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Hybrid sorbent with thioetheric sites

P. TZVETKOVA, P. VASSILEVA, N. NIKOLOVA, L. LAKOV, O. PESHEV*
Bulgarian Academy of Sciences, Institute of General and Inorganic Chemistry, Acad. G. Bonchev Str., Block 11, Sofia 1113, Bulgaria
E-mail: adsor@svr.igic.bas.bg

Harmful substances polluting air, water and soil are formed in many industrial processes. So the synthesis of new adsorbents able to remove them is a topic which receives much attention [1–4]. Silicon-organic hybrid materials are found to possess good sorption and other relevant properties due to their large surface area and the possibility of varying the organic substituent bonded to the silicon atom [5–8]. On the other hand, sulphur-containing ligands are more selective towards heavy metals than are their oxygen and nitrogen analogues. That is why sulphur-organic compounds have been used in modifying silica gel and preconcentrating metal ions from aqueous solutions [9–12].

The present paper deals with the synthesis of a new adsorbent based on tetraethyl orthosilicate (TEOS) and 2,2′-thiodiethanol (TDE). Its sorption properties with respect to cadmium, lead and mercury, which are often industrial pollutants, have been investigated.

The adsorbent was synthesized by the classical sol-gel method [13], the end product resulting from hydrolysis and polycondensation of TEOS ($Si(OC_2H_5)_4$) and TDE ($S(CH_2CH_2OH)_2$). The optimum volume ratio between the two reactants is 2:1. A change in favor of TDE reduces the porosity and increases the elasticity of the product, which leads to a drop in the adsorption capacity.

The first stage of the procedure comprised hydrolysis of TEOS at room temperature for one hour under intense stirring with a magnetic stirrer, followed by addition of TDE and agitation of the mixture to complete homogenization. The resulting sol solution was dried at 100 °C. Subsequent heating at 175 °C for 72 h yielded a brown powdery product, which was washed with distilled water to eliminate unreacted compounds. This product was characterized as follows.

Its specific surface area was found to be 50 m^2/g (in BET-type measurement [14]). The X-rays study performed with a Philips apparatus using Cu K_α-radiation, $\lambda = 1.54178$ A^0, and a graphite monochromator showed an amorphous structure. Its sulphur content amounted to 18 wt% as determined by X-ray fluorescence analysis with a VA-620 apparatus.

The IR spectra were recorded on a Bruker spectrometer within the range of 400–4000 cm^{-1} using KBr tablets. They are shown in Fig. 1 for the initial compounds (TEOS, TDE) and the sorbent. As known, the characteristic bands of the IR spectra of silicon-organic compounds arise from vibrations of the silicon atoms, their intensity being much stronger than that of the bands due to carbon atoms [15]. This is also evidenced by the IR spectrum of the sorbent obtained. At 1105 cm^{-1} it appears as the band of the Si—O group, which is embedded in a cross-linked silicon-organic polymeric structure. Such a structure is also suggested by the fact that the sorbent is neither dissolving nor swelling in the solvents used in NMR-spectroscopy as well as by its thermal stability up to 250 °C.

The sorption behavior with respect to Hg (II), Cd (II) and Pb (II) was examined under static conditions at 20 °C. Experiments were carried out in 50 ml flasks where 0.25 g sorbent and 25 ml acid solution of the metal ion to be sorbed were placed. The initial concentrations of these solutions were 5 mg/l for Cd (II) and Pb (II), while the Hg (II) required 50 mg/l because with lower concentrations the device used for AAA required preliminary concentrating of the solution. Desired pH-values were adjusted by adding a few drops of diluted HNO_3 or NH_4OH. Then an intense stirring for a definite time was applied in order to attain the adsorption equilibrium whereupon the sorbent was eliminated by filtering. The residual metal ion concentration in the liquid phase was determined by flame AAA with a Pye Unicam SP 192 apparatus. Analytical grade reagents were used.

The kinetic curves of sorption for Hg (II), Cd (II) and Pb (II) are shown in Fig. 2. As seen, saturation is reached in about 45 min. Yet in the case of Hg (II) a second step of the kinetic isotherm is being formed much

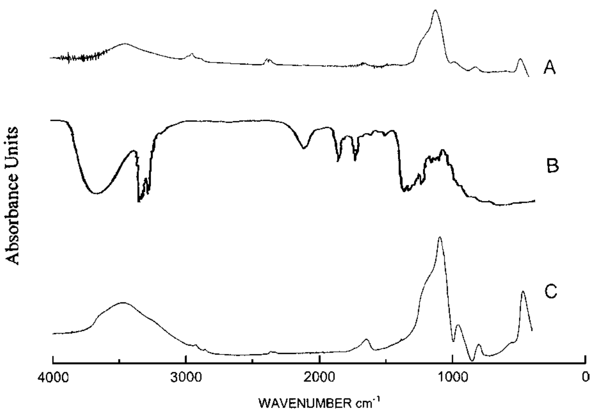

Figure 1 IR-spectra of the initial compounds and the synthesized product: (A) hydrolyzed TEOS, (B) 2,2′-thiodiethanol, TDE and (C) sorbent obtained.

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*Author to whom all correspondence should be addressed.

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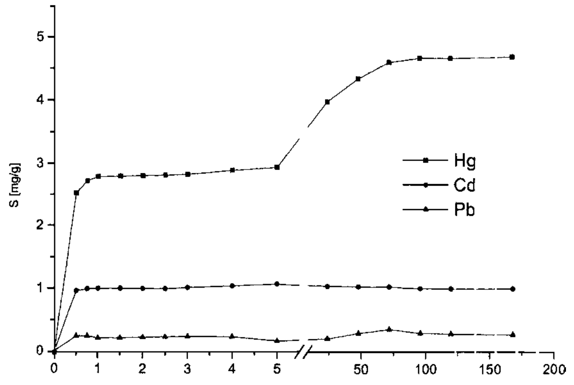

Figure 2 Kinetic isotherms of sorption for Cd (II), Pb (II) and Hg (II).

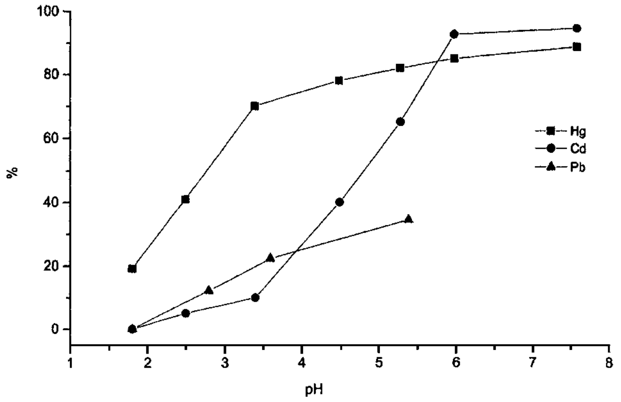

Figure 3 Extracted fraction of the metal ions (in %) as dependent on pH.

more slowly and the sorption equilibrium needs more than 70 h to occur. This slow step could be associated with the cross-linked structure of the solid where new adsorption sites gradually become accessible.

The total uptake expressed as extracted fraction of the metal (in %) proves strongly dependent on the solution pH as inferred from Fig. 3. The sorbent under consideration is highly efficient towards Hg (II) over a wide range of pH values (3.5–7.6). In the case of Cd (II) the corresponding values are between 5.5 and 7.6. With lead ions a low sorption is observed over the whole pH interval investigated (<40% extraction). This ability of sorbing the different metal ions to different degrees might be used for their separation and concentration.

The sulphur site is a soft base [16], which means that it shall have a high affinity for soft acids (e.g., Hg (II), Cd (II) and a low one for borderline acids such as Pb (II). The results obtained are in agreement with this rule: Hg (II) and Cd (II) are sorbed better than Pb (II) within the pH range studied. In the acid region, sulphur sites alone seem to be accessible to sorption since the oxygen ones are likely to be protonated. In a neutral medium simultaneous participation of both kinds of sites may be the case, which will explain the increase of sorption with pH, lead ions making no exception.

At a pH-value of about 6, saturation of the sorbent with Hg (II) and Cd (II) is attained whereas with Pb (II) no trend to reaching constant sorption is observed. This value can thus be considered optimal for assessing the static sorption capacity. The latter was measured upon addition of 25 ml of metal ion solution with a concentration of 200 mg/l to 0.25 g sorbent. The results are (in mg metal per g sorbent): 20.5 for Hg (II), 2.5 for Cd (II) and 2.0 for Pb (II). Hence the sorbent under consideration could be used for a selective removal of mercury ions from aqueous solutions.

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