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LETTERS TO THE EDITOR

Agar-immobilized Metal Sulfides and Their Sorption Power with Respect to Ag(I) Ions

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Thin-film systems based on sulfides of various *p* and *d* elements (MS) efficiently sorb noble and toxic metals from wastewater and spent process solutions by the ion-exchange mechanism. Previously such systems were prepared in most cases by chemical deposition of metal sulfides in the form of microcrystalline films on various supports (cellulose [1], cellulose triacetate [2], glass [3]). All these sorbents are characterized by micrometric particle size, which limits their performance in sorption of noble and toxic metals, if for no other reason than long sorption time. In [4] we suggested a procedure for preparing gelatin-immobilized metal sulfide matrix systems with quasimolecular level of MS dispersity. Sorption of metal ions, in particular, Ag(I), from wastewater and spent process solutions with such sorbents is fairly fast and complete. However, the gelatin layers exhibit relatively poor adhesion to the polyethylene terephthalate support and can exfoliate, which complicates further operation and utilization of the sorbent. Therefore, it is preferable to use polymer systems in which the nanometric particle size of the immobilized metal sulfides is preserved but no foreign support is required. One of polymeric materials suitable for this purpose is agarose, linear polysaccharide built from regularly alternating residues of 3-O-substituted β-D-galactopyranose (occasionally, 6-O-methyl-β-D-galactopyranose) and 4-O-substituted 3,6-anhydro-α-L-galactopyranose. Agarose is the main component of agar natural polymer recovered from red algae [5]. Agar-immobilized metal sulfide matrices (MS–AIM) are prepared in two steps. In the first step, agar is added into an aqueous solution containing an appropriate metal salt (nitrate, chloride, sulfate); the mixture is heated to 90–95°C and added with a buret or pipet into a vessel with water cooled to 10–15°C. The globules formed in the process are treated in the second step at room temperature with an aqueous solution of sodium sulfide to obtain the desired metal sulfide MS (M = Cu, Zn, Pb, etc.) by exchange reactions. These globules are fairly stable to aqueous solutions at widely varied pH (from 2 to 13) and temperature (up to 100°C) and to physicomechanical stresses. According to elemental analysis, the particle size of the sulfides implanted in MS-AIM is 10–15 nm on the average and does not exceed 20 nm.

The results of chemical analysis of the products formed by sorption of Ag(I) ions from $AgNO_3$ aqueous solutions on CuS-AIM, ZnS-AIM, and PbS-AIM, in combination with the kinetic curves of the process, show that in all the cases, as expected, the metal ions in MS-AIM were replaced by Ag(I) ions according to the following scheme (immobilized species are given in braces):

$$\{MS\} + 2Ag^{+}_{soln} \longrightarrow \{Ag_2S\} + M^{2+}_{soln}.$$

The conversion with CuS is 95% in 24 h and 99% in 48 h; with ZnS, 82% in 24 h and 95% in 48 h; and with PbS, 70% in 24 h and 97% in 48 h. Thus, almost 100% conversion with each of the MS-AIMs studied can be attained in a relatively short time (2–3 days). Thus, the agar-immobilized metal sulfide matrices are good sorbents for Ag(I), well competing with gelatin-immobilized metal sulfide matrix systems prepared in [4].

The kinetic curves of the M(II)/Ag(I) ion exchange (M = Cu, Zn, Pb) show that, in solutions with low (10^{-5}–10^{-4} M) Ag(I) concentrations, the highest ion-exchange capacity for Ag(I) ions is exhibirted by PbS-AIM, and the lowest, by CuS-AIM. In more concentrated (>10^{-3} M) Ag(I) solutions, the pattern is opposite: CuS-AIM shows the highest capacity, and PbS-AIM, the lowest capacity.

The substances immobilized in MS-AIM were isolated by heating to 70–80°C, washing of the resulting mass with a large volume of hot (90–95°C) distilled water, and separation of the precipitate formed from this hot solution by filtration. The elemental analysis of the isolated substances was performed by X-ray fluorescence spectroscopy under the conditions indicated in [4].

Copper sulfide CuS. Found, %: Cu 66.2; S 33.8. CuS. Calculated, %: Cu 66.47; S 33.53. Zinc sulfide ZnS. Found, %: Zn 67.3; S 32.7. ZnS. Calculated, %: Zn 67.10; S 32.90. **Lead sulfide PbS.** Found, %: Pb 86.3; S 13.7. PbS. Calculated, %: Pb 86.60; S 13.40.

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