

# REMOVAL OF ALIZARIN RED BY SUPERMACROPOROUS CROSS-LINKED CHITOSAN MONOLITH SORBENTS

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## Abstract

Here, we report the fabrication of supermacroporous monolith sorbents for acidic dye removal via chitosan cross-linking with ethylene glycol diglycidyl ether (EGDGE) in acidic medium at sub-zero temperature. The developed porous structure with the thickness of polymer walls in the range of a few microns and a high content of primary amino groups determined the high sorption capacity of the sorbents toward Alizarin Red in a broad pH range (2–8). Due to the cross-linking via hydroxyl groups of the chitosan, the static sorption capacity of the fabricated materials was higher than that of chitosan flakes, even for sorbents cross-linked at EGDGE:NH<sub>2</sub>-chitosan with molar ratio 2:1. The monolith sorbents were mechanically stable and supported flow rates up to 300 bed volumes per hour. The breakthrough curve of Alizarin Red sorption showed that the effective dynamic sorption capacity was 283 mg/g, and 100% of the dye could be removed from the solutions with concentration of 100 mg/L. The monoliths can be regenerated with 0.3s M NaOH solution and used in several consecutive cycles of sorption/regeneration without loss of efficacy.

**Keywords:** chitosan, cryogel, dye, sorption

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## 1. Introduction

One of the most important fields of chitosan application is wastewater and drinking water treatment. Its high binding capacity to the different types of pollutants, including heavy metal ions, dyes, and dissolved organic matter determine the multi-functionality of the chitosan-based materials and the high interest for fabrication of different forms of sorbents, including beads, microspheres, membranes, and fibres. As a rule, shaping of chitosan sorbents proceeds via precipitation of chitosan from aqueous acidic solutions using organic solvents or alkali, which is laborious and not an environmentally sound process. The materials obtained by this method are soluble in acidic media and can have limiting applications as catalyst supports [1] and sorbents [2]. Usually, insolubility of chitosan-based materials in a wide pH range is provided by covalent cross-linking using different types of cross-linking reagents, among those most popular are glutaraldehyde [3], epichlorohydrin [4], and diglycidyl ethers of glycols [5]. However, for a long time it was believed that only dialdehydes showed sufficiently high reactivity in acidic media and can be used for fabrication of porous cross-linked materials via cryogelation or in the presence of inorganic or organic templates. The chitosan sorbents crosslinked with ethylene glycol diglycidyl ether in acidic media were not stable and dissolved during sorption at pH 2.0–3.0 [6]. Recently, we have shown that using hydrochloric acid solutions as a reaction media allows for efficient chitosan cross-linking with diglycidyl ethers of glycols, even at subzero temperature, yielding supermacroporous monolith materials [7]. Unlike dialdehydes, the cross-linking reaction in this case involves mainly hydroxyl group of chitosan; thus, chitosan amino groups remain free for interaction with metal ions or anionic pollutants.

Here, we investigate sorption properties of supermacroporous monolith chitosan materials cross-linked with ethylene glycol diglycidyl ether (EGDGE) toward the anionic dye Alizarin Red. The presence of textile effluents is a challenging issue in many countries. They are difficult to treat due to the high resistivity of the dyes to aerobic digestion and oxidizing agents [6]. Moreover, even at very low dye concentrations, the wastewaters are coloured and cannot be discharged into the environment. This makes sorption the first choice method for treatment of this type of waste. Chitosan and other polysaccharides were extensively studied as biosorbents for dye removal [6,8,9]; however, to the best of our knowledge, supermacroporous chitosan-based monoliths applicable under dynamic conditions have not been yet reported.

## 2. Materials and Methods

### 2.1. Materials

Chitosan was purchased from BioLog Heppe GmbH (Germany), the degree of acetylation (DA) was determined by  $^1\text{H}$  NMR spectroscopy to be 0.9; the viscosity-average molecular weight was 30 kDa. Ethylene glycol diglycidyl ether (EGDGE) and Alizarin Red S were purchased from J&K Scientific (China) and Sigma–Aldrich, respectively.

### 2.2. Fabrication and Characterization of Supermacroporous Chitosan Sorbents

Supermacroporous cross-linked chitosans were fabricated by cryogelation techniques as described in [7]. Briefly, cross-linking agent EGDGE was added dropwise under constant stirring into 3% chitosan solution in 0.47% hydrochloric acid at the molar ratios to amino group, 2:1, 1:1, 1:2, and 1:4. pH of the chitosan solution was preadjusted to 5 with 0.1M HCl. To obtain monolith EGDGE/chitosan sorbents, the 1 ml of solutions was immediately placed into the plastic syringe with an internal diameter of 4.8 mm and kept in a freezer at  $-10^\circ\text{C}$  for 12 days. The unreacted materials were thoroughly washed with

0.1 M solution of hydrochloric acid and then with water. The materials are further referred to as EGDGE/CH\_2:1- EGDGE/CH\_1:4, where ratio indicates molar ratio of EGDGE to chitosan amino groups.

Morphology of the fully hydrated sorbents was determined using environmental scanning electron microscope (ESEM) equipped with the Peltier cooling stage (Quanta 200 FEG, Thermofisher, USA). The maximal flow rate was determined by passing distilled water through the syringes (diameter of 4.8 mm, bed height of 6 cm) filled with swollen cryogels using a peristaltic pump (Ismatec, Germany), the flow rate was recalculated from ml/h to bed volumes per hour (b.v./h) to account for geometrical parameters of the column.

X-ray diffraction (XRD) analysis of the chitosan samples has been performed using DRON-3 multipurpose diffractometer (Russia) equipped with CuK $\alpha$ - irradiation source, Ni-filter, medium wavelength ( $\lambda$ ) 1.5418 Å.

### 2.3. Alizarin Red S Adsorption on Chitosan Sorbents

The Alizarin Red S dye adsorption isotherm on supermacroporous chitosan sorbent was obtained by the batch method as follows: 5 mg of the dry EGDGE/CH\_1:4 sorbent was shaken for 24 h with 5 mL of Alizarin Red S solution in water (pH 5.6 without pH adjustment) containing from 25 to 1000 mg/L of the dye. pH dependence of the Alizarin Red adsorption was investigated on EGDGE/CH\_1:4 from solutions with the dye concentration of 500 mg/L, maximal sorption capacities of EGDGE/CH were determined from solutions with dye concentration of 1000 mg/L, in all cases solid: liquid ratio was 1:1000, pH 5.6. The equilibrium concentration of the dye was determined spectrophotometrically using UV-1650PC spectrophotometer (Shimadzu, Japan) at the wavelength 520 nm, pH of the standard solutions for calibration and of all solutions after the sorption was adjusted to 8.8 with 0.1 M NaOH solution. The adsorbed amounts were calculated using the difference in initial and equilibrium concentrations of the dye, the sorption isotherm was fitted using the Langmuir equation.

Dynamics of Alizarin Red S sorption on monolith EGDGE/CH\_1:4 sorbent was investigated as follows: dye solution with a concentration of 20 mg/L, pH 5.6 was fed through a syringe filled with 1 ml of supermacroporous sorbent (inner diameter, 4.8 mm; bed length, 6 cm) at a rate of 20 b.v. (bed volumes)/h. The samples were collected every 5 mL, the dye concentration in eluates was determined spectrophotometrically as described above. The effective dynamic adsorption capacity was calculated assuming the breakthrough at 10% of the initial dye concentration.

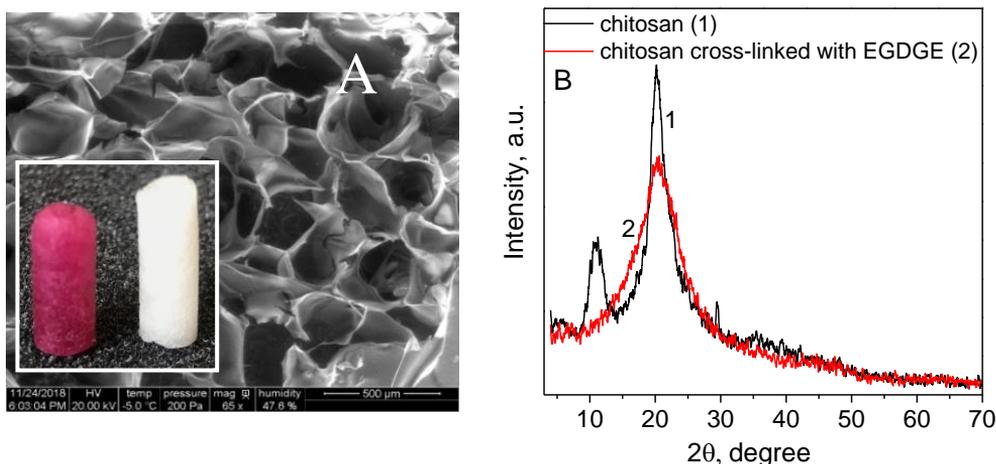
For evaluation of efficacy of Alizarin Red desorption the dye was preadsorbed on EGDGE/CH\_1:2 sorbent from solution with a concentration of 20 mg/L, pH 5.6, solid:liquid ratio 1:1000. After 24 h sorbent (5 mg) was separated from the solution, and 1 ml of eluent (0.01M NaOH, 0.1M NaOH, 0.3M NaOH) was added. The dye concentration in eluate was determined spectrophotometrically after pH adjustment to 8.8 with 1–5 M HCl solutions. Efficacy of sorbent regeneration in consecutive cycles was determined using the same procedure and 0.3M NaOH solution as eluate. The regeneration of the monolith in column is described in section 3.

## 3. Results and Discussion

The cross-linking and granulation significantly affect mechanical and hydrodynamic properties of the chitosan. While ionic cross-linking does not assure stability in acidic media, covalent crosslinking usually yields harder but also more fragile materials [7]. To assure applicability under dynamic conditions of sorption and to avoid high backpressure chitosan beads are fabricated with swelling degree up to 100–300% and relatively large bead size [1], so intraparticle diffusion is often a limiting stage of the sorption. Negative

side of high cross-linking degree required for fabrication of chitosan-based materials for column application at  $\text{pH} < 5$  is reduction of sorption capacity due to the involvement of amino groups in cross-linking process. For example, chitosan beads cross-linked with EGDGE in alkaline media had 1.5-fold lower sorption capacity to acidic dyes compared to virgin chitosan flakes [10].

The advantage of supermacroporous chitosan-based sorbents obtained via cryogelation is interconnected porous structure with the thickness of polymer walls in the range of few microns (Fig. 1A) that significantly facilitate accessibility of the binding sites for solutes. At the same time, despite high swelling degrees, sorbents have good mechanical and hydrodynamic properties supporting flow rate up to 300 bed volumes per hour (Table 1). Fig. 1B shows XRD patterns of chitosan flakes and supermacroporous chitosan cross-linked with EGDGE, both are in free base form. Only for the virgin chitosan two wide reflections with maxima at  $10.9^\circ$  and  $20.1^\circ$ , corresponding to (020) and (110) planes, respectively, were observed indicating relatively low degree of crystallinity typical for chitosan with high deacetylation degree [11]. Amorphization of chitosan structure after cross-linking with EGDGE is evidenced from the absence of the reflection at  $\sim 10.9^\circ$  in XRD pattern. The loss of chitosan crystallinity can be also beneficial for its sorption performance.



**Figure 1.** A) SEM images of supermacroporous chitosan cross-linked with EGDGE at a EGDGE to chitosan molar ratio of 1:2 [insert, photo of EGDGE/CH\_1:4 sorbent before (right) and after (left) Alizarin Red sorption]. B) X-ray diffraction (XRD) pattern of original chitosan and chitosan cross-linked with EGDGE (both in free base form).

Sorption properties of the supermacroporous chitosans cross-linked with EGDGE at different molar ratios have been preliminary investigated in batch tests. Fig. 2A shows that Alizarin Red was removed by EGDGE/CH\_1:4 with efficiency 95–97% from solutions with dye concentration 500 mg/L in pH range 2–8, confirming applicability of the cross-linked material for the treatment of acidic textile effluents. The isotherm of Alizarin Red sorption of supermacroporous chitosan sorbent is of high affinity type (Fig. 2B), the maximum sorption capacity is 803 mg/g. 100% of dye removal was observed for initial Alizarin Red concentrations up to 100 mg/L. Such characteristics are significantly better in comparison with other materials earlier investigated for Alizarin Red uptake. For example, maximal sorption capacities toward this dye were 40.12 mg/g for chitosan coating on the surface of magnetite [12], 127 mg/g for chitosan beads impregnated with

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ionic liquid Aliquat-336 [13], 88.50 mg/g and 34.13 mg/g for graphene oxide and bare graphite powder, respectively [14].

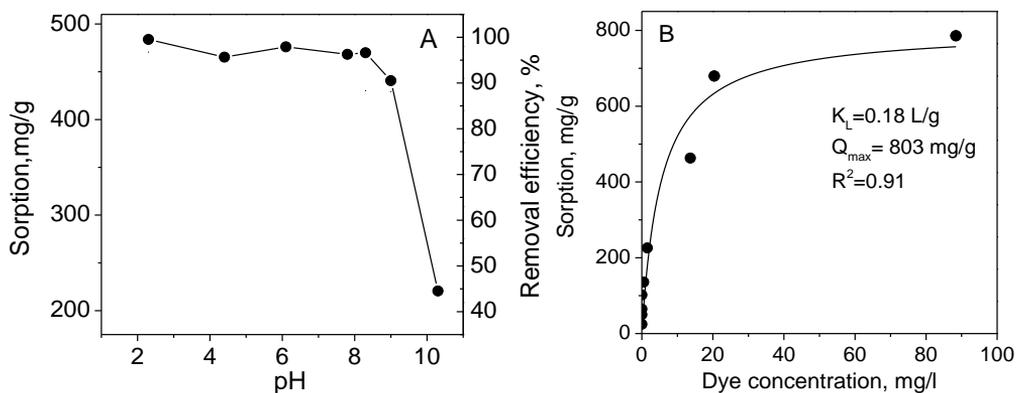
**Table 1.** Swelling, mechanical, and hydrodynamic characteristics of supermacroporous chitosans cross-linked with EGDGE.

EGDGE to chitosan molar ratio	Young's modulus, kPa [7]	Swelling in water (%) [7]	Maximal flow rate (b.v./h)
2:1	75±14	2061	>300
1:1	72±10	2407	>300
1:2	63±11	2368	>300
1:4	35±8	3292	250
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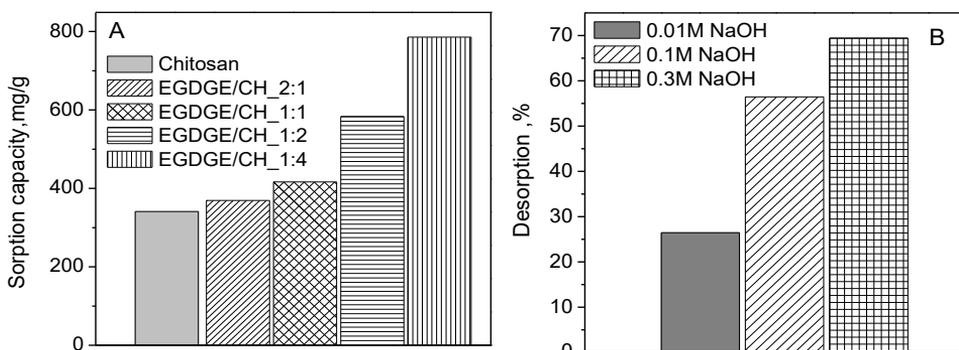
As mentioned above, chitosan cross-linking with EGDGE in acidic medium at sub-zero temperature involves mainly hydroxyl groups [7]; therefore, high sorption capacity observed for the fabricated supermacroporous materials can account for the high content of free amino groups, loss of crystallinity, and better accessibility of the sorption sites due to the interconnected porous structure. Fig. 3A shows that the fabricated cross-linked chitosans have even higher sorption capacity than that of virgin chitosan flakes, which decreases with an increase in the cross-linking degree.

The possibility to regenerate the sorbent and use it in several adsorption/desorption cycles is important for applications, especially assuming the cost of chitosan-based materials. It was previously reported that alkaline solutions provide the highest efficacy for elution of acidic dyes from chitosan and chitosan-containing composite sorbents [15]. Fig. 3B shows that efficacy of Alizarin Red desorption increases symbatically with NaOH concentration in the range 0.01–0.3mol/L and reaches 70%. Applicability of the material in several consecutive cycles is demonstrated in Fig. 4A. One can see that Alizarin Red removal efficacy was 100% in three cycles at the desorption efficacy 70–80%.

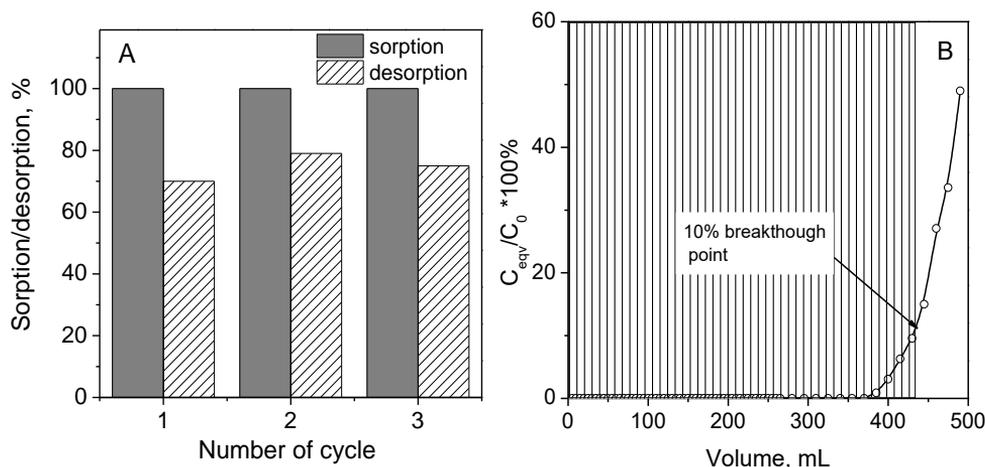


**Figure 2.** Dependence of Alizarin Red sorption on pH (dye concentration, 500 mg/L) (A) and isotherm of Alizarin Red sorption (pH=5.6) (B) on EGDGE/CH\_1:4 (solid to liquid ratio 1:1000; T=25°C).

Breakthrough curve for Alizarin Red adsorption on monolith EGDGE/CH\_1:4 sorbent shows that the fabricated material provide 100% of dye removal at flow rate 20 bed volumes per hour, however, effective dynamic sorption capacity at 10% of breakthrough dye concentration was 286 mg/g, so complete or very high efficacy of the dye removal was possible at this flow rate only when less than 35% of the sorption sites were occupied. However, even this value of dynamic sorption capacity is higher than full static sorption capacities for earlier reported materials [12–14]. After passing through the column 490 bed volumes of the dye solution, the monolith sorbent was regenerated using 8 bed volumes of 0.3M NaOH solution. The dye removal efficacy in the second cycle of sorption under dynamic conditions was 100% for the first 200 bed volumes passed through the column.



**Figure 3.** A) Maximum sorption capacity of sorbents cross-linked at various EGDGE to chitosan molar ratios (pH=5.6). B) Efficacy of Alizarin Red desorption from EGDGE/CH\_1:2 sorbent using alkaline eluents.



**Figure 4.** A) Efficacy of sorption/desorption of Alizarin Red on EGDGE/CH\_1:4 (dye concentration, 20 mg/L; solid to liquid ratio, 1:1000; pH, 5.6; eluent, 0.3 M NaOH). B) Breakthrough curve of Alizarin Red sorption on EGDGE/CH\_1:4 monolith (dye concentration, 20 mg/L; flow rate, 20 bed volumes/h; pH, 5.6).

#### 4. Conclusions

Here, we report the fabrication, characterization, and investigation of sorption properties of a new supermacroporous monolith cross-linked chitosan material for removal of anionic dyes. We have demonstrated that a high content of free amino groups, loss of crystallinity due to cross-linking, and better accessibility of the sorption sites due to the interconnected porous structure result in a sorption capacity toward Alizarin Red dye that is higher than that of virgin chitosan flakes. The fabricated sorbent provides efficacy of dye removal of 100% in the pH range of 2–8 at dye concentration up to 100 mg/L, and it had an effective dynamic sorption capacity of 283 mg/g. The sorbent can be regenerated with 0.3 M NaOH solutions and used in several sorption/desorption cycles without loss of efficacy.

#### 5. Acknowledgements

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