Adsorption of anionic surfactants from aqueous solution by high content of primary amino crosslinked chitosan microspheres

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ABSTRACT

High content of primary amino crosslinked chitosan microspheres (ACCMs) were synthesized and characterized with IR, XRD and SEM technologies. Subsequently, ACCMs were adopted to adsorb three common anionic surfactants from aqueous solution: sodium dodecyl benzene sulfonate (SDBS), sodium lauryl sulfate (SLS), and sodium dodecyl sulfonate (SDS). The adsorption performances were evaluated based on different variables such as the pH, contact time, temperature and initial concentration of the anionic surfactants. Moreover, the adsorption were investigated with kinetic models, equilibrium isotherms and thermodynamic models. The experimental results indicated that the adsorption processes were fitted very well with a pseudo-second-order model. The adsorption isotherms could be better described by Langmuir model rather than Freundlich model. The adsorption of SDBS was a spontaneous, exothermic process. While the adsorption of SLS and SDS were spontaneous, endothermic. The adsorption processes were complex physical-chemistry adsorption models, which are dominated by physisorption. Furthermore, this study found that the material had strong absorption abilities for anionic surfactants, the saturation adsorption capacity of ACCMs were 1220 mg/g for SDBS, 888 mg/g for SLS, and 825 mg/g for SDS at pH 3.0 and 298 K, respectively. The adsorption capacity was reduced only 5.7% after 8 cycles of the adsorption-desorption processes.

1. Introduction

Many industries, including textile industry, catering industry, tanneries, chemical factories, and our daily life release a great amount of wastewater containing anionic surfactants. Due to the hydrophilic and hydrophobic groups on the molecule, anionic surfactant molecules could accumulate and generate an isolation layer under the water surface. This would limit the reoxygenation process and reduce the dissolved oxygen in water. Besides, the anionic surfactants containing effluents could apparently increase the solubility of hydrophobic persistent organic pollutants, such as PCBs, lindane, and PAHs [1,2], and result in acute and chronic toxicity [3]. Therefore, the overloaded anionic surfactants are regarded as a serious threat to the water ecological balance. Multiple techniques have been applied to water treatment in terms of anionic surfactants containing effluents, such as adsorption [4], microbial degradation [5], electrochemical degradation [6], photoeletrocatalytic oxidation [7] and so on [8]. Among these methods, adsorption has its own advantage based on its high efficiency of treatment, simple operation procedure and commercial available adsorbent.

Chitin is one of the most abundant natural polymer in the terrestrial biosphere. And it is a kind of renewable and low-cost material. Chitosan was prepared after de-acetylation of chitin. Previous researches found that chitosan had enormous potential to adsorb pollutions, such as heavy metal [9] and dyes [10]. Furthermore, under acid conditions, chitosan had high adsorption capacity to anionic surfactant due to the electrostatic attraction between anions and the protonated amino groups [4]. However, chitosan was soluble in acid and had low mechanical strength and small surface area, limiting its adsorption performance. To overcome these drawbacks, chitosan microspheres were synthesized with self-crosslinking reactions between the chitosan molecules. Besides, Schiff-base was composited [11] to protect the active sites of adsorption.

There are a large number of researches focused on the adsorption of heavy metal and dye onto chitosan [9,10,12–14]. But studies of anionic surfactants are very scarce and are limited to SDBS [4,13]. No information is available about different anionic surfactants. This paper firstly evaluated the adsorption of chitosan for a class of anionic surfactants: sodium dodecyl benzene sulfonate (SDBS), sodium lauryl sulfate (SLS), and sodium dodecyl sulfonate (SDS).

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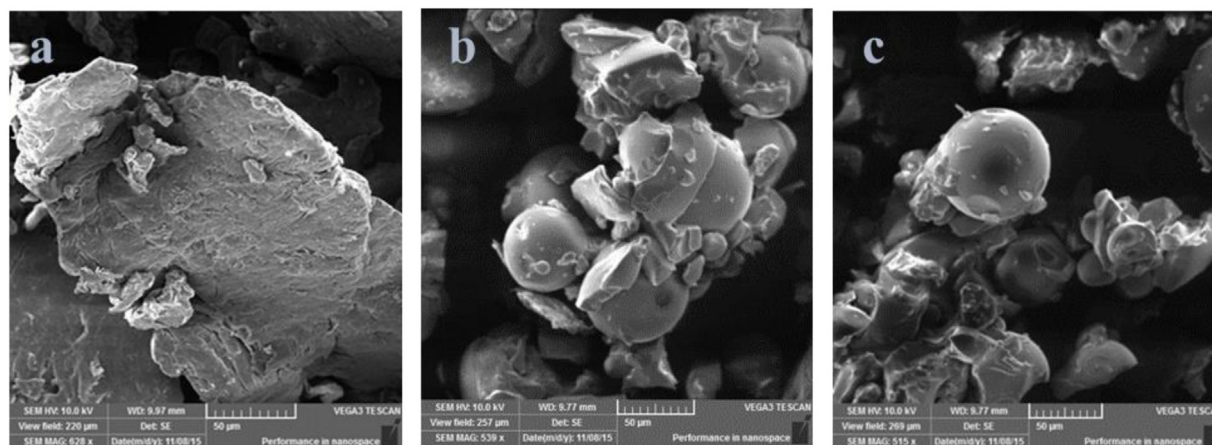 *E-mail address:* whf@usst.edu.cn (H. Wen).

Fig. 1. SEM images of chitosan (a) and ACCMs (b and c).

With studying the adsorption equilibrium, kinetics and thermodynamics processes, the adsorption mechanism of anionic surfactants on ACCMs was elucidated. Moreover, the performance of adsorbent was evaluated in terms of the saturated adsorption capacity and reusability.

2. Experimental

2.1. Chemicals

Chitosan in powder form (deacetylation degree of 85%–95%) and methylene blue (indicator grade) are commercially available from Shanghai Chemical Reagent Co., China. Basic brilliant blue BO (C.I. 42595) can be purchased from Shanghai Santai Dyestuff Chemical Factory. Liquid paraffin, Span 80 and Triton X-100 were chemical grade. Other reagents (SDBS, SLS, SDS, formaldehyde, epichlorohydrin, HCl, H_2SO_4, acetic acid, NaOH, etc.) were analytical grade. These chemicals were purchased from Shanghai Chemical Reagent Co., China.

2.2. Preparation of high amino ACCMs

The amino radical ACCMs were synthesized by the inverse suspension method [15]. The synthetic process could be described by Fig.s1 briefly. Firstly, Formaldehyde, precrosslinker, reacted with amino groups of chitosan to generate the Schiff-base to shield the active adsorb sites of adsorbent. Then, the chitosan molecules were connected with each other by epichlorohydrin (ECH). Finally, the Schiff-base was removed by HCl solution, and the primary amine of chitosan molecules was generated.

Chitosan (5.0 g) was dissolved in 100 mL of 4.0% (v/v) acetic acid solution; and then 100 mL liquid paraffin was added. After the mixture was stirred for 10 min, three drops of emulsifier span-80 was added into it. The suspension was stirred and emulsified for 10 min at 50 °C. After that, 6.0 mL formaldehyde was added, and the mixture was stirred for 1 h at 60 °C. The temperature was increased up to 70 °C, the pH value of the mixture was adjusted to 10 with addition of 5.0% (w/v) NaOH solution. Extra 3.0 mL 37% (w/v) ECH was added into the chitosan suspension. Right after that, the NaOH solution was added dropwise continually to maintain the pH value of the mixture to be around 10. Meanwhile the mixture was stirred for 3 h. The prepared chitosan derivative was filtered and purified for 24 h by extraction with the petroleum ether in a Soxhlet apparatus. The derivative was then soaked in 0.1 mol/L HCl solution for 9 h. It was filtered and rinsed by NaOH solution and deionzed water. Finally, the chitosan particles was dried in the air oven at 40 °C.

2.3. Characterization

ACCMs and chitosan were characterized on an X-ray diffractometer (XRD) (D8 ADVANCE, Bruker Corporation, the Germany) with Cu Kα radiation (λ = 1.5419 Å). The scanning electron microscopy (SEM) images were taken with a scanning electron microscopy (SEM, Tescan vega3, operated at 10 kV). The Fourier transform infrared (FT-IR) spectra of ACCMs and chitosan were tested with a Nicolet 6700 spectrometer within the range of 400–4000 cm^{-1}.

2.4. The methods of measuring the concentration of the anion surfactant solution

The concentration of SDBS and SLS solution were measured with alkaline brilliant blue BO spectrophotometry [16]. 5.0 mL 0.2 mmol/L alkaline brilliant blue BO solution, 5.0 mL pH buffer solution (0.6 mol/L H_3PO_4-0.6 mol/L NaH_2PO_4), distilled water, a certain volume of test solution, and 1.0 mL 0.2% (w/v) emulsifier OP solution were one by one in order added into a 50 mL volumetric flask and diluted with water to the exact volume. The absorbance of the solution was measured in 1.00 cm quartz cells at 570 nm after 5 min by 732N type visible spectrophotometer (Shanghai Jingke Industrial Co., China). The concentration of the SDS solution was measured by methylene blue spectrophotometry [17].

2.5. Determination of saturation adsorption capacity of ACCMs

It started with distribution of 100 mL of the anionic surfactants solutions with different initial concentrations (10, 20, 50, 100, 200, 300, 400, 500, 1000, 2000 mg/L) into different 250 mL closed Erlenmeyer flasks. The pH of the solution was adjusted to a value of 3.0 ± 0.2 with 0.5 mol/L H_2SO_4, and then 50 mg ACCMs was added. The flasks were placed into a water bath and shaken at 120 rmp and under 25 °C for 24 h. From the above methods, the equilibrium concentration of anionic surfactants can be determined. The adsorption capacity, q_e (mg/g) of the adsorbent for anionic surfactants at equilibrium status was calculated with following Eq. (1):

$$q_e = \frac{(c_0 - c_e)V}{m} \tag{1}$$

Where c_0 and c_e (mg/L) represent the concentration of the anionic surfactants at initial and equilibrium status, respectively. V (L) is the volume of anionic surfactants solution, and m (g) is the mass of adsorbent.