



Original Research Article

Effective Removal of Methyl Green from Aqueous Solution Using Epichlorohydrin Cross-Linked Chitosan

Zahra Bashandeh, Aliakbar Dehno Khalaji*

Department of Chemistry, Faculty of Science, Golestan University, Gorgan, Iran

ARTICLE INFO

Article history

Submitted: 09 May 2021

Revised: 27 June 2021

Accepted: 08 July 2021

Available online: 11 July 2021

Manuscript ID: [AJCA-2105-1259](https://doi.org/10.22034/AJCA.2021.285520.1259)DOI: [10.22034/AJCA.2021.285520.1259](https://doi.org/10.22034/AJCA.2021.285520.1259)

KEYWORDS

Epichlorohydrin

Cross-linked

Chitosan

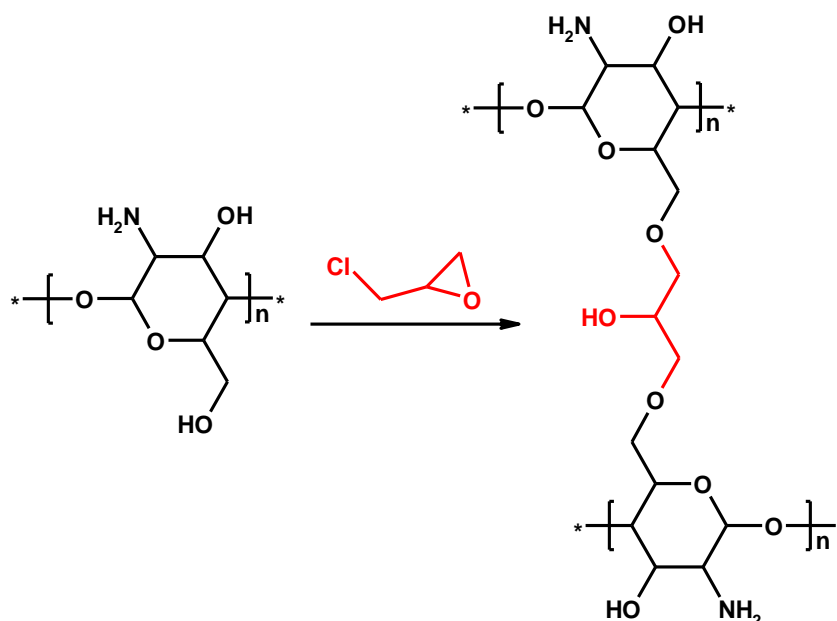
Adsorbent

Methyl green

ABSTRACT

Epichlorohydrin cross-linked chitosan (EP-Cs) was prepared was characterized using Fourier transform infrared spectroscopy (FT-IR), X-ray powder diffraction (XRD), thermal gravimetry (TG-DTA) and differential calorimetric analysis (DSC), and used as adsorbent for methyl green (MG) removal. Epy-Chit was soaked in methyl green solution with concentration of 40 mg/L using a batch adsorption system, to measure the adsorption capacity of the EP-Cs and the percentage of MG removed from the aqueous solution. The optimum MG adsorption on EP-Cs occurred at pH 7.8, agitation time of 60 minute and adsorbent dosage of 0.02 g were observed. Adsorption results show that the EP-Cs exhibited the excellent performance for the MG removal from aqueous solution. This study suggests that EP-Cs could be explored as an adsorbent for removing other organic pollutants.

GRAPHICAL ABSTRACT



* Corresponding author: Dehno Khalaji, Aliakbar

✉ E-mail: alidkhalaji@yahoo.com

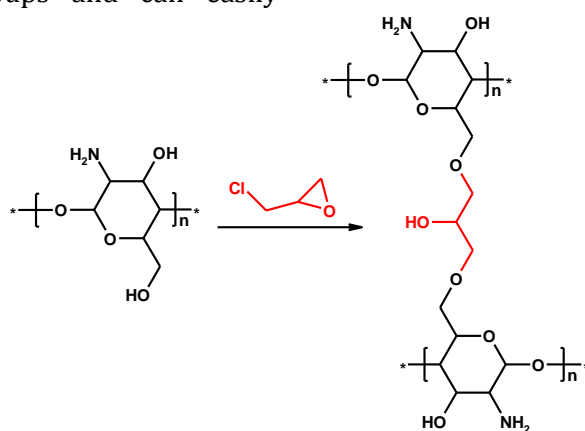
© 2021 by SPC (Sami Publishing Company)

Introduction

Currently, different organic dyes were used in various industries such as leather, food, paper, plastics and others industries [1]. About 10 to 20 percent of these dyes are present in the effluent of these industries and may enter the environment [2]. Due to the degradation resistance, high stability, string colority and high toxicity of the azo-dyes against light and heat, so they can be present in nature for a long time. In this case, they cause a lot of damage to the environment [3] and so called as eco-toxic substances [4]. Therefore, the removal of these dyes from the effluent of these industries is one of the important goals in reducing environmental pollution. So far, many methods have been used to remove these dyes from the environment (water and soil) [5-8]. Of all the available methods, the adsorption method is used as an efficient, effective, low-cost and convenient method to remove various dyes such as methyl green [9], congo red [10], bromophenol blue [11], crystal violet [12], and methyl green [13-15]. Then, it is important to develop new adsorbents for removal of various dyes with highly adsorption capacity and very fast separation rates. Chitosan, as a natural macromolecule, and its derivative are of the best adsorbents to remove of the various dyes [16-20], because they have a large number of free amino and hydroxyl groups and can easily

coordinate with various metal ions [21] or intermolecular interaction (O-H...N, O-H...π, N-H...N) with various dyes [9]. Obeid et al. [19] synthesized new chitosan/maghemite composite and used it for the adsorption of methyl green. Tsai *et al.* [18] prepared crosslink chitosan microspheres via emulsion polymerization using glutaraldehyde as crosslinking agent to adsorption of methyl green from aqueous solution. Ke *et al.* [9] successfully modified chitosan with quaternary ammonium salt and then used it as an adsorbent for the removal of methyl green [9]. Yuvaraja *et al.* [16] reported aminated chitosan Schiff base for the methyl green removal. Methyl green (as a cationic dye) used as change solution color in biology and medicine [22] and a histochemical reagent [23]. The major application of MG is for dyeing in the textile industry [24] and also used as indicator dyes due to their pH sensitivity [25]. Recently, various adsorbents have been used for removal of methyl green from aqueous solution [13-15].

Continuing the previous work [26], in the present study, epichlorohydrine cross-linked chitosan (abbreviated as EP-Cs) was prepared by reaction of chitosan with epichlorohydrine as crosslinked agent and characterized by FT-IR, XRD, TGA and DSC analysis. In addition, adsorption properties for methyl green removal of EP-Cs from aqueous solution under varied experimental conditions were investigated.



Scheme 1. Preparation of Epichlorohydrin cross-linked chitosan (EP-Cs)

Experimental

General

Chitosan, glacial acetic acid, ethanol and epichlorohydrine were purchased from Merck and Sigma-Aldrich Companies. They were used without further purification. FT-IR spectra were recorded with Perkin-Elmer FT-IR spectrophotometer using KBr disks from 4000–400 cm^{-1} . TGA curve was recorded by the Perkin-Elmer TGA analyzer in air atmosphere at a flow rate of 20 $^{\circ}\text{C}/\text{min}$ (25–700 $^{\circ}\text{C}$). DSC analysis was recorded using DSC analyzer Model 60A, Shimadzu. XRD patterns were determined by Bruker AXS-D8 X-ray diffractometer ($2\theta = 10\text{--}80^{\circ}$). SEM images were recorded on the TESCAN Vega Model scanning electron microscope. UV-Vis spectra were carried out with UV-Visible spectrophotometer (Perkin-Elmer).

Preparation of EP-Cs

The steps for preparing the EP-Cs are as follows: Chitosan (1 g), 20 mL ethanol and 2 mL glacial acetic acid were added into a three-necked flask, subsequently stirring at 50 $^{\circ}\text{C}$ for 1 h on a hiter-stirre. Then, 1 mL of epichlorohydrine was added dropwise, and the mixture continuously reacted at 70 $^{\circ}\text{C}$ for about 6 h. The pale cream precipitates were filtered off, washed and dried.

Adsorption Experiments

The EP-Cs (0.005, 0.01 and 0.02 g) and 20 mL of methyl green solution with initial concentration of $C_0 = 40 \text{ mg/L}$ were mixed in a 250 mL flask, following shaking on a room temperature at $\text{pH} \approx 8$ and. The EP-Cs was removed and the concentration of MG remaining in solution (C_e) was measured by UV-Vis spectroscopy at 632 nm. Also, the effect of contact time was studied

between 0 to 60 min. Percentage of adsorption (R%) was calculated using equation (Eq. 1) below:

$$R\% = \frac{(C_0 - C_e) \times 100}{C_0} \quad (1)$$

Results and Discussion

Characterization of EP-Cs

The FT-IR spectra of chitosan and EP-Cs are shown in Figure 1. The broad band at around 3435 cm^{-1} was assigned to the overlap between -OH and $-\text{NH}_2$ stretching vibrations [9,19], while the several bands were appeared at wavenumbers between 3500–3100 cm^{-1} , confirming the removed of some of hydroxyl groups during the modification [9,19]. The two peaks at about 2920 and 2875 cm^{-1} were assigned to the C-H vibration of aliphatic hydrogen [9,19]. The two peaks at about 1650 and 1600 cm^{-1} in chitosan are assigned to the C-O stretching along the N-H deformation [18]. While in the FT-IR spectrum of EP-Cs there are two peaks at 1650 and 1558 cm^{-1} . The peak at 1558 cm^{-1} was due to $-\text{NH}$ deformation [26], and 1411 cm^{-1} showed the C-N amine group [26]. The peak at about 1089 cm^{-1} is due to C-O-C in the pyranose ring of chitosan [14].

The X-ray diffraction patterns of chitosan and EP-Cs are shown in Figure 2. The shoulder peak and a small broad peak at $2\theta = 14.50^{\circ}$ and 23.65° showed that the chitosan polymer was amorphous [14,16]. In the EP-Cs, a new peak at 12.02° appeared and also the two broad peaks at about of 18.32° and 21.22° appeared. These changes confirmed the preparation of EP-Cs.

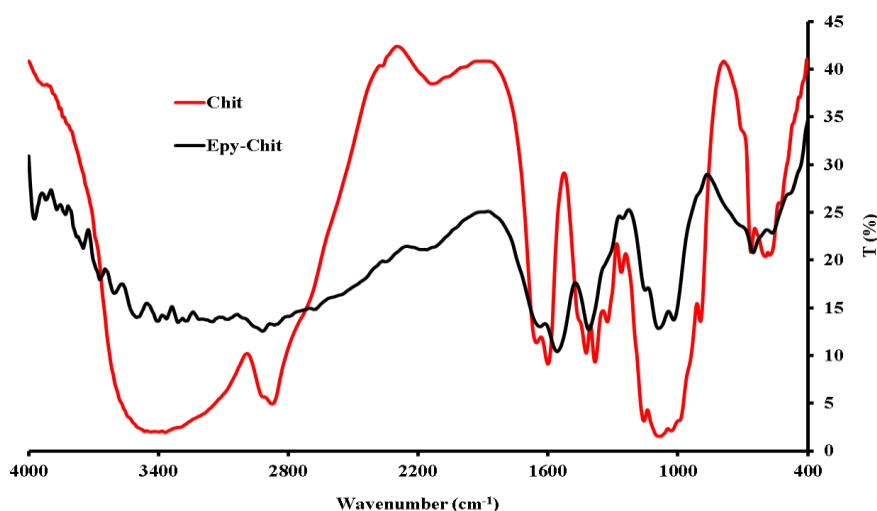


Figure 1. FT-IR spectra of the chitosan and EP-Cs

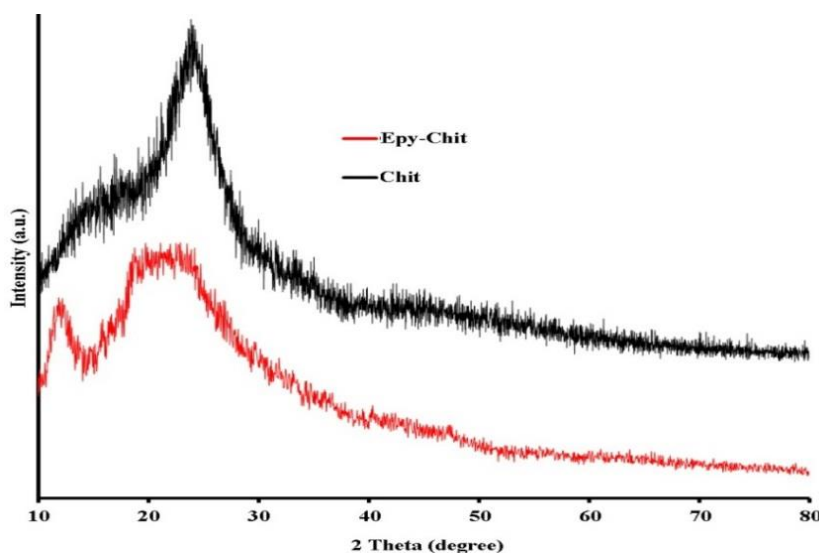


Figure 2. XRD patterns of the chitosan and EP-Cs

Thermal gravimetry (TG) and differential thermal analysis (DTA) of EP-Cs are shown in Figure 3. TGA of EP-Cs shows three stages of mass loss. It is stable until 75 °C, and after that about 20% of its weight has been losses in the temperature range of 75 to 175 °C that may be attributed to losing physically adsorbed moisture or ethanol solvent [27,28]. The second stage of weight losses (42%) begins from 175-375 °C assigned to the thermal decomposition of pyranose ring [27,28]. At the third stage the loss

of weight was 16% at 825 °C and a residual mass of 22% was observed [29].

Differential scanning calorimetry (DSC) curve of EP-Cs (Figure 4) shows an endothermic peak at 108 °C assigned to the evaporation of moisture and ethanol molecules adsorbed on the compound [30], while an exothermic peak appeared at 297 °C, corresponding to the decomposition of the pyranose chain [30]. Figure 4 showed that the EP-Cs is a slightly less stable than chitosan; chitosan shows the exothermic peak at 306 °C [30].

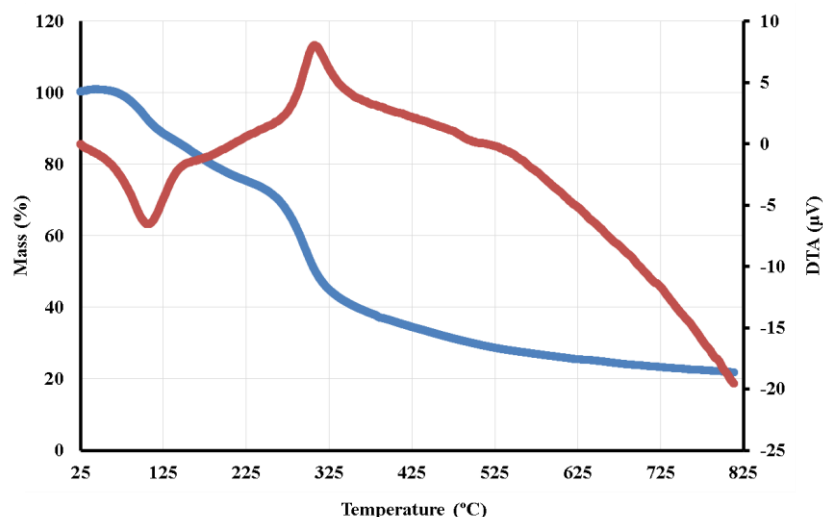


Figure 3. TGA-DTA curves of EP-Cs

Adsorption Properties

One of the most important parameters on the removal of dye from aqueous solution is the pH of solution [9,16]. Rida et al. reported the MG removal percentage is about 77% at pH = 8 using activated carbon [31]. Then, we examined the removal of methyl green by EP-Cs at pH = 8 and considered the effect of adsorbent dosage and contact time of the removal percentage of methyl green.

The effects of EP-Cs mass quantity in the range of 0.005–0.02 g on the absorbance of MG solution

and the removal of the MG are shown in Figures 5 and 6, respectively. Figure 5 shows the absorbance of solution decreased by increasing the adsorbent dosage from 1.249 to 1.005, 0.09 and 0.057, respectively, due to the increase in the adsorbent surface areas and hence increase the active functional sites on the adsorbent [32]. Figure 6 shows the study of adsorption of MG at the presence of various adsorbent dosages. After 60 min of contact time, percentage adsorption of MG onto EP-Cs was 19.53, 92.79 and 92.7% for 0.005, 0.01, and 0.02 g of EP-Cs.

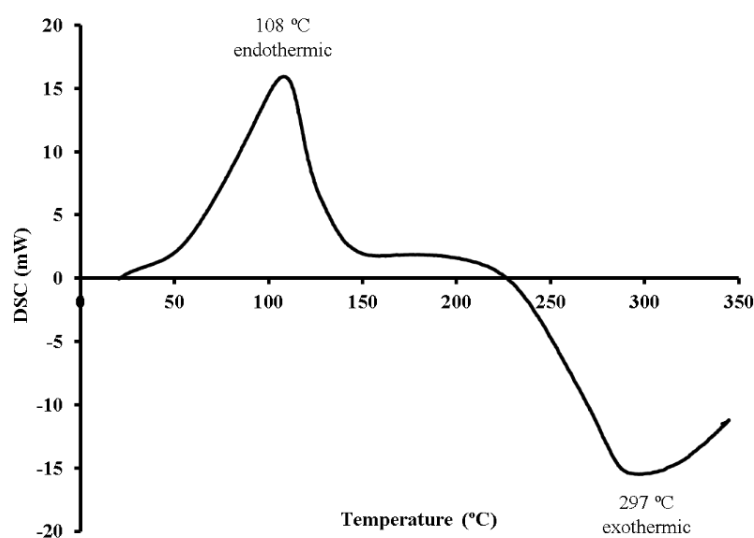


Figure 4. DSC curve of EP-Cs

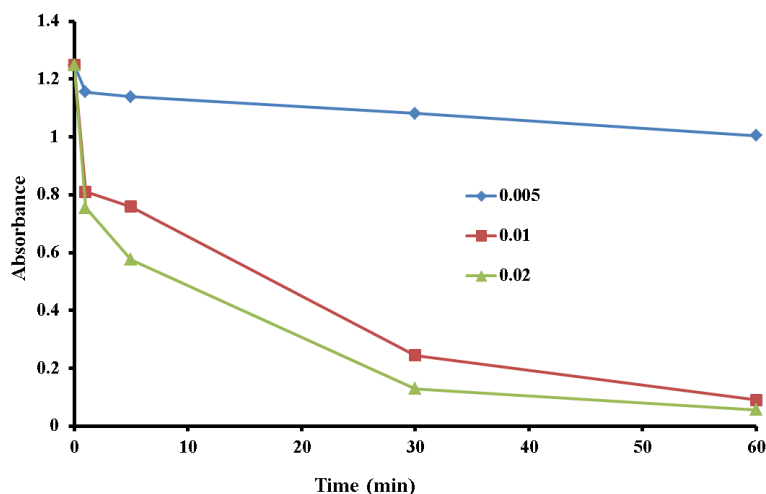


Figure 5. Effect of adsorbent dosage on the absorbance of MG solution at various contact times

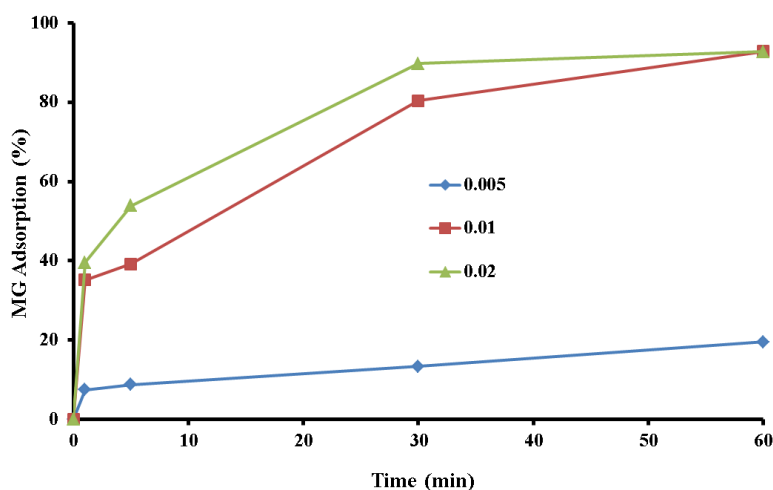


Figure 6. Effect of adsorbent dosage on the MG removal at various contact time

Conclusion

The epichlorohydrin cross-linked chitosan (EP-Cs) adsorbent was successfully prepared and characterized by FT-IR, XRD, TG/DTA and DSC analysis. The removal of MG dye was investigated and the effect of adsorbent dosage and contact time were studied. Results showed that the adsorption percentage of EP-Cs was highly dependent on the adsorbent dosage and contact time. The adsorption rate increased with increasing the adsorbent dosage and also contacts time. Then the EP-Cs can act as a

potential sorbent to remove of various dyes from aqueous solution.

Fund

This work was supported by the Golestan University.

Acknowledgements

Thanks to Golestan University for its scientific help.

Disclosure statement

No potential conflict of interest was reported by the authors.

ORCID

A. D. Khalaji : 0000-0002-1787-2951

References

- [1] B.E. Reed, M.R. Matsumoto, J.N. Jensen, R. Viadero, W. Lin, *Water Environ. Res.*, **1998**, *70*, 449–473. [[CrossRef](#)], [[Publisher](#)]
- [2] C. Smaranda, M. Gravilescu, D. Bulgrin, *Int. J. Environ. Res.*, **2011**, *5*, 177–188. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [3] S. Chen, J. Zhang, C. Zhang, Q. Yue, Y. Li, C. Li, *Desalination*, **2010**, *252*, 149–156. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [4] S. Yavari, N.M. Mahmodi, P. Teymouri, B. Shahmoradi, A. Maleki, *J. Taiwan Ins. Chem. Eng.*, **2016**, *59*, 320–329. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [5] H.D. Kiriarachchi, K.M. Abouzeid, L. Bo, M.S. El-Shall, *ACS Omega*, **2019**, *4*, 14013–14020. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [6] C. Song, H. Li, Y. Yu, *RSC Adv.*, **2019**, *9*, 9421–9434. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [7] F. Gu, J. Geng, M. Li, J. Chang, Y. Cui, *ACS Omega*, **2019**, *4*, 21421–21430. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [8] C. Shen, Y. Pan, D. Wu, Y. Liu, C. Ma, F. Li, H. Ma, Y.A. Zhang, *Chem. Eng. J.*, **2019**, *374*, 904–913. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [9] P. Ke, D. Zeng, K. Xu, J. Cui, X. Li, G. Wang, *ACS Omega*, **2020**, *5*, 24700–24707. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [10] L. Ai, Y. Zeng, *Chem. Eng. J.*, **2013**, 215–216, 269–278. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [11] H.A. Al-Aoh, *Desalin. Water Treat.*, **2018**, *110*, 229–238. [[CrossRef](#)], [[Google Scholar](#)]
- [12] N. Alizadeh, M. Mahjoub, *J. Nanoanalysis*, **2017**, *4*, 8–19. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [13] M. Bahgat, A.A. Farghali, W. El Roubay, M. Khedr, M.Y. Mohassab-Ahmad, *Appl. Nanosci.*, **2013**, *3*, 251–261. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [14] W. Yin, S. Hao, H. Cao, *RSC Adv.*, **2017**, *7*, 4062–4069. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [15] A. Maghni, M. Chelamallah, A. Benghalem, *Acta Phys. Pol. A*, **2017**, *132*, 448–450. [[CrossRef](#)], [[Google Scholar](#)]
- [16] G. Yuvaraja, D.Y. Chen, J.L. Pathak, J. Long, M.V. Subbaiah, J.C. Wen, C.L. Pan, *Int. J. Biol. Macromol.*, **2020**, *146*, 1100–1110. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [17] L. Zhai, Z. Bai, Y. Zhu, B. Wang, W. Luo, *Chin. J. Chem. Eng.*, **2018**, *26*, 657–666. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [18] F.C. Tsai, N. Ma, T.C. Chiang, L.C. Tsai, J.J. Shi, Y. Xia, T. Jiang, S.K. Su, F.S. Chuang, *J. Water Process Eng.*, **2014**, *1*, 2–7. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [19] L. Obeid, A. Bee, D. Talbot, S.B. Jaafar, V. Dupuis, S. Abramson, V. Cabuil, M. Welschbillig, *J. Coll. Interface Sci.*, **2013**, *410*, 52–58. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [20] D. Yang, L. Qiu, Y. Yang, *J. Chem. Eng.*, **2016**, *61*, 3933–3940. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [21] A. Homayonfard, M. Miralinaghi, R. Haji Seyed Mohammad Shirazi, E. Moniri, *Water Sci. Technol.*, **2018**, *78*, 2297–2307. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [22] A. Nezazadeh-Eihieh, Z. Shams-Ghahfarokhi, *J. Chem.*, **2013**, *11*, 104093. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [23] J.R. Baker, E.G.M. Williams, *Quart. J. Micr. Sci. J. Cell Sci.*, **1965**, *106*, 3–13. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [24] W. Azmi, R.K. Sani, U.C. Banerjee, *Enzyme Microb. Technol.*, **1998**, *22*, 185–191. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]

- [25] C. Fleischmann, M. Lievenbrück, H. Ritter, *Polymers*, **2015**, *7*, 717–746. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [26] M. Sanati, A.D. Khalaji, A. Mokhtari, M. Keyvanfard, *Prog. Chem. Biochem. Res.*, **2021**, *4*, 319–330. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [27] T.M. Tamer, M.A. Hassan, A.M. Omer, W.M.A. Baset, M.E. Hassan, M.E.A. El-Shafeey, M.S. Mohy Eldin, *Process Biochem.*, **2016**, *51*, 1721–1730. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [28] M.A. Hassan, A.M. Omer, E. Abbas, W.M.A. Baset, T.M. Tamer, *Sci. Rep.*, **2018**, *8*, 11416. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [29] M. Sahin, N. Kocak, G. Arslan, H.I. Ucan, *J. Inorg. Organomet. Polym.*, **2011**, *21*, 69–80. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [30] F.S. Pereira, S. Lanfredi, E.R.P. Gonzalez, D.L. da Silva Agostini, H.M. Gomes, R. dos Santos, *J. Therm. Anal. Calorim.*, **2017**, *129*, 291–301. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [31] P. Sharma, B.K. Saikia, M.R. Das, *Colloids Surf. A*, **2014**, *457*, 125–133. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [32] S. Cinar, U.H. Kaynar, T. Aydemir, S.C. Kaynar, M. Ayvacikli, *Int. J. Biol. Macromol.*, **2017**, *96*, 459–465. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)].

HOW TO CITE THIS ARTICLE

Zahra Bashandeh, Aliakbar Dehno Khalaji*. Effective Removal of Methyl Green from Aqueous Solution Using Epichlorohydrine Cross-Linked Chitosan. *Adv. J. Chem. A*, **2021**, 4(4), 270-277.

DOI: 10.22034/AJCA.2021.285520.1259

URL: http://www.ajchem-a.com/article_133377.html