An intensive study on the magnetic effect of mercapto-functionalized nano-magnetic Fe$_3$O$_4$ polymers and their adsorption mechanism for the removal of Hg(II) from aqueous solution

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HIGHLIGHTS
- Magnetic effect was clearly observed during the process of Hg(II) removal by SH-Fe$_3$O$_4$-NMPs.
- Various characterization techniques were applied to investigate the adsorption mechanism.
- Hg(II) could be reduced to Hg$_2$Cl$_2$ during the adsorption process, and the magnetic nuclei might play an important role.

GRAPHICAL ABSTRACT
The adsorption process of Hg(II) by SH-Fe$_3$O$_4$-NMPs was found highly related to the content of Fe$_3$O$_4$ magnetic core in the adsorbents. Hg(II) was found to be partial reduced to Hg$_2$Cl$_2$ in which the Fe$_3$O$_4$ magnetic core in the adsorbents might play an important role.

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ABSTRACT
A series of mercapto-functionalized core–shell structured nano-magnetic Fe$_3$O$_4$ polymers (SH-Fe$_3$O$_4$-NMPs) with different amount of magnetic core were synthesized and characterized by XRD, EA, VSM, TG–DTG and XPS. Their applications as adsorbents for Hg(II) removal from aqueous solutions were intensively investigated. The adsorption process of Hg(II) by SH-Fe$_3$O$_4$-NMPs was found highly pH dependent and related to the content of Fe$_3$O$_4$ magnetic core in the adsorbents. The optimized content of magnetic core for SH-Fe$_3$O$_4$-NMPs was found to be at 5.88%. Kinetic studies showed that the adsorption of Hg(II) by SH-Fe$_3$O$_4$-NMPs followed pseudo-second-order model, suggesting a chemisorption process. Activation energy ($E_a$) for the Hg(II) removal was found to be 22.1 kJ mol$^{-1}$, indicating that the diffusion process might be the rate-controlled step. Thermodynamic studies suggested that the adsorption processes of Hg(II) onto the SH-Fe$_3$O$_4$-NMPs were endothermic and entropy favored in nature with the enthalpy changes ($\Delta H_h$) at 7.26–16.54 kJ mol$^{-1}$ and the entropy changes ($\Delta S_h$) at 27.60–56.78 J mol$^{-1}$ K$^{-1}$. The adsorption processes fit the Langmuir isotherms well with the maximum adsorption capacities of Hg(II) onto the SH-Fe$_3$O$_4$-NMPs at 129.9–256.4 mg g$^{-1}$ with the content of Fe$_3$O$_4$ in SH-Fe$_3$O$_4$-NMPs varying from 0% to 22.37%. The selective adsorption of Hg(II) by SH-Fe$_3$O$_4$-NMPs can be achieved when Ca$^{2+}$, Mg$^{2+}$, Na$^+$ or Cu$^{2+}$ ions coexisted. XRD and XPS analyses results of the adsorbents before and after Hg(II) adsorption suggested that Hg(II) ions had been successfully adsorbed onto SH-Fe$_3$O$_4$-NMPs via