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Integrated ion imprinted polymers-paper composites for selective and sensitive detection of Cd(II) ions

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HIGHLIGHTS

- IIPs are first grafted on the low-cost A4 print paper to develop an integrated paper-based device.
- As an imprinted composite, the adsorption capacity is 155.2 mg g^{-1} and the imprinted factor is more than 3.0.
- As an analytical method, the limit of detection is 0.4 ng mL^{-1}.
- Based on the water quality standards, it could be used to determine Cd(II) ions in drinking water.

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ABSTRACT

Paper-based sensor is a new alternative technology to develop a portable, low-cost, and rapid analysis system in environmental chemistry. In this study, ion imprinted polymers (IIPs) using cadmium ions as the template were directly grafted on the surface of low-cost print paper based on the reversible addition-fragmentation chain transfer polymerization. It can be applied as a recognition element to selectively capture the target ions in the complex samples. The maximum adsorption capacity of IIPs composites was 155.2 mg g^{-1} and the imprinted factor was more than 3.0. Then, IIPs-paper platform could be also applied as a detection element for highly selective and sensitive detection of Cd(II) ions without complex sample pretreatment and expensive instrument, due to the selective recognition, formation of dithizone-cadmium complexes and light transmission ability. Under the optimized condition, the linear range was changed from 1 to 100 ng mL^{-1} and the limit of detection was 0.4 ng mL^{-1}. The results were in good agreement with the classic ICP-MS method. Furthermore, the proposed method can also be developed for detection of other heavy metals by designing of new IIPs.

1. Introduction

Cadmium (Cd) pollution has raised public concern in the world due to their toxicity, persistence and bio-accumulative nature. Most importantly, cadmium can travel long distances from the source of emission by atmospheric transport [1]. Environmental cadmium exposure can cause a variety of adverse health effects, especially on the bone, kidney and lung. The U.S. Environmental Protection Agency (EPA) classified Cd(II) as a human carcinogen at low levels of exposure. The World Health Organization recommend a 3 ng mL^{-1} standard for Cd(II) ions in drinking water [2]. In response to such a strict standards, it is urgent to design a sensitive and reliable analytical platform for the determination of Cd(II) ions in environmental samples. To date, a variety of well-established methods have been created for monitoring Cd(II) ions, such as flame atomic absorption spectrometry (FAAS) [3], inductively coupled plasma atomic emission spectrometry (ICP-AES) [4], and inductively coupled plasma mass spectrometry (ICP-MS) [5,6]. But, these methods require expensive equipment, complex sample pretreatment and highly special operators. Especially in the treatment of cadmium

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pollution emergency, rapid and simple monitoring is very necessary to protect human health and the environment [7,8]. Therefore, an on-site analytical platform with portable size, easy operation, low cost, fast response and high sensitivity should be proposed for heavy metal analysis.

Nowadays, paper as a substrate has drawn much attention in analytical chemistry because of its flexible, portable, lightweight, low cost, capillary action and the ability to store reagents [9–12]. Rattanarat et al. reported a paper-based analytical device for colorimetric and electrochemical detection of heavy metals [13]. Compared with the standard method in certified laboratories (more than $100/sample), it is a simple, rapid and inexpensive technology, which is suitable for the minimally trained individuals or even everyday citizens. However, due to the low exchange capacity, paper can only be used as a solvent carrier or substrate. The sensitivity and accuracy of paper-based device are dependent on the introduction of selective probe. In fact, the main composition of paper is cellulose fiber, which can be further modified to prepare multifunction polymers and then develop an integrated paper-based device. These technologies are beneficial to further improve the accuracy and sensitivity of the analytical method. Loípez Marzo et al. developed an integrated paper-based immunosensing system for the determination of Cd(II) ions [14]. The detection principle is based on the recognition of Cd-ethylenediaminetetraacetic acid complex by the monoclonal antibody and colorimetric detection due to the aggregation of gold nanoparticles. However, the introduction of monoclonal antibody will potentially increase the cost and complexity of paper-based device, and the lifetime is usually short. Recently, much effort has been paid on the replacement of biological receptors with artificial recognition materials, due to their high selectivity, remarkable mechanical stability, improved shelf-life and low cost [15,16].

Based on the key-and-lock model, ion imprinting is a type of template-assisted synthesized technology that leads to the formation of highly selective imprinted cavities in a 3D-polymeric network [17]. After removal of the target ions, imprinted cavities are complementary not only in the shape and size, but also in the orientation of functional groups generated in the polymerization process [18]. Furthermore, IIPs have several advantages including ease of preparation, low cost, easy storage, reusability and harsh environment utility [19,20]. Thanks to the predetermined recognition ability, ion imprinting polymers (IIPs) with high selectivity for target ions can be used to improve the selectivity and sensitivity of the paper-based analytical device without further introduction of other selective probes. However, slow rebinding is the drawback of the IIPs, because the recognition cavities are deeply embedded in the polymer matrix [15]. Especially for the paper-based system, the bulk polymerization of IIPs on the paper will cause many adverse effects, such as increase in weight, loss of flexible ability, decrease of translucent and transferring of liquid solution.

Compared with the conventional IIPs, the surface imprinted polymerization can be used for not only effective integration of multi-functional materials but also for improvement of mass transfer and binding kinetics. Reversible addition-fragmentation chain transfer (RAFT) polymerization has been proven to successfully prepare IIPs with controlled morphology, homogeneous distribution of imprinted sites and terminal functionality [21,22]. Up to now, there are few reports on the preparation of IIPs on the surface of paper as the substrate using RAFT strategies. In this study, thin print paper was oxidized using hydrogen peroxide to introduce enough hydroxyl groups and then grafted with RAFT initial agent. Subsequently, IIPs were synthesized on the surface of print paper by RAFT strategy using cadmium ions as the template, methylacrylic acid and polyethyleneimine as the monomers. The adsorption capacities, binding kinetics and the selective recognition mechanism were studied. Based on the high selectivity of IIPs, pink color of dithizone-cadmium complex and light transmission ability, a simple, rapid and sensitive colorimetric assay was proposed for the determination of cadmium ions in environmental samples.

2. Experimental

2.1. Chemicals and reagents

Cadmium acetate, ethylene glycol dimethacrylate (EGDMA), polyethylenimine (PEI, MW 600), 3-chloropropyltrimethoxysilane, 2,2-azobisisobutyronitrile (AIBN), sodium N,N-diethyldithiocarbamate trihydrate and methacrylic acid (MAA) were obtained from the Sigma Company (St. Louis, MO, USA). A4 print paper was obtained from Deli Group Co Ltd. Dimethyl sulfoxide (DMSO), dithizone (DTZ), hydrochloric acid (HCl), hydrogen peroxide (H_2O_2), acetone, ethanol and sodium hydroxide were purchased from the Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). MAA and EGDMA were purified prior to use via general distillation method in vacuum under nitrogen protection to remove the polymerization inhibitor. AIBN was recrystallized from cooled methanol and dried at room temperature in a vacuum. Potential interferences (1 mg mL^{-1}), such as Cu(II), Pb(II), Zn(II), Ni(II), Ca(II), Ag(I), Mn(II), Hg(I), Al(III), Co(II), Fe(III), Mg(II), Fe(II), As(III) and Ba(II) were all purchased from the National Institute of Metrology of China. Ultrapure water was available from a Milli-R04 purification system (Millipore, Germany). The stock solution was diluted as required to obtain standard solutions containing 1–100 μg L^{-1} Cd(II) ions. Water samples were collected from the East Lake and the Yangtze River, and then stored at −4 °C until analysis. The chemical oxygen demand

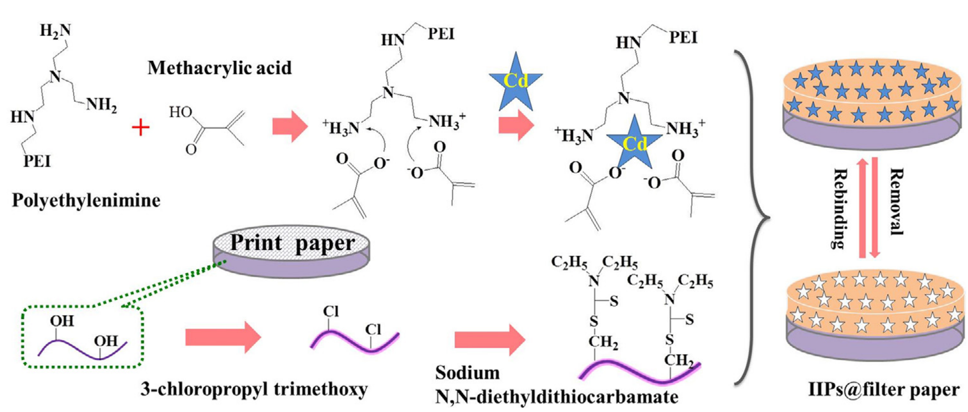

Fig. 1. The preparation procedure of IIPs composites.