A New Purification Process of Solanesol Based on Chemically Modified Diatomite

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Abstract. Diatomite is a kind of natural material with adsorption capacity and it’s widely used in industry. The main purpose of this paper is to study the influence of hydrochloric acid concentration and modification time on the modification effect of diatomite. This article describes a modified method of diatomite, which can not only reduce the purification cost, but also improve the separation efficiency of solanesol. The results show that when the concentration of hydrochloric acid is 3 mol/L and the treatment time is 50 minutes, the modification effect of diatomite is the best. The determination of the optimum technological conditions is conducive to the separation and purification of Solanesol by diatomite, and lays a foundation for the further development and utilization of diatomite.

1. Introduction
Diatomite is a kind of biogenic siliceous sedimentary rock, which is mainly composed of diatoms and other microalgae from tens of thousands of years ago [1-3]. These diatoms belong to individual micro unicellular algae, whose shape is generally only ten to tens of microns. The density of diatomite is 1.9-2.35 g/cm³, the loose density is 0.34-0.56 g/cm³, the specific surface area is 10-60 m²/g, the pore volume is 0.46-0.98 cm³/g, and the melting point is 1650°C - 1750°C. The special porous structure of diatomite can be observed under the electron microscope (Figure 1). Its shell micropores are generally tens of nanometers to a few microns, with loose texture, high porosity and strong adsorption capacity [4-6]. In addition, diatomite has stable chemical properties and does not react with any strong acid except hydrofluoric acid. Because there are a lot of hydroxyl groups on the surface and in the pore of diatomite, hydrogen bonds can be formed between the hydroxyl groups, which has a certain reaction activity and is weakly acidic.

The separation of natural products mostly uses macroporous resin as stationary phase, which has high preparation cost, complex processing process, and the waste is not suitable for treatment, which will cause certain environmental pollution problems. Through the modification of diatomite, it can be used as a stationary phase for the separation of natural products, which can not only reduce the use of resin materials, but also greatly reduce the cost of natural product separation and improve the separation efficiency. At the same time, it provides a good technical support for the comprehensive utilization of agricultural waste and the improvement of quality and efficiency of agricultural production [7-8]. In this paper, through the surface modification of diatomite, we prepared a special
material which can be used for the separation and purification of Solanesol in tobacco extract. It can improve the efficiency of solanesol molecular separation and greatly reduce the purification cost.

![Figure 1. Microstructure of diatomite](image-url)

2. Experimental

2.1. Materials and Reagents
The materials and drugs involved in this test include diatomite, sodium nitrite, sodium hydroxide, hydrochloric acid, sulfuric acid, aniline, potassium bisulfate, ammonium sulfamate and N-(1-naphthyl) ethylenediamine hydrochloride.

2.2. Experimental Equipment
The experimental equipment includes spectrophotometer, constant temperature water bath pot, electronic analytical balance, constant temperature water bath oscillator, electric blast drying oven and pH meter.

2.3. Experimental Methods

2.3.1. Modification of diatomite
Firstly, 3.0g diatomite was put into the grinding bottle, then the modifier hydrochloric acid solution was added into the grinding bottle, and then the grinding bottle was put into the constant temperature water bath oscillator to oscillate, and the modification temperature and time were controlled. After modification, the modified diatomite is washed to neutral and then filtered. Finally, the diatomite filtrate obtained in the previous step was dried to constant weight in an electric blast drying oven to obtain modified diatomite. 0.5g modified diatomite was put into a grinded flask containing 50ml aniline solution, and the grinded flask was put into a constant temperature water bath oscillator. After shaking at 25°C for 30min, the grinded flask was taken out and filtered. The filtered filtrate water sample was taken to analyze the concentration of aniline. The influence of hydrochloric acid concentration and modification time on the modification effect of diatomite was investigated to determine the optimal process conditions.

2.3.2. Adsorption of solanesol on modified diatomite
0.5g modified diatomite was placed in a grinding flask containing 50ml simulated solanesol n-hexane, and then put into a constant temperature water bath oscillator to oscillate. The adsorption time and temperature were controlled. After the adsorption, take out the grinded flask and filter it to analyze the aniline concentration in the filtered methanol. The influence of different modified diatomites on the enrichment rate of Solanesol in methanol extract was studied, and the optimum process conditions of modified diatomite were determined.

2.4. Static Adsorption Experiment of SSO-MIP
Weigh a certain mass of solanesol dissolved in methanol as adsorption solution, weigh 200mg of solanesol molecularly imprinted polymer, add it into 40mL of adsorption solution, stir and adsorb for 4
hours at 30°C, then centrifuge the adsorbed mixed solution for 30min. Solanesol concentration in the solution before and after adsorption was detected by ultra-high liquid chromatography. The adsorption amount of solanesol molecularly imprinted polymer was calculated with the formula as follows.

\[ Q = \frac{(C_0 - C)W}{W} \] (1)

\( C_0 \) is the concentration of solanesol before adsorption, \( C \) is the concentration of solanesol after adsorption, \( V \) is the volume of adsorption solution, \( W \) is the mass of MIP.

2.5. Determination of Solanesol Concentration

Accucore Vanquish C18\(^{+}\) (100 mm × 2.1 mm, 1.5μm) chromatographic column was used. The mobile phase was pure methanol. The detection wavelength was 210nm, the column temperature was 30°C, the flow rate was 0.2 mL/min, and the injection volume was 5μL. Under these conditions, the concentration of solanesol was detected. The results are shown in Figure 2.

![Figure 2. Liquid chromatogram of Solanesol in methanol solution](image)

2.6. Preparation of Standard Curve

Accurately weigh 0.050 g of solanesol dissolved in methanol and fix the volume to 100mL to obtain 0.50g/L of solanesol methanol solution. Solanesol methanol solutions of 0.50 g/L were accurately measured of 5.00, 2.00, 1.00 and 0.20 mL and diluted to 10 mL, respectively. Solanesol methanol solutions of 0.25, 0.1, 0.05 and 0.01 g/L were obtained. The concentration of solanesol has a good linear relationship with the peak area between 0.01 g/L and 0.5 g/L, \( R^2=0.99399 \). The standard curve is shown in Figure 3.

![Figure 3. The standard graph of solanesol in methanol solution](image)
3. Results and Discussions

3.1. Influence of the Hydrochloric Acid Concentration on Adsorption Performance of MIP

Figure 4. The influence of hydrochloric acid concentration on the adsorption performance of MIP

Figure 4 is a graph showing the effect of changing the hydrochloric acid concentration on the adsorption performance of the polymer. It can be seen from the figure that with the increase of the hydrochloric acid concentration from 1 mol/L to 5 mol/L, the adsorption capacity of MIP both increases first and then decreases. When the hydrochloric acid concentration is 3 mol/L, the adsorption capacity of MIP reaches the maximum. It means the concentration of hydrochloric acid has an important influence on the modification effect of diatomite. With the increase of hydrochloric acid concentration, the surface roughness of diatomite particles increases, and more grooves and holes are formed. This will increase the specific surface area and pore volume of the particles, thus increasing the adsorption capacity of diatomite. When the concentration of hydrochloric acid is more than 3mol/L, the excess hydrochloric acid will be disordered in the polymer with the increase of hydrochloric acid dosage. Therefore, excessive hydrochloric acid reduced the recognition and adsorption capacity of solanesol molecularly imprinted polymer.

3.2. Influence of the Treatment Time on Adsorption Performance of MIP

Figure 5. The influence of treatment time on the adsorption performance of MIP

Figure 5 showing the effect of changing the treatment time on the adsorption performance of the
polymer. It can be seen from the figure that the adsorption capacity of solanesol-molecularly imprinted polymers increases first, and then decreases as the treatment time increases from 20 minutes to 60 minutes. When the treatment time is 50 minutes, the adsorption capacity of MIP reaches the maximum. This reflects that the treatment time also has an important influence on the modification effect of diatomite. This is because with the increase of treatment time, the contact between the modifier and diatomite is closer, and the interaction opportunities are more, which can effectively enhance the adsorption capacity of diatomite. However, when the treatment time was more than 50 minutes, the adsorption capacity decreases slightly, which may be due to the reaction equilibrium moving in the direction of unfavorable adsorption.

4. Conclusion
The modified diatomite was obtained by modifying diatomite with hydrochloric acid solution. The effects of the hydrochloric acid concentration and treatment time on the adsorption of solanesol were studied. The optimized process conditions were obtained: the hydrochloric acid concentration was 3 mol/L and the treatment time was 50 minutes. SSO-MIP was synthesized under the optimal synthesis process. The modified diatomite can effectively improve the separation speed of solanesol and reduce the purification cost.

5. Acknowledgments
This research was supported by Finance Science and Technology Project of Hainan Province (No. ZDYF2020084), Central Public-interest Scientific Institution Basal Research Fund (No. BSRF202105), Key scientific and technological projects of Xinjiang production and Construction Corps (No. 2021AB007), Science and technology Project of the Ninth Agricultural Division of Xinjiang production and Construction Corps (2020JS015), and Changzhou Science and Technology Program (No. CE202022).

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