Formulation of multilayer magnetic Cu$^{2+}$ and Ni$^{2+}$ – imprinted sorbents based on humic acids

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The technique for formulation of magnetic ion-imprinted sorbents aimed at specific metal ions seems to be the most attractive for the design of materials with various sizes, shapes, compositions and morphology, which provide important opportunities for adjusting and controlling the physicochemical properties of the collected materials and create an important perspective for them application. To obtain magnetic selective ion-imprinted sorbents, preliminary encapsulation of Fe$_3$O$_4$ nanoparticles into the HA matrix was used, on the surface of which by successive “crosslinking” it is possible to create several layers that add rigidity to the structure and also protect magnetite from the destruction of aggressive substances. Fe$_3$O$_4$ nanoparticles were obtained by chemical precipitation by the addition of FeCl$_2$ and FeCl$_3$ solutions in the ratio 2:3 in NH$_4$OH medium. The optimal reaction parameters for the formation of the Fe$_3$O$_4$/HA nanocomposite were determined, where the concentration was 0.2 g of HA per 1 g of Fe$_3$O$_4$. The time of introducing HA into magnetite medium was determined, which amounted to 20 sec.

A technique has been developed for producing magnetic multilayer selective ion-imprinted sorbents with the formation of a crosslinked 3D structure of the composite based on ammonium humate, phenylene diamine (FDA), solutions of target metal ions (Cu$^{2+}$, Ni$^{2+}$). The resulting magnetic multilayer ion-imprinted materials (IIM) are selective with respect to the target metals. The multilayer sorbents provide the integrity of the structure of magnetite. Such multilayer magnetic ions-imprinted sorbents can be used repeatedly in the technique of magnetic separation. The magnetic solid phase sorption characteristics of the adsorption process were studied. The effects of various parameters on the extraction efficiency such as pH of solution, the amount of adsorbent, extraction time, the type and concentration of eluent were systematically investigated. Furthermore, the thermodynamic and kinetic properties of the adsorption process were studied to explore the internal adsorption mechanism.

Removal of the Ni(II), Cu(II) from the imprinted material and creation of cavities for hosting Cu(II) was proved by comparison of the response of IIM/HA/FDA to template with that of non-imprinted material (NIM/HA/FDA). The relative selectivity coefficients of Me-IIM for Cu(II)/Co(II), Cu(II)/Cd(II), Cu(II)/Zn(II), and Cu(II)/Pb(II) were determined. The experimental data fit well with the Langmuir adsorption isotherm. The max Cu/Ni-adsorption capacity obtained from the Langmuir isotherm is 256 and 167 mg/g for Cu(II)/Ni(II) IIM, respectively.