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Selective separation of salicylic acid from aqueous solutions using molecularly imprinted nano-polymer on wollastonite synthesized by oil-in-water microemulsion method

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ABSTRACT

Highly effective molecularly imprinted nano-polymer on wollastonite (nano-WMIP) was prepared by imprinting technique using oil-in-water emulsion polymerization in the presence of salicylic acid (SA) as template. The adsorption behavior of nano-WMIP including adsorption kinetic, isotherms, selective adsorption, recognition, and effects of initial pH, ionic strength, initial concentration, adsorption temperature, and amount of adsorbents were investigated in detail. Moreover, the selective recognition of nano-WMIP was further investigated by HPLC toward analogs of SA. The relative selectivity coefficients for *p*-HB, MS, and MP were 113.4, 8.049, and 6.239, respectively, showing that much higher selectivity of SA on nano-WMIP was obtained than that of wollastonite-based non-imprinted polymer (nano-WNIP).

1. Introduction

Salicylic acid (SA) is a prominent medicine intermediate to produce lopirin, fenamifuril, diflunisal, salicylamide, and benorylatum. Moreover, it is frequently applied as the main component of cosmetic owing to its excellent role in getting rid of horniness, shrink pores, and trivial wrinkles [1]. However, heavy use of SA in chemicals, petrochemical, pharmaceutical, pesticide industries has caused the increasing concentration of SA in wastewater, surface water, and even groundwater. SA-contained water can induce headaches and nausea, and even harm the liver and kidney of human being [2]. The Environmental Protection Agency (EPA) has listed SA on the priority pollutants list. Thus, it is necessary to remove SA from wastewaters before discharging into the environment.

In regular monitoring, photocatalytic degradation [3,4], chemical coagulation [5], solvent extraction [6], membrane separation [7], and adsorption [8], have been employed to remove SA from wastewater. Among these processes, adsorption is an efficient and economically feasible method for the removal of organic pollutants [9]. The commonly used adsorbents are activated carbon, alumina, silica, and ferric oxide. However, these adsorbents always cannot effectively remove SA from wastewater for their poor selectivity and regeneration and for SA often with a relative low concentration.

Molecularly imprinted polymers (MIP) have been regarded as ideal adsorbents to treat wastewater for their predetermined selectivity of targeted substance, high adsorption capacity, easy regeneration and relative low cost [10,11]. However, the study of removal of SA from wastewater by MIP is scarcely reported. Thus, it is of great significance to study the usage of MIP to remove SA from wastewater. During the process of preparation of MIP, considerably high quantities of cross-linking agents are used to preserve the shape and size of the cavities formed. But the kinetics and equilibrium behaviors of MIP are poor due to the nature of extensive cross-linking. Surface imprinting technique, which builds the recognition system on the support materials, could be such an alternative method to prepare the favorable MIP [12]. Most studies with imprinted polymers have been carried out using the surface imprinting method and focused on selective binding, transport, and separation [13,14]. Although, the above methods can promote the selective recognition of target molecules and speed of the imprint molecules for the imprint sites, they are not environmental friendly because of excess of organic solvent used and the adsorption capacity of the polymer are limited. Therefore,

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it is urgent to develop a new "green" molecularly imprinted polymer with more imprinted cavities and excellent performance.

Microemulsions are thermodynamically stable, clear or translucent micellar solution comprised of oil, water, and surfactant [15]. The microemulsion method is often used to synthesize nanoparticles with specific size and morphology. The advantage of the method is the ability to control the particle size or shape-controlled nanoparticles with narrow size distribution, which are easily incorporated into a variety of substances to form nanocomposites or assembled into higher-order nanostructures. Over the past few decades, microemulsion technique has attracted particular attention because the aqueous phase dispersed into the oil phase can form a transparent microemulsion. In view of the green chemistry, the oil-in-water (O/W) microemulsions structure has several advantages over more the (water-in-oil) W/O microemulsion: water phase and oil phase ratio is far greater than 1, consumption organic matter less and relatively low cost.

Using microemulsion method with imprinting technique can prepare various imprinting nanoparticles with higher specific recognition and adsorption capacity of the target molecular comparing to imprinting polymers of large particle size [16]. However, these imprinting nanoparticles often show low recycling rate for their very small particle size. If these imprinting nanoparticles can be grafted on some supports, the recycling rate of the used imprinting particles will be greatly enhanced.

Therefore, in the present work, the imprinting nanoparticles for SA were synthesized by oil-in-water microemulsion and then grafted onto wollastonite (WAT) by immobilization. Using WAT as the support is because it is a potential and easy available imprinting material with high chemical, mechanical and thermal stability [17]. The prepared wollastonite-based MIP (nano-WMIP) showed highly selective adsorption of SA from aqueous solution with high recycling rate. The recognition mechanism of nano-WMIP on SA was discussed. And the adsorption equilibrium selectivity and regeneration of nano-WMIP were also investigated by the batch mode experiments.

2. Materials and methods

2.1. Materials

WAT was supplied by Jilin Hua'ou Wollastonite Co. in China. Prior to use, it was activated with 3.0 M HNO_3 to increase the hydroxyl groups on their surfaces. Divinylbenzene (DVB), styrene (St), dodecyltrimethylammonium bromide (DTAB), and potassium persulfate were all purchased from Chemical Reagent (Shanghai, China). *p*-Hydroxybenzoic acid (*p*-HB), salicylic acid (SA), methyl salicylate (MS), methyl paraben (MP), and 4-vinylpyridine (4-VP) were all supplied by Sinopharm Chemical Reagent (Shanghai, China). All other chemicals used were of analytical grade and obtained commercially. Ultra pure water used throughout the experiments was obtained from laboratory purification system.

2.2. Synthesis of nano-WMIP

The overall synthetic procedure of wollastonite based molecularly imprinted nano-polymer (nano-WMIP) is represented in Fig. 1. Firstly, 1.0 g of CTAB, 0.06 g of SA, 2.5 mL of methanol and 20 mL of water were mixed by high shear dispersion for 1 h in order to form micelles in the water. Then a mixture of 2 mL of St, 0.5 mL 4-VP and 1 mL of DVB was added dropwise into the micelle formed solution for 2 h. The monomer penetrated into the micelles in aqueous media. The activated WAT was added into the above microemulsion. Then, 0.04 g of the initiator (potassium persulfate) was added into the mixed solutions and the polymerization proceeded for 3 h at 70 °C. The residual surfactants were removed by excess methanol and then extracted with mixed solvents of

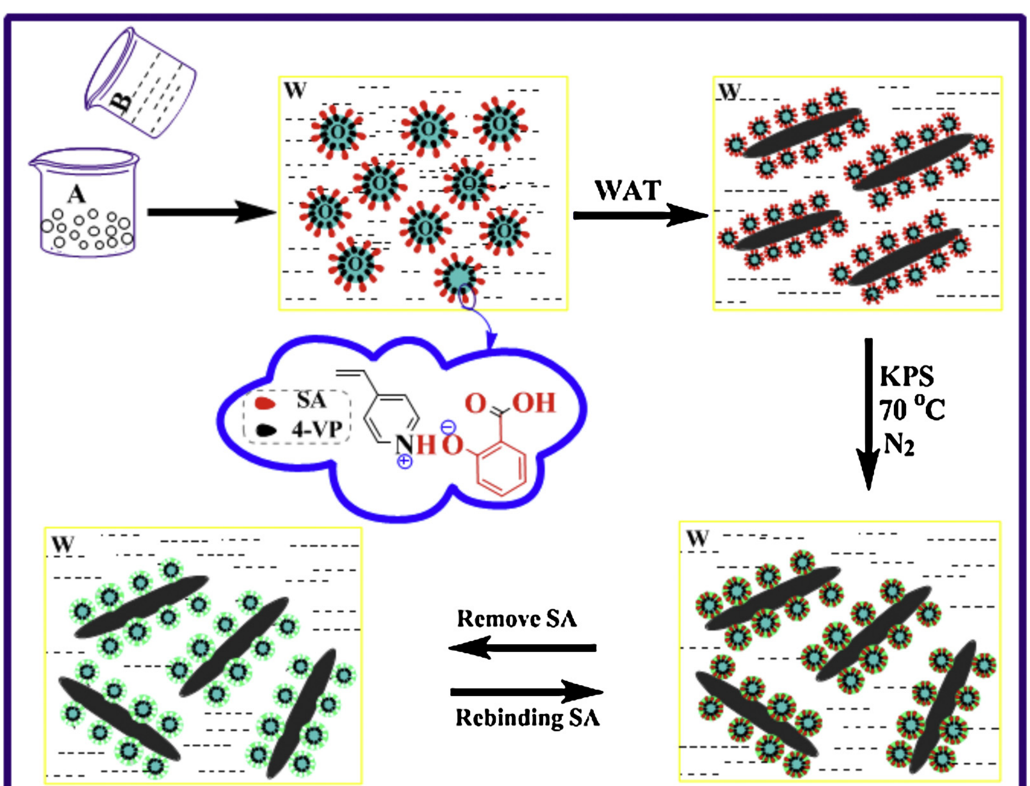

Fig. 1. Schematic procedure of nano-WMIP preparation. (O: oil phase solution; W: water phase solution). A: Ultrapure water, dodecyltrimethylammonium bromide (DTAB), methanol, and salicylic acid (SA); B: divinylbenzene (DVB), styrene (St), 4-vinylpyridine (4-VP).