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$CsPbBr_3$@MOF-5-Based Single Drop Microextraction for in-situ Fluorescence Colorimetric Detection of Dechlorination Reaction

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Abstract : Chlorobenzene homologues (CBHs) are a category of environmental pollutants that can not be ignored. They can stay in the environment for a long period and are potentially carcinogenic. The traditional degradation method of CBHs is dechlorination followed by sample preparation and analysis. This is not only time-consuming and laborious, but the detection and analysis processes are used in conjunction with large-scale instruments. Therefore, this can not achieve rapid and low-cost detection. Compared with traditional sensing methods, colorimetric sensing is simpler and more convenient. In recent years, chromaticity sensors based on fluorescence have attracted more and more attention. Compared with sensing methods based on changes in fluorescence intensity, changes in color gradients are easier to recognize by the naked eye. Accordingly, this work proposes to use single drop microextraction (SDME) technology to solve the above problems. After the dechlorination reaction was completed, the organic droplet extracts Cl^- and realizes fluorescence colorimetric sensing at the same time. This method was integrated sample processing and visual in-situ detection, simplifying the detection process. As a fluorescence colorimetric sensor material, $CsPbBr_3$ was encapsulated in MOF-5 to construct $CsPbBr_3$@MOF-5 fluorescence colorimetric composite. Then the fluorescence colorimetric sensor was constructed by dispersing the composite in SDME organic droplets. When the Br^- in $CsPbBr_3$ exchanges with Cl^- produced by the dechlorination reactions, it is converted into $CsPbCl_3$. The fluorescence color of the single droplet of SDME will change from green to blue emission, thereby realizing visual observation. Therein, SDME can enhance the concentration and enrichment of Cl^- and instead of sample pretreatment. The fluorescence color change of $CsPbBr_3$@MOF-5 can replace the detection process of large-scale instruments to achieve real-time rapid detection. Due to the absorption ability of MOF-5, it can not only improve the stability of $CsPbBr_3$, but induce the adsorption of Cl^-. Simultaneously, accelerate the exchange of Br- and Cl^- in $CsPbBr_3$ and the detection process of Cl^-. The absorption process was verified by density functional theory (DFT) calculations. This method exhibits exceptional linearity for Cl^- in the range of 10^{-2} - 10^{-6} M (10000 µM - 1 µM) with a limit of detection of 10^{-7} M. Whereafter, the dechlorination reactions of different kinds of CBHs were also carried out with this method, and all had satisfactory detection ability. Also verified the accuracy by gas chromatography (GC), and it was found that the SDME we developed in this work had high credibility. In summary, the in-situ visualization method of dechlorination reaction detection was a combination of sample processing and fluorescence colorimetric sensing. Thus, the strategy researched herein represents a promising method for the visual detection of dechlorination reactions and can be extended for applications in environments, chemical industries, and foods.

Keywords : chlorobenzene homologues, colorimetric sensor, metal halide perovskite, metal-organic frameworks, single drop microextraction

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