Effect of organic solvents on dyes adsorbed by calcium alginate

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Abstract. Sodium alginate aerogel prepared by vacuum freeze-dry method was first crossed bonding in organic solvent. Using 95 % ethanol as an organic solvent, the organic solution of calcium chloride has retained the original morphological structure of aerogel, which has better adsorption property. Then sodium ions were replaced by calcium ions through cross-linking reaction to gain the porous calcium alginate aerogel. After natural drying, product is completed. The experimental parameters such as the contact time, pH, temper and dosage prove the adsorption properties of methylene blue on the porous calcium alginate aerogel.

1. Introduction
The usage of dyes can cause serious physiological problems such as vomiting, rapid heart rate, diarrhea, shock, cyanosis, jaundice, quadriplegia\cite{1} and environmental issues. Therefore, it is very important to develop a low-cost method to remove dyes from wastewater. Adsorption has been used for many years because it is simple, safe, reliable, efficient, and relatively inexpensive. It is important to find adsorbents with high efficiency and large adsorption capacity. Adsorption of dye materials from aqueous solutions include: activated carbon, zeolite, agricultural waste\cite{2}, natural polymer materials\cite{3}, clay\cite{4}, silicate\cite{5}. Sodium alginate (SA) is a linear polysaccharide extracted from natural seaweed. It is biocompatible, non-toxic, highly viscous, and relatively inexpensive compared to other polymer materials.

In this experiment, the porous sodium alginate (SA) aerogel obtained by the freeze-drying method was cross-linked by placing calcium chloride in ethanol solution to prepare calcium alginate (CaA) having a 3D network structure. Because SA is insoluble in ethanol, the sample obtained by cross-linking in ethanol almost completely retains the entire shape of the aerogel, and also retains the excellent performance of the aerogel in terms of adsorption.

2. Materials and methods

2.1 Materials
Sodium alginate (SA, viscosity >400 mpa. S, shandong jiejing group); Anhydrous calcium chloride (analysis of pure, molecular weight 110.98, national drug reagent); 95% ethanol (analysis of pure, Shanghai wokai biotechnology co., LTD.); Methylene blue (analysis pure, tianjin guangcheng chemical reagent co. LTD.). Water bath constant temperature oscillator (shz-82a, jiangsu jincheng...
guosheng experimental instrument factory); Refrigerator (bcd-215kaw, Qingdao haier co., LTD.); Freeze-drying machine (fd-1b-50, Beijing boyikang experimental instrument co., LTD.).

2.2 Preparation of calcium alginate membrane
Put the Sodium alginate into deionized water and stirred by a magnetic stirrer until it was dissolved completely. The weight ratios of sodium alginate to deionized water were 1–8%. When the SA is completely dissolved, set it for 24 hours to remove the bubbles. Then the solution is placed in a refrigerator for 24 hours. In order to obtained SA aerogel, the frozen samples were placed in a freeze-drying machine to freeze and dry. Dissolve calcium chloride in 95% ethanol. Then put SA aerogel into calcium chloride ethanol solution for 30 minutes. After crosslinking, CaA products with aerogel morphology were obtained. After CaA products dried in the natural environment, the CaA aerogel finally completed.

3. Results and discussion

3.1 Characterization of calcium alginate aerogel

![Fig. 1. Photographs of (a) sodium alginate (b) calcium alginate cross-linked in ethanol (left) in water (right).](image)

Figure 1a shows that the SA aerogels frozen in the refrigerator has a smooth surface and picture b is come from (a) which has been divided into two aerogels with same size. Respectively, the SA aerogels immersed in the calcium chloride solution which is full of ethanol (left) and water (right). As we can see from picture (a), SA aerogel obtained a kind of spongy solid structure with loose surface. SA aerogel is immersed in aqueous solution of calcium chloride and in ethanol solution of calcium chloride. It makes the calcium ions connect to the α-L-guluronic acid blocks between α-L-guluronic acid and β-D-mannuronic acid chains to form calcium alginate membrane[6]. Picture b compared with the SA aerogels soaking by water and ethanol. It can be seen that the SA, which is immersed in water, shrinks in volume and its surface becomes densification. Basically, it loses its original appearance. However, the SA, crosslinked in ethanol, almost retains all the forms of aerogels, and the loose surface structure is preserved. SA, crosslinked in ethanol, retains aerogel morphological structure, which has better adsorption performance.
Figure 2 shows the scanning electron microscopy (SEM, JSM 6700F, JEOL Ltd., USA) of CaA. The electron micrograph of CaA obtained in the water (Figure 2a). It can be seen that the CaA surface is uneven. There are many small convex folds, but the holes are not obvious to see. The electron micrograph of CaA obtained in the calcium chloride solution of ethanol (Figure 2b). It shows CaA are flat and dense, which has visible holes. The difference between a and b is due to different solvents. The water makes the gel atrophy and wrinkles. Moreover, the hole becomes to shrink and many small pores disappeared. SA does not dissolve in the ethanol, so it does not affect the aerogel structure. At the same time, the vacuum freeze-drying method[7] is an effective method to fabricate the porous structure based on sublimation. In the process of drying, only the water is sublimated and SA is preserved. This leave a large number of holes, forming a spongy structure. The porous structure can provide a large number of channels for MB passage and provide more adsorption sites, thereby improving the diffusion efficiency and adsorption efficiency of the dye.

3.2 The adsorption properties of the CaA
The CaA gas gel treated with different solvents SA (1-8%) has different adsorption properties. Fig. 3a and b show the adsorption properties and removal rates. The adsorption properties of SA treated with different solvents are different (Fig. 3a). The adsorption properties of SA which has been crosslinked in water is irregular and the adsorption amount was approximately 518mg/g. At the same time, it can be seen that the adsorption of SA on MB after crosslinking in ethanol is regular. With the increase of concentration of SA, the adsorption capacity was increased slowly, reaching the maximum adsorption capacity of 567mg/g at the concentration of SA at 5%. With the concentration of SA continue increasing, the adsorption capacity decreases slowly. The adsorption quantity changes may due to the changes of specific surface area of adsorbent, with the increase of SA concentration, adsorbent pore number more, at the same time its density enhanced. But its volume is become smaller. At this time, the leading role is the more quantity of holes and bigger specific surface area, so the adsorption quantity increased. With the concentration of SA reaching at 5%, SA has maximum specific surface area and the adsorption properties reach at maximum capacity. As the concentration of SA continues to increase, the density of adsorbent becomes dominant, the specific surface area become smaller. Similarly, the changing in the removal rate of (Fig. 3b) diagram is similar to adsorption property. The removal percentage reaches 83% and the removal percentage of SA treated by ethanol reaches 95% at the weight ratio at 5%. The biggest removal percentage points higher than 12%. Thanks to the protective effect of ethanol on aerogel structure. After the SA aerogels were crosslinked in ethanol, the appearance and shape were basically preserved and the volume did not change significantly. The SA crosslinked in the water, the volume is reduced, and the appearance and shape have changes a lot. The aerogel structure was destroyed. So the aerogel crosslinked in ethanol have a larger specific surface
area and better adsorption properties.

![Graph](image)

**Fig. 3.** The (a) adsorption capacity and (b) removal rate properties of the sodium alginate (1% ~ 8%) treated with different solvents on MB.

4. **Conclusion**

The SA crosslinked in the water, the volume is reduced, and the appearance and shape have changes a lot. The aerogel structure was destroyed. So the aerogel crosslinked in ethanol have a larger specific surface area and better adsorption properties.

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