

# Preparation of efficient and recyclable regenerated silk fibroin film and sericin carbon aerogel for water pollution treatment

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The growing industrialization has released a large amount of toxic and hazardous wastes such as organic dyes, oils and organic solvents to the environment. They not only damage the ecological environment, but also seriously threaten to human health. Dyes are an important part of daily life. They have been extensively used in the textile, paint and pigment manufacturing industries<sup>[1]</sup>. It is estimated that 1.6 million tons of dyes are produced annually worldwide, and 10-15% of this volume is released via effluents<sup>[2]</sup>. It is obvious that direct discharge has created serious problems for water resources. For example, the presence of dyes in water might be hazardous to many life forms<sup>[3]</sup>. The oil spill is another global challenge facing our society. It not only damages the fragile ecological environment, but also poses a long-term threat to human health<sup>[4]</sup>. In April 2010, the Macondo 252 wellhead spilled more than 1 million barrels of crude oil into the northern Gulf of Mexico (nGoM), causing extreme pollution<sup>[5]</sup>. Existing wastewater purification technology, adsorption process is a popular choice which enables complete capture and complete disposal without the production of toxic by-products, and is simple and effective<sup>[6]</sup>. Zeolite, sawdust and wool fibers which are natural materials -have been widely used in Sewage purification treatment due to their porous structure and high specific surface area. However, the low adsorption efficiency and the poor selectivity limit its application in wastewater purification<sup>[7]</sup>.

Silk is a natural protein polymer composed of silk fibroin and sericin. Silk fibroin has superior biodegradability and biocompatibility<sup>[8]</sup>, so most studies have focused on its biomedical and biotechnological applications. Silk fibroin has both hydrophilic nature and amphoteric properties and can interact with a variety of dye types, making it a potential biosorbent for dye wastewater treatment<sup>[9]</sup>. Sericin contains 18 kinds of amino acids, and the content of polar amino acids such as serine, aspartic acid and threonine exceeds 70%, which gives the sericin good water solubility<sup>[10]</sup>. Silk gum has inherent properties such as hydrophilicity, oxidation resistance, cell viscosity, biodegradability, and pollution resistance. These inherent physical and chemical properties of sericin make it ideal as a biosorbent to selectively remove contaminants from aqueous environments<sup>[11]</sup>. Therefore, we use silk fibroin and sericin to make different materials to treat dyes, oils and organic solvents in sewage.

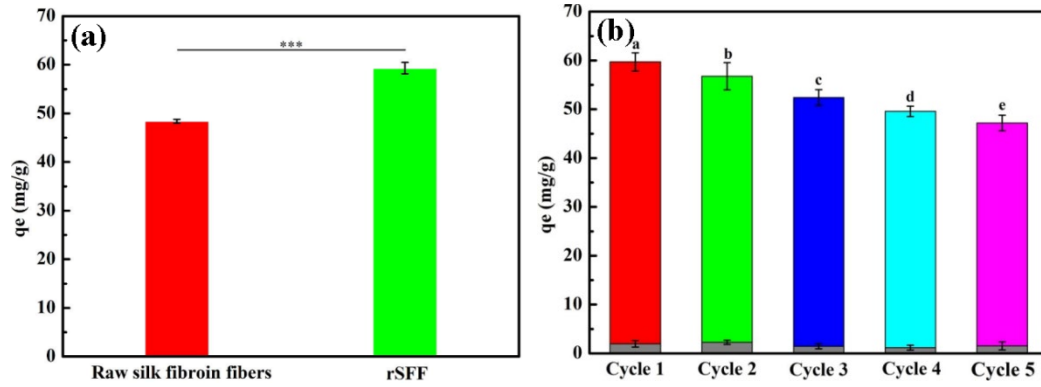


Fig.1 Adsorption and Recyclability study of rSFF: (a) the comparison of Raw silk fibroin fibers and rSFF; (b) Recyclability study of rSFF

In this work, two different components of silk, silk fibroin and sericin, were successfully used to prepare two different porous materials for water treatment-regenerated silk fibroin film (rSFF) and sericin carbon aerogel (SCB). ① Preparation of regenerated silk fibroin using silk fibroin material and its adsorbability to azo dyes (acid yellow 11, naphthol orange and direct orange S) was measured. At optimal conditions, the adsorption capacity of rSFF for acid yellow 11 reached up to 59.71 mg/g, which was 1.23-fold higher than that of raw silk fibroin fibers. More importantly, rSFF exhibited a high level of flexibility and functionality as well as a good shaping ability, which were crucial for its practical application (fig 1a). Fig 1b shows that rSFF had potential to be reused in a number of treatment cycles. After five cycles, its adsorbability to acid yellow 11 remained as high as 47.20 mg/g. Finally, a scale-up experiment was performed for rSFF, and the results indicated that it was feasible for rSFF to extend the practical application. ② Sericin carbon (SCB) aerogel was successfully prepared by freeze-drying and tube furnace carbonization. The adsorption properties of SCB aerogels on organic solvents and oils are shown in fig 2. The results indicated that, the adsorption efficiency of SCB for organic solvents and oils is high. Among them, the adsorption efficiency of ethanol is the lowest, which is 73.7 times of the weight of SCB; the adsorption efficiency to chloroform is the highest, which is 193.7 times its own weight. Again, the adsorption efficiency of other organic solvents and greases is higher than 73 times of its own weight. In addition, the high adsorption efficiency of SCB is also recyclable, which are shown in fig 2d. After 5 cycles, its adsorption efficiency can still reach 59 times of its own weight, which is higher than commercial absorbent (10-30 times). It is worth mentioning that sericin is the industrial waste of the silk industry. The use of sericin as a precursor to prepare the absorbent material can not only reduce the discharge of the sericin-containing wastewater, but also the organic solvent and oil through the prepared materials. In summary, both absorbent materials have large adsorption properties and can be reused. It has a positive effect on the treatment of water pollution.

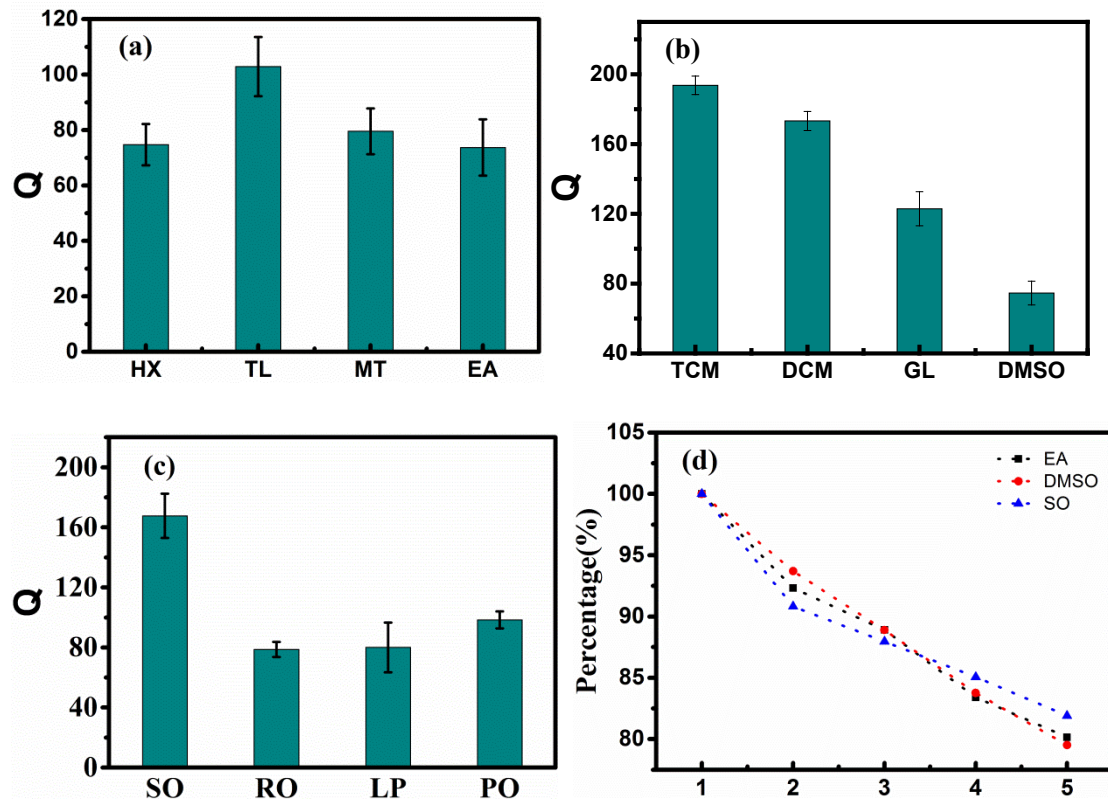


Fig.2. Adsorption and Recyclability study of SCB aerogel: (a) Adsorption of organic solvents with a density less than water, Hexane, Toluene, Methanol, Ethanol. (b) Adsorption of organic solvents with a density greater than water, Trichloromethane, Dichloromethane, Glycerol, Dimethyl sulfoxide. (c) Oil adsorption, Soybean oil, Rapeseed oil, Liquid paraffin, Pump oil. (d) Recyclability study of SCB aerogel, Ethanol, Soybean oil and Dimethyl sulfoxide.

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