Preparation and Adsorption Properties of Novel Anionic Starch Microspheres

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Absrtact: In recent years, with the rapid development of our national economy, the current industrial development is very fast, the scale is increasing, the discharge of industrial wastewater is increasing, and the pollution of water resources in our country is also serious. Because many kinds of dye wastewater contain many non-degradable organic substances, their presence in water not only affects the propagation of light, This makes it impossible for multiple ecosystems and microbial systems in the water to quickly complete photosynthesis and maintain metabolism; Heavy metal waste water can go through the food chain and cause irreversible poisoning in humans, and adsorption methods are used to remove some of the toxic effects that cannot be achieved. Degradation of pollutants in the process of removal has a very important role. The aim of this study was to prepare neutral starch microspheres from natural soluble starch and to prepare a new kind of green and degradable anion starch microspheres by anion reaction. It was used as adsorbent to treat methylene blue positive dyestuff wastewater and heavy metal ion wastewater represented by copper and lead. The adsorption properties and adsorption mechanism of methylene blue and Cu^{2+}, Pb^{2+} were analyzed from the point of view of thermodynamics and kinetics. The results provide some theoretical basis and application basis for wastewater treatment.

1. Preparation and Characterization of Anionic Starch Microspheres

Ordinary neutral starch microspheres play a major role in adsorption, so their adsorption strength and selective adsorption capacity are not very strong. Through the ionization modification of starch microspheres, the active group can be improved, thus the adsorption and selective adsorption ability of starch microspheres can be improved. After anion modification of starch microspheres, some positive charge drugs and some cations in industrial wastewater can be adsorbed. Therefore, it is of great significance to study the synthesis of anionic starch microspheres. Some related reports have been reported on the synthesis of ionic starch microspheres. Li Bingzheng, Mao Zhihuai and others (2009) used Na3P30 as crosslinking agent to complete the second crosslinking and anion reaction, thus the anionic starch microspheres were obtained. However, as a secondary crosslinking agent, Na3P30 itself still needs to be prepared, and the preparation of Na3P30 itself is more complicated. In this paper, chloroacetic acid is mainly used as anion reagent. Thus, a new kind of anionic starch microspheres can be prepared.

2. Materials and Methods

2.1 Reagents and Instruments

2.1.1 Reagent

Soluble starch (chemical pure, Tianjin Bodi Chemical Co., Ltd.), Sodium hydroxide (Analytical Pure, Xi'an Chemical Reagent Factory) and Span 60 (Chemical Pure, Chinese Medicine Group Chemical Reagent Co., Ltd.), Soybean oil (on the market) and epichlorohydrin (analytical pure, Tianjin chemical reagent factory), acetic acid ethyl acetate (analytical pure, Tianjin Bodi chemical co., Ltd) and acetone (analytical pure), Tianjin Bodi Chemical Co., Ltd) and anhydrous ethanol (Analytical pure, Xian Sanpu Fine Chemical Plant)

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2.1.2 Instruments

DF-101 S constant temperature heating magnetic agitator (Zhengzhou the Great Wall Science & Trade Co., Ltd.) and Spark Brand Glass instrument Air flow Dryer (Zhengzhou the Great Wall Technology & Trade Co., Ltd), There are also UV754 ultraviolet spectrometer (Shanghai Precision Scientific instrument Co., Ltd), SHZ-88 desktop water bath constant temperature oscillator (Jiangsu Cang Tai City Experimental equipment Factory), 101-2 drying box (Shanghai Experimental instrument Factory of the people's Republic of China), Biological microscope (Chongqing Optoelectronic instrument Co., Ltd.), Flying Pigeon TDL-40B bench centrifuge (Shanghai Anting Scientific instrument Factory), JJ-1 Precision Enhancement Electric Mixer (Changzhou Guohua Electric Co., Ltd.), BX320D Electronic Analytical balance (mouthpiece), SKC-2000 Particle size Analyzer (UK), JSM-6360LV scanning Electron Microscopy (), NEXUS Fourier Infrared Spectrometer) (USA)

2.2 Experimental methods

2.2.1 Preparation of neutral starch microspheres

A proper amount of soluble starch was added to the 2 mol/L NaOH solution which was relative to the soluble starch, which was stirred sufficiently and activated at 60 ℃ for 30 min, so that it could be used as water phase. Add proper soybean oil to three flasks, add Span60, to it, install electric stirrer and constant temperature water bath on it, and heat it to 60 ℃ so that Span60 can dissolve completely. And it is cooled to 40 ℃ as oil phase.

Slowly add the water phase to the oil phase, and the stirring speed is effectively controlled. The appropriate choice is to use a microscope to observe. After stirring and dispersing for 30 mi, it can be observed that the emulsion is evenly dispersed, then added to epichlorohydrin during the holiday period, then reacted at 40 ℃ for 6 hours, then took out another emulsion to remain static, then removed the oil phase from the upper layer. The lower crosslinks were eluted repeatedly by acetic acetate ethyl acetate anhydrous ethanol and acetone and kept dry in a drying box to obtain yellow powder microspheres.

2.2.2 preparation of Anionic starch Microspheres

1 g neutral starch microspheres were selected, then 80% ethanol solution was added to the microspheres. Then 20% NaOH solution and 0.25 g chloroacetic acid solution were added to the solution. It was agitated at 55 ℃ so that it could react fully, using 20% HCl solution and neutral solution to satisfy pH=11, washing the sample with 80% ethanol solution and no Cl^- (silver nitrate solution test) in the washing solution. Then place the sample in a drying box and keep it dry.

2.2.3 Characterization and Properties of Microspheres

2.2.3.1 Characterization of a novel Anionic Microsphere

Scanning electron microscopy (SEM) was used to observe the morphology, size and distribution of soluble starch and anion microspheres after vacuum gold plating. There is also a need to compare their own differences and changes.

The functional group prepared its own soluble starch and anion starch microspheres into KBr tablets by IR spectroscopy, and then measured them by IR to record the infrared spectra in the range of 400-4000 cm. Then it analyzes its own differences and changes.

The average particle size and particle size distribution of the microspheres were measured by means of SKC-2000 photo-permeable particle size analyzer after the proper amount of anionic starch microspheres were dispersed evenly using anhydrous ethanol as solvent.

2.2.3.2 Study on adsorption of methylene blue by anionic starch microspheres

The preparation of methylene blue standard reserve solution put methylene blue in drying oven and drying at low temperature. Accurately weigh 1.000 g methylene blue in a beaker, then add a small amount of deionized water. The methylene blue was stirred until completely dissolved, then transferred to the volumetric bottle, diluted to 1000mL with deionized water, and swayed to obtain a

solution of concentration of 1000mg / L. 1000mg solution is used as methylene blue mother liquor and stored in dark place.

Different concentrations of methylene blue solution were prepared from the above standard solution with deionized water.

The standard curve of methylene blue was drawn by diluting methylene blue solution with deionized water concentration of 1000mg. The concentration of methylene blue was 2? 3? Methyl blue solution. The deionized water was used as a blank in the UV-Vis spectrophotometer and the absorbance value was measured at the maximum absorption wavelength of 665nm. The absorbance value was drawn on the vertical coordinate and the methylene blue solution concentration was drawn on the transverse coordinate to prepare the standard curve.

Anion starch microspheres adsorbed methylene blue 1g completely dry anion starch microspheres were added into 50mL 50mg / L methylene blue solution and oscillated in a constant temperature water bath oscillator for 2 hours and centrifuged. The absorbance of supernatant was determined by ultraviolet spectrophotometer and the concentration was obtained by methylene blue standard curve.

3. Results and Discussions

3.1 Scanning electron microscope analysis

In this figure, a and b show the scanning electron micrographs of soluble starch and anion starch microspheres, the magnification is 500 times of the scanning electron microscope, c and d are 2000 times of that of the anion starch microspheres. The soluble starch was irregular and uneven in size, while the anion starch microspheres had smooth surface and spherical shape. It can be seen from c and d diagrams that there are some pores on the surface of anion starch microspheres. However, anion microspheres have a high degree of erection, which may be caused by the preparation of microspheres by emulsification and crosslinking. Emulsion liquid when emulsified by mechanical stirring The size distribution of droplets is very wide, so the connection of microspheres is inevitable in emulsification and transportation.

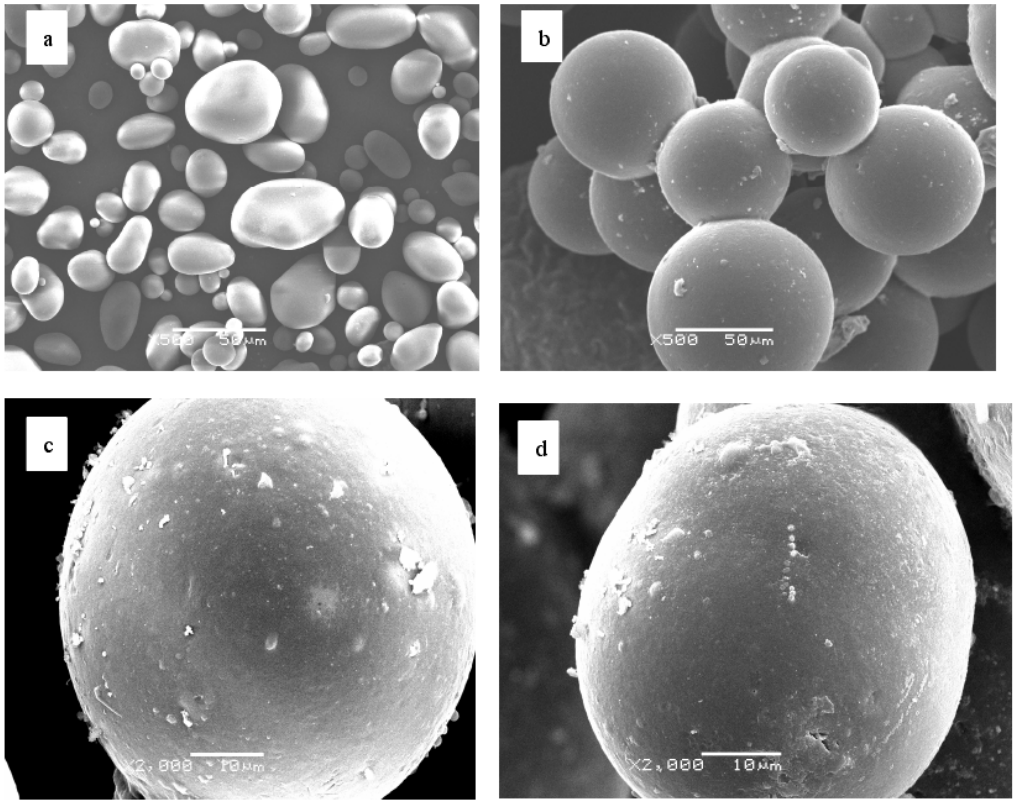

Fig. 1 SEM of soluble starch and anionic microspheres

3.2 IR (FTIR) analysis

In this diagram, a and b are infrared spectra of soluble starch and anion starch microspheres, respectively. The spectra of soluble starch and anion starch microspheres were obviously different. In the region of 3400 cm^{-1} -2920 cm^{-1}, the soluble starch and anion starch microspheres had strong and wide peaks, indicating that there was a light alkali before and after crosslinking, but it could be seen that the anion starch microspheres had a smaller peak width. It is possible that soluble starch due to crosslinking reduces the binding of hydrogen bonds. At 930cm^{-1}1650cm^{-1}, soluble starch was found at 1647cm^{1} . There are six visible peaks at 4 cm^{1}115 8 cm^{-1} 10 81 cm^{-1} 1021 cm 1931cm^{-1}. There are obvious peaks in 1081cm^{-1} and weak peaks in 1021cm^{-1}. In the same region the spectrum of anion starch microspheres was significantly different from that of soluble starch. The peak at 1158 cm^{-1}931 cm-' becomes invisible, the peak at 1081 cm weakens, and the peak at 1022 cm is stronger. Peak pair crystallinity at 1081 cm 'and 1021cm^{-1} The changes are very sensitive. The peak value at 1081 cm^{-1} is related to the shape or crystallization of starch, and the peak value increases with the increase of crystallinity, while the peak value at 1021 cm is the characteristic peak of the amorphous region of starch, which decreases with the increase of crystallinity. The crystallinity of soluble starch decreased as a result of crosslinking and anion reaction, which was consistent with the change of peak strength of 1081 cm^{-1} and 1021 cm^{-1}. The new peaks of 1605 cm^{-1} and 1420 cm^{-1} were also observed in the anionic starch microspheres. It's characteristic suction. The peak of the shuttle group (Chang 2006). All these spectral changes confirmed the successful preparation of anion starch microspheres.

3.3 Particle size analysis and particle size distribution of microspheres

The results of the particle size measurement of the sample show that the particle size of the microspheres is a normal distribution, and that the particle size of the microspheres is basically uniform. And there was no wide distribution and bimodal distribution. The particle size of the microspheres with more than 90% was kept at 100. Below.

4. Conclusion

Soluble starch was used as raw material, epichlorohydrin itself as crosslinking agent, Span60 as emulsifier, soybean oil as oil phase, and then neutral starch microspheres were synthesized by inverse emulsion method. Then the neutral starch microspheres were used as the main raw materials and then modified by chloroacetic acid to prepare a new type of anionic starch microspheres. Then the products were characterized by scanning electron microscopy and infrared spectroscopy, which showed that the preparation of anion starch microspheres had been completed. The adsorption capacity of anionic starch microspheres for methylene blue was used as an index to complete single factor and orthogonal. The optimum conditions for the synthesis of anionic starch microspheres were as follows: the reaction temperature should be kept at 50 ℃, the specific reaction time should be kept at 5 h, and the dosage of 80% ethanol was 5.5 mL, sodium hydroxide 0.9 g. Amount of chloroacetic acid 0.3 g.

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