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# A novel crosslinked β-cyclodextrin-based polymer for removing methylene blue from water with high efficiency

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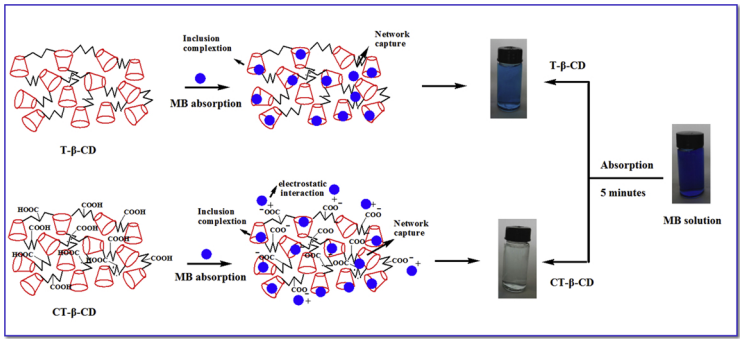
## GRAPHICAL ABSTRACT




## ARTICLE INFO

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## ABSTRACT

In this work, a novel crosslinked porous β-cyclodextrin-based polymer containing carboxylic acid groups (CT-β-CD) was synthesized successfully and characterized by SEM, FTIR, $^{13}C$ solid-state NMR, water-contact-angle measurement, and TGA. The resultant CT-β-CD with triple absorption effects including inclusion complextion, porous network capture, and electrostatic interaction was employed as an adsorbent for removing methylene blue dye from aqueous solution, which exhibited several advantages such as high absorption capacity ($q_{max}$ = 672 mg/g), rapid absorption rate, good recyclable ability, and selective adsorption for cationic dyes. The influences of initial MB concentration, absorption time, and pH value on the absorption behavior of CT-β-CD for MB were also investigated. In addition, it was found that the pseudo-second-order kinetic and the Langmuir model for adsorption isotherm could be used to describe the MB absorption behavior of CT-β-CD.

## 1. Introduction

The massive discharge of organic dye from industry has seriously polluted the water resource and caused great damage to human survival [1–5]. Several physical, chemical, and biological methods, such as membrane filtration, ozonation, coagulation, precipitation, adsorption, and fungal decolarization, are used for the removal of various dyes from wastewater [6–8]. In recent years, much attention has been paid to the design and synthesis of new generation adsorption reagents to separate various pollutants from water, which are anticipated to possess several advantages including high efficiency, cost effectiveness, low energy consumption, as well as good recyclable ability.

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As an inexpensive sustainably-produced cyclic oligosaccharide, β-cyclodextrin (β-CD) is one of the most promising environment-friendly materials for removing dyes or other pollutants from water by adsorption. It is well known that β-CD can encapsulate various contaminants to form well-defined host-guest inclusion complexes because its interior cavity provides a relatively hydrophobic environment into which an apolar pollutant can be trapped. According to this purpose, a number of adsorbents based on β-CD materials have been developed for the removal of different contaminants [9–28]. Alsbaiee et al. achieved a high-surface-area mesoporous β-cyclodextrin-based polymer (CDP) by crosslinking β-CD with rigid aromatic group, which could rapidly separate different organic micropollutants (2,4-dichlorophenol, 2-naphthol, 1-naphthyl amine, metolachlor, bisphenol A, bisphenol S, ethinyl oestradiol, propranolol hydrochloride) with adsorption capacities ranging from 15 to 200 times greater than those of activated carbon [16]. As reported by Gogoi et al., a $CeO_2$/β-CD hybrid was obtained from the utilization of a combination method based on precipitation and sol-gel processing for efficient absorption and degradation of organic dyes from aqueous solution at room temperature [28]. Badruddoza et al. fabricated a novel carboxymethyl-β-CD (CM-β-CD) containing $Fe_3O_4$ nanoparticle, which could be handled easily by using magnetic field for dye absorption [17]. Because the affinity of β-CD for basic (cationic) dyes is low, Crini et al. developed a crosslinked CDP using epichlorohydrin as crosslinking agent in the existence of carboxymethylcellulose (CMC). However, the absorption capacity of resultant CMC-β-CD for cationic methylene blue (MB) was only 57 mg/g [10]. Similarly, Ebadi et al. used silica nano hollow spheres (SNHS) to modify β-CD for the removal of MB from aqueous solution and the absorption capacity of resultant SNHS-β-CD was only about 60 mg/g [20]. Zhao et al. synthesized a crosslinked CDP with an absorption capacity of 105 mg/g using citric acid as crosslinking agent, $NaH_2PO_4$ as catalyst, and polyvinyl alcohol (PVA) as additive. They suggested that the acidic carboxyl groups and ester groups in their CDP were helpful in the adsorption to basic positively charged MB [14].

Up to now, it is still a challenge to overcome the poor removal performance of CDP compared to other conventional absorbents [16]. To fully exploit the potential of CDP as an absorbent especially for cationic dyes, a novel porous tetrafluoroterephthalonitrile (TFPN)-crosslinked β-CD derivative containing carboxylic acid groups (abbreviated as CT-β-CD) has been synthesized and used to remove cationic methylene blue (MB) dye from water in this work. The influences of different experimental parameters, such as initial MB concentration, absorption time, and the pH value of MB solution, on the absorption behavior of CT-β-CD were systematically investigated. The adsorption isotherm and adsorption kinetic of CT-β-CD for MB were examined to identify the possible absorptive mechanism. In addition, the recycled utilization and the selective absorption ability of CT-β-CD were also explored.

## 2. Experimental

### 2.1. Materials

β-cyclodextrin (β-CD, 98%), tetrafluoroterephthalonitrile (TFPN, 99%), and potassium carbonate ($K_2CO_3$, 99%) were purchased from Macklin (Shanghai, China). MB ($C_{16}H_{18}ClN_3S{\cdot}3H_2O$) was obtained from Aladdin (Shanghai, China). N,*N*-dimethylformamide (DMF, AR), dichloromethane ($CH_2Cl_2$, AR), tetrahydrofuran (THF, AR), ethanol ($CH_3CH_2OH$, AR), hydrochloric acid (HCl, AR), methanol ($CH_3OH$, AR), and sodium hydroxide (NaOH, AR) were purchased from Xi-Long chemical company in China and used without purification.

### 2.2. Synthesis and characterization of sorbents

As presented in Fig. 1, the TFPN-crosslinked β-CD (abbreviated as T-β-CD) used in this work was synthesized as follow. 27 ml dried THF and 5 ml dried DMF were added to the mixture of 0.5 g TFPN, 0.962 g β-CD, and 1.23 g $K_2CO_3$ in nitrogen using a syringe. The crosslinked reaction was carried out for 48 h under stirring. Finally, the reaction product was filtered, washed with HCl (1 M), distilled water, THF, $CH_2Cl_2$ in sequence, and dried to obtain the T-β-CD. The derivative of T-β-CD (abbreviated as CT-β-CD) was obtained from the following procedure: dried T-β-CD powder and 20% NaOH solution ($V_{water}$:$V_{ethanol}$ = 1:1) were added into a single neck round-bottom flask equipped with a condenser, the resultant mixture was stirred at 120 °C under reflux for 24 h and then filtered. The filtride was added into 40 mL aqueous solution with a pH value of 4–5 adjusted by dropwises of HCl solution and then heated at 120 °C under reflux for 2 h. Finally, the resultant mixture was filtered, washed by water and methanol for several times, and then dried at 70 °C in a vacuum oven for 24 h.

### 2.3. Characterization

A scanning electron microscope (SEM, Zeiss Merlin) was used to observe the microstructure of CT-β-CD. Fourier-transform infrared (FTIR) spectra were recorded on a Bruker Vertex70 equipment in the range of 400 $cm^{-1}$–4000 $cm^{-1}$ with the resolution of 4 $cm^{-1}$ and each sample was scanned for 20 times. UV–vis adsorption spectra were recorded on a Shimadzu spectrophotometer (UV2550). The pore characteristic of CT-β-CD was investigated by the mercury intrusion porosimetry (MIP, AtuoPore IV 9500 V1.09). The zeta potential of CT-β-CD was studied by the Malvern equipment (ZS90). The $^{13}$CNMR experiments were performed on Bruker AVANCE III 600 spectrometer at a resonance frequency of 150.9 MHz. $^{13}$C NMR spectra were recorded using a 4 mm MAS probe and a spinning rate of 10 kHz. A contact time of 2 ms and a recycle delay of 5 s were used for the $^{13}$CNMR measurement. The contact angle was measured with the static contact angle measuring instrument (model JC2001C, Shanghai Zhongchen Digital Technology Equipment Co., Ltd., China). The Diamond (Perkin Elmer, USA) thermal gravimetric analyzer (TGA) was employed to analyze thermal degradation of samples, which were heated from 30 °C to 800 °C under argon flow at heating rate of 10 °C/min.

### 2.4. MB adsorption experiments

In order to explore the adsorption properties of CT-β-CD for MB influenced by different experimental factor, batch MB adsorption experiments of CT-β-CD and T-β-CD were conducted using 100 mL reagent bottles with definite volume of MB solution at different initial concentration under a shaker speed of 170 rounds/min. The pH value of MB solution in the range of 3–11 was adjusted by dropwisely adding 0.1 M NaOH or 0.1 M HCl solutions. Adsorption kinetic experiments were performed by mixing 10 mg of adsorbent into 25 mL of MB solution with an initial concentration of 38 mg/L at 30 °C. After adsorption, the resultant suspension was filtered using a 0.2 μm PTFE membrane filter and the residual MB was determined by a UV–vis spectrophotometer (U-2550) at the maximum wavelength of 664 nm [16]. The adsorption capacity $q_t$ (mg/g) and removal rate (%) were calculated according to the following equations:

$$q_t = \frac{(C_0 - C_t)V}{M} \quad (1)$$

$$\text{Removal}(\%) = \frac{(C_0 - C_t)}{C_0} \quad (2)$$

where $C_0$ (mg/L) and $C_t$ (mg/L) were the MB concentration at initial time and t minute during absorption process, correspondingly. V (mL) was the volume of the MB solution and M (mg) was the mass of adsorbents.