isotherms recorded on a NOVA 2200 instrument (Quantachrome, US) at 196ºC. The pore size distribution functions were calculated by the BJH method based on the desorption curve. Before measurements the samples were degassed for 2 h at 180ºC under residual pressure of 1×10^{-4} mm Hg.

Table 1 presents the porosity (pore volume by benzene sorption) and yield of the samples at different technological stages of treatment. It is seen that chemical modification causes both the porosity and yield of the end product to increase relative to those in the case of activation of preliminarily carbonized PET. Treatment with concentrated sulfuric acid yields pore volume of 0.20–0.22 cm^3 g^{-1} by benzene sorption. In the case of vapor activation the porosity increases to 0.8 cm^3 g^{-1}, and for direct activation of sample II the pore volume by benzene sorption V_s does not exceed 0.14 cm^3 g^{-1}.

Sample I exhibits a polymodal pore structure comprised of micro and meso pores; its specific surface area was estimated by the BET method at 1034 m^2 g^{-1} (Table 2). Sample II prepared by direct activation is dominated by micro pores with a small size whose filling with nitrogen takes very long time. The specific surface area achieved for sample II was estimated at 218 m^2 g^{-1} (Table 2).

The results of tests with tracers are fully consistent with the data on the pore structure of the samples. For example, the sorption capacity of sample I with respect to I_2 nearly 4-fold exceeds that of sample II. This suggests a sharp increase in the amount of micro pores whose surface area varies from 128 for sample II to 807 m^2 g^{-1} for sample I (Table 2). Hence, treatment with H_2SO_4 actually affords high pore structure parameters.

Figure 1 demonstrates a sharp rise in the adsorption isotherm for Methylene Blue (MB), recorded for sample I, at low equilibrium concentrations. At MB concentrations of 300–400 mg l^{-1} the adsorbent tends to saturation, with the sorption capacity of 250–280 mg g^{-1} for MB. This value is comparable with that for highly porous commercial carbons [8]. At the same time, sample II is virtually incapable of MB sorption. Our results confirm the expediency of treatment of PET matrixes with H_2SO_4.

Table 2 presents the physicochemical and sorption properties of the samples we used in examinations of the selectivity with respect to transition metal ions.

The sorption isotherms for Ni^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, and Mn^{2+} ions, presented in Fig. 2, suggest that sample

Table 1. Pore volume dynamics by benzene sorption in different technological stages of treatment

Sample no.	Treatment stage	Process characteristics		Yield, %	Pore volume by benzene sorption, cm^3 g^{-1}
		T, °C	τ, min		
I	Treatment with sulfuric acid	140	15	27	0.22
	Steam activation	850	60	15	0.8
II	Carbonization	200–650	30	–	0.008
	Steam activation	850	60	8	0.14

Table 2. Pore structure and sorption properties of the samples examined for sorption of transition metal ions

Sample no.	Bulk density, g cm^{-3}	pH of water extract	SEC, meq g^{-1}		S_{BET}, m^2 g^{-1}	S_{meso}, m^2 g^{-1}	S_{micro}, m^2 g^{-1}	ΣV_s, cm^3 g^{-1}	V_{micro}, cm^3 g^{-1}	Sorption of MB, mg g^{-1}	Sorption of I_2, %
			HCl	NaOH							
I	0.119	6.9	0.6	0.1	1034	227	807	0.75	0.31	290	95
II	0.547	6.2	0.2	0.1	218	90	128	0.14	0.09	18	25

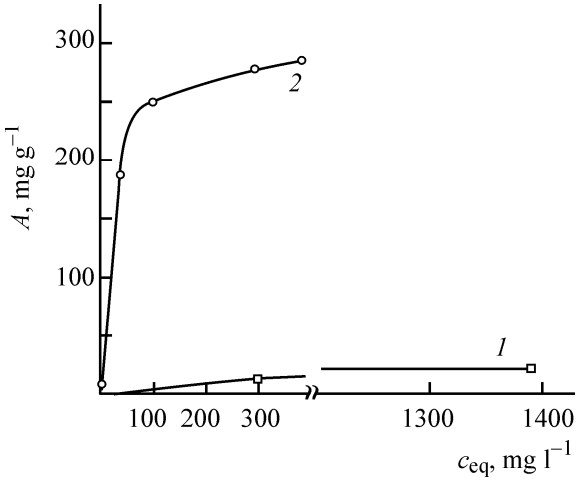

Fig. 1. Sorption capacity A with respect to MB vs. equilibrium solution concentration c_{eq} for sample (*1*) II and (*2*) I.

I is superior to sample II in selectivity. Moreover, at low equilibrium concentrations of the metal ions, the highest selectivity is exhibited with respect to Cu^{2+}, Zn^{2+}, and Ni^{2+} ions. As to Co^{2+} and Mn^{2+} ions, they are sorbed in insignificant amounts; their adsorption is appreciably enhanced only upon the equilibrium concentration of 15–20 mg l^{-1} is achieved. On the whole, the achieved sorption capacities agree well with those of commercial activated carbons.

The sorption efficiency in each specific case was estimated by comparison of the K_d values for samples I and II under standard conditions: c_{eq} = 1 mg l^{-1}. The diagram in Fig. 3 presents the K_d values and shows that samples I and II exhibit the highest sorption selectivity with respect to Cu^{2+} and Zn^{2+} cations. The sorption capacity of sample I exceeds that of sample II by a factor of 2, 2.3, 3, and 2 for Cu^{2+}, Zn^{2+}, Co^{2+}, and Mn^{2+}, respectively. For the remaining cations K_d increases 2–3 times in changing from sample II to sample I.

The sorbability of the examined cations varies as $Cu^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+} > Mn^{2+}$ for sample I and as $Cu^{2+} > Ni^{2+} > Zn^{2+} > Co^{2+} > Mn^{2+}$ for sample II.

Sorption studies with the model solution simulating process effluents discharged by electroplating industry, heat and power plants, and other enterprizes (Figs. 4a, 4b) showed that the sorption selectivity varies as $Mn^{2+} > Ni^{2+} > Co^{2+}$. The total sorption capacity was estimated at nearly 1.1 mg g^{-1} for sample II and 2.2 mg g^{-1} for sample I.

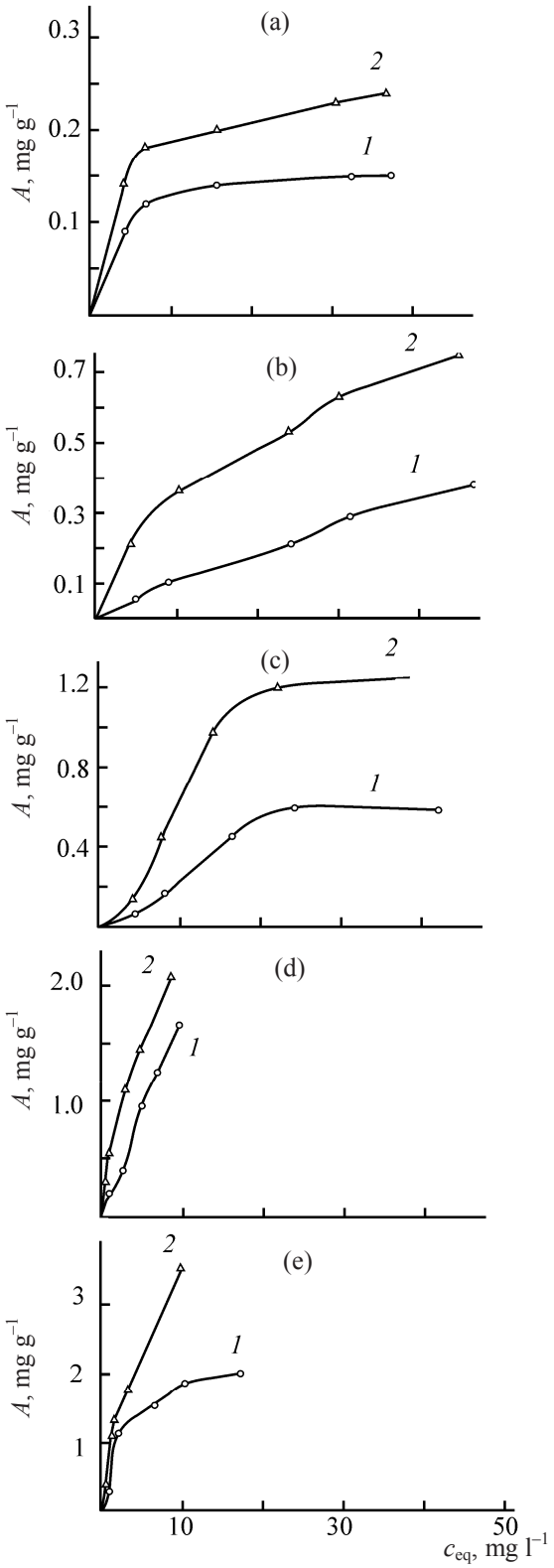

Fig. 2. Isotherms of adsorption of (a) Co^{2+}, (b) Ni^{2+}, (c) Mn^{2+}, (d) Zn^{2+}, and (e) Cu^{2+} ions with sample (*1*) II and (*2*) I. (A) Sorption capacity and (c_{eq}) equilibrium solution concentration; the same for Fig. 4.

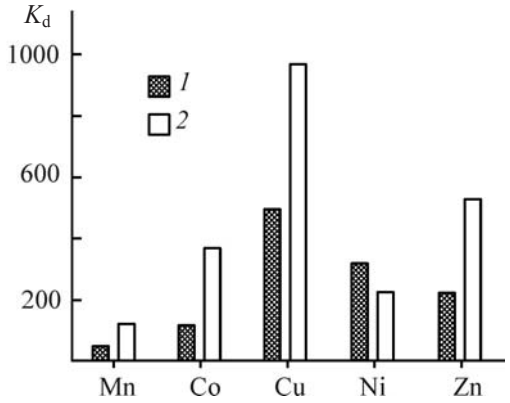

Fig. 3. Diagram of K_d values achieved for samples (*1*) II and (*2*) I, calculated at c_{eq} = 1.0 mg l^{-1}.

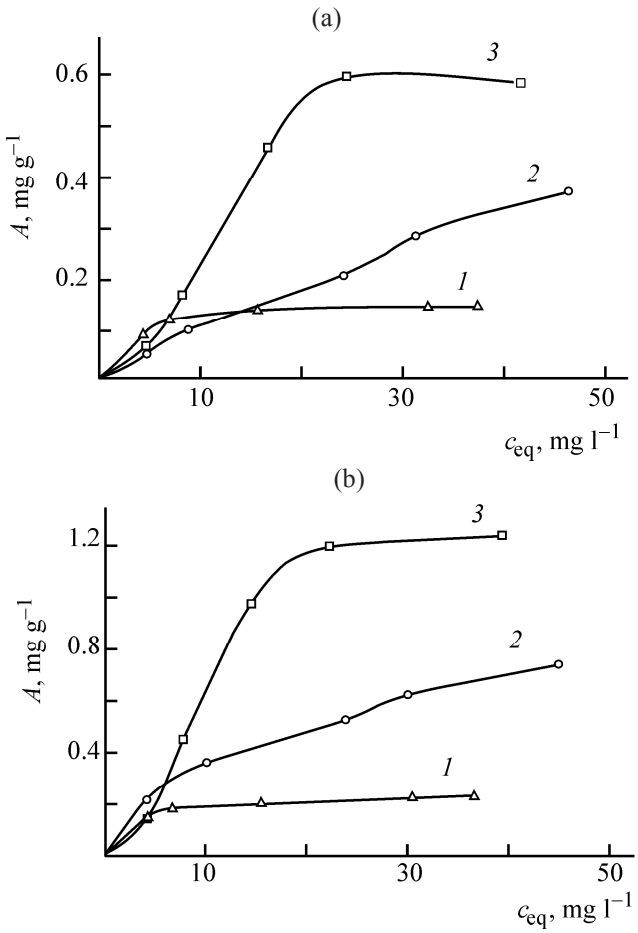

Fig. 4. Isotherm of adsorption of (*1*) Co^{2+}, (*2*) Ni^{2+}, and (*3*) Mn^{2+} ions from the model solution simulating process effluents with samples (a) I and (b) II.

Thus, PET containers and packages can be converted into highly porous activated carbons exhibiting a fairly high selectivity with respect to heavy metal ions in aqueous solutions discharged by metallurgical and electroplating industries, heat power plants, and other enterprizes.

CONCLUSIONS

(1) A new type of activated carbons was obtained by treating spent polyethylene terephthalate containers and packages with sulfuric acid, followed by activation with overheated steam. The carbons exhibit more developed pore structure and higher sorption capacities with respect to Methylene Blue compared to the carbons untreated with sulfuric acid.

(2) The selectivity series $Cu^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+} > Mn^{2+}$ were established under standard conditions for samples of the activated carbons prepared by the procedure involving sulfuric acid treatment against that for samples obtained by carbonization under acid-free conditions.

(3) Model experiments with solutions simulating process effluents showed that the selectivity for both types of samples varies as $Mn^{2+} > Ni^{2+} > Co^{2+}$.

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