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# Fabrication of a porous hydrangea-like $\text{Fe}_3\text{O}_4@\text{MnO}_2$ composite for ultra-trace arsenic preconcentration and determination

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## Abstract

$\text{Fe}_3\text{O}_4@\text{MnO}_2$  magnetic composite microsphere with hierarchical shells structure has been synthesized through a facile two-step hydrothermal reaction for ultra-trace arsenic enrichment. Scanning electron microscopy and transmission electron microscopy images clearly indicated that the as-synthesized material is a porous hydrangea-like morphology, as well as the size of the composite microspheres and the widths of pore are related to the reaction conditions. The  $\text{N}_2$  adsorption-desorption isotherms demonstrated that the specific surface areas and pore volume of  $\text{Fe}_3\text{O}_4@\text{MnO}_2$  with 8 h hydrothermal synthesis are  $121.9260 \text{ m}^2 \text{ g}^{-1}$  and  $0.21 \text{ cm}^3 \text{ g}^{-1}$ , respectively. The enrichment performance of composites depends on their compositions, and the recovery of As(III) on  $\text{Fe}_3\text{O}_4@\text{MnO}_2$  with Mn/Fe ratio 1:2 was 1~2.3 times of that on other ratios. In comparison with As(V), experimental data indicated that the prepared composites have faster adsorption rate for As(III). In addition, slurry sampling chemical hydride generation technology can effectively remove and reduce the adsorbed As(III) or As(V) to the gaseous product, thus ensuring that the composite is at least repeated over 5 times. Under the optimized conditions, the detection limit of the proposed method was  $2.9 \text{ ng L}^{-1}$  and relative standard deviation of 4.8% for  $0.1 \text{ } \mu\text{g L}^{-1}$  As(III) was obtained. The linear calibration range was  $0.01\text{-}1.5 \text{ } \mu\text{g L}^{-1}$ . The accuracy of the method was verified through analysis of the certificated reference materials. The proposed method has been applied to the determination of inorganic As in natural water samples.

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