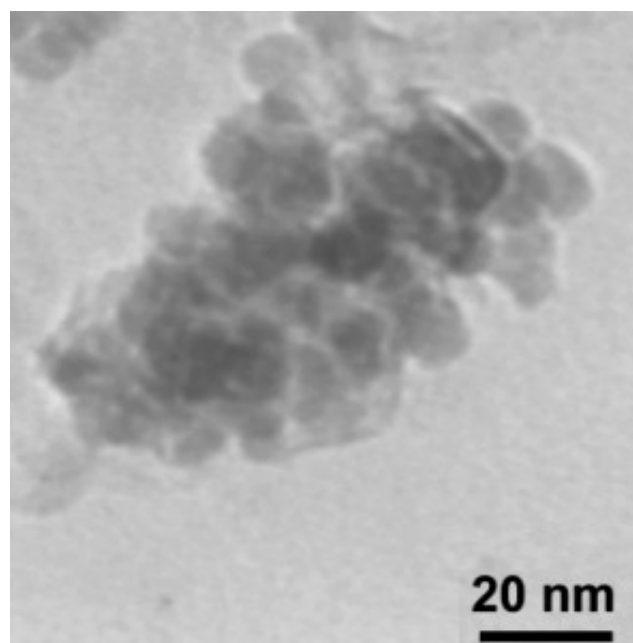


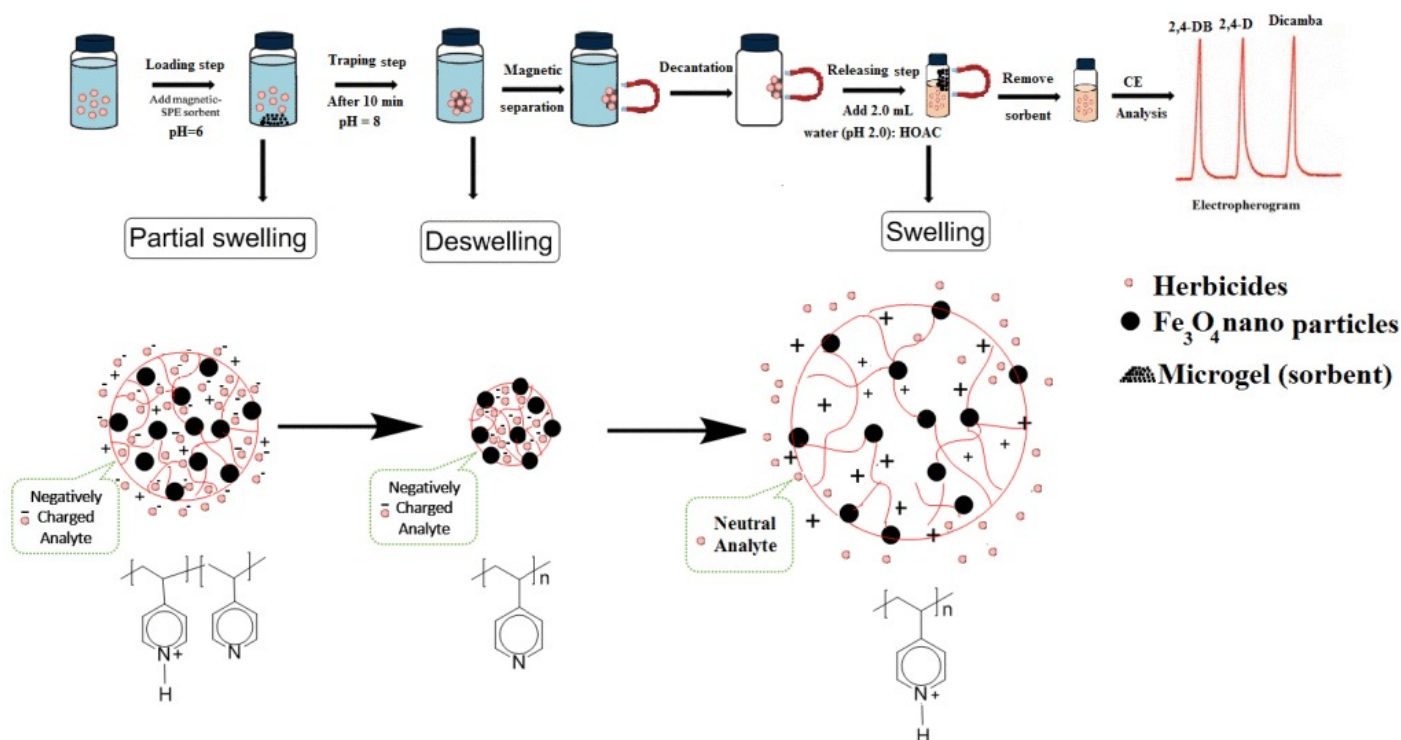
Application of pH-sensitive magnetic microgel in environmental samples

Phenoxy acid herbicides are phytotoxic compounds employed to kill annual and perennial broad leaved weeds in gardens and crops. Phenoxy acid herbicides such as 2,4-dichlorophenoxyacetic acid (2,4 - D), 4 - (2,4 - dichlorophenoxy) butanoic acid (2,4-DB), and 3,6-dichloro-2-methoxybenzoic acid (dicamba) are among the 10 most important herbicides. Due to their high polarity and solubility in water these acidic herbicides can be released from harvest fields and cause the pollution of surface and ground waters. The World Health Organization (WHO) regulations set the maximum contaminant level (MCL) of phenoxy acid herbicides in drinking water at 70 ng mL^{-1} . Therefore, their presence in water sources is highly objectionable for human and animal consumption. Due to the fact that groundwater and river water are the major sources of drinking water, monitoring the acidic and polar herbicides in these water sources is quite necessary.



Introducing new sorbents is an interesting and debatable issue in the field of sample preparation. In this study, for the first time, a pH-sensitive magnetic microgel, $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-poly}(4\text{-vinylpyridine})$, was introduced as a smart sorbent. The synthesis procedure of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-P4VP}$ pH-sensitive organic-inorganic hybrid microgels includes a “grafting from” strategy, with $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-Br}$ nanoparticles as the crosslinker and 4VP as the monomer via an ATRP reaction. The living radical polymerization allows coating of the polymer on the surface of Fe_3O_4 in a controlled fashion, resulting in a good dispersibility of the particles in a suitable media. The TEM observation shows that $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-P4VP}$ microgel contains many small black spheres, which are Fe_3O_4 MNPs (Fig. 1).

The extraction procedure for the analytes using $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-P}_4\text{V}_p$ pH-sensitive magnetic microgel sorbent is shown in Figure 2. Extracting the herbicides from standard solutions and real samples is accomplished through three steps: loading, trapping, and desorption. The loading step happens in 200 mL of the water sample containing 100 ng mL^{-1} of each herbicide with the pH adjusted to 6.0. Then, 100 mg of dried microgel is suspended in the aqueous solution and the sample is stirred for 10 min. In trapping step, the pH of the sample is increased up to 8.0 in order to trap the analytes inside the microgel. Then, the sorbent is isolated from the sample solution by applying an external magnetic field, and the sample solution is removed. During desorption step, 2.0 mL (water (pH = 2.0): HOAC (5%, v/v)) solution as an eluent is added to the magnetic sorbent and shaken. This mixture is again exposed to an external magnetic field and the clear solution of the eluent, containing the eluted herbicides is introduced to a microvial for the capillary electrophoresis (CE) analysis.



The proposed method has various important advantages and benefits compared to the other extraction methods. First of all, the mentioned system does not need toxic solvents for the elution of herbicides from the microgel and instead, the only solvent was distilled water; therefore, it can be referred to as a green extraction system. Secondly, this method is quite simple, fast, and accurate for herbicide extraction due to magnetic separation process. Thirdly, the designed system is smart due to the pH sensitive characteristic of the microgel. Therefore, coupling CE with the proposed method can provide good and sensitive results for the determination of these herbicides in environmental samples. As the mechanism of the adsorption and desorption was based on changing the pH value and only aqueous medium was used as the effluent solvent, this method

was introduced as a green method for extraction. These advantages ensure that pH-sensitive microgels have a strong potential as new sorbents in future sample pretreatment technique.

Publication

[Application of pH-sensitive magnetic nanoparticles microgel as a sorbent for the preconcentration of phenoxy acid herbicides in water samples.](#)

Tabani H, Khodaei K, Bide Y, Zare FD, Mirzaei S, Fakhari AR
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