Epichlorohydrine crosslinked chitosan cinnamaldehyde Schiff base: Synthesis, characterization, thermal studies and its application in adsorption of methyl green

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Research Article

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Abstract

Epichlorohydrine crosslinked chitosan cinnamaldehyde Schiff base (Epy-Chit-cin) had been synthesized by the reaction of epichlorohydrine, chitosan and trans-cinnamaldehyde (weight ratio 1:1:1) and characterized by FT-IR, UV-Vis, TG-DTA, DSC and XRD. The efficiency of the prepared Epy-Chit-cin was studied for the methyl green (MG) dye removal from aqueous solutions. The effects of pH, adsorbent dosage and contact time on the adsorption process were evaluated. Results showed that the equilibrium of MG adsorption by Epy-Chit-cin was reached at 120 min contact time and the maximum adsorption capacity obtained 98.47 at the presence of 0.02 g of Epy-Chit-cin.

Introduction

Pollution by various organic dyes [1–4] and heavy metal ions [5–6] is a great threat for human health and environment due to their stability, toxicity, non-biodegradability. Most of organic dyes are cheap, very easy to obtain, more stable (not easily decomposed under natural conditions) and widely used to color products in various industries such as textiles, leather and plastics [1–4]. These organic days can damages the balance of the ecosystem [2]. Therefore, remove of them from wastewaters is necessary. Until now, various techniques have been reported for remove of various dyes such as biological degradation [7], oxidation [8] chemical coagulation and adsorption [1–4, 9–14]. Chitosan, as a natural polymer, is harmless to humans [3], eco-friendly, nontoxic and also not expensive [2]. Due to containing many amine and hydroxyl groups on chitosan and its derivatives, they used as a good adsorbent for remove of various dyes [2–5, 11–14]. Rahmi et al. [2] reported the maximum adsorption capacity of 20.408 mg/g for the methylene blue removal using H_2SO_4 crosslinked magnetic chitosan nanocomposite beads. Cinar et al. [4] prepared nano-ZnO/chitosan composite beads as an efficient removal of RB5. The maximum adsorption capacity has been found to be 189.44 mg/g.Ke et al. [11] reported methyl green removal from wastewater using the modified chitosan by quaternary ammonium salt. We can modify chitosan using various crosslinking agents such as terephthaldehyde [15], glutaric acid [16] and epichlorohydrine [17], to improve its mechanical performance.

In this paper, an epichlorohydrine crosslinked chitosan cinnamaldehyde Schiff base (Epy-Chit-cin) (Scheme 1) was synthesized and used as adsorbent for removal of methyl green from aqueous solutions. The effects of pH, dosage of Epy-Chit-cin and contact time on the adsorption of methyl green were discussed.

Experimental

Materials and characterization techniques

Chitosan, epichlorohydrine, trans-cinnamaldehyde, glacial acetic acid, and ethanol were purchased from Sigma-Aldrich and Merck Co. and were used as received without further purification. Perkin-Elmer FT-IR spectrophotometer was used for the recording FT-IR (KBr disks, 4000–400 cm^{-1}) spectrum. The Perkin-

Elmer TG-DTA analyzer was used for the thermogravimetry analysis in air atmosphere at a flow rate of 20 ºC/min (25-825 ºC). DSC analysis of compounds was recording DSC analyzer Model 60A, Shimadzu, Japan. XRD patterns were determined by Bruker AXS-D8 X-ray diffractometer (2θ = 10-80 º), and SEM images were recorded on the TESCAN Vega Model scanning electron microscope. UV-Vis spectra were carried out with UV-Visible spectrophotometer (Perkin-Elmer).

Synthesis of Epy-Chit-cin

This compound was prepared based on the method mentioned in the literature [17] and with some modifications as follows. Chitosan (2 g) was suspended in 100 mL of ethanol-glacial acetic acid (95:5 v/v) and stirred at room temperature. After 10 min, 10 mL ethanolic solution of epichlorohydrine (1 mL) was slowly added and the reaction mixture was stirred at 80ºC for 6 h. Then, 10 mL ethanolic solution of trans-cinnamaldehyde (2 mL) was added and stirred for about 12 h at 80 ºC, up to a pale yellow solid precipitated. The mixture was cooled and the solid was filtered off, washed with cold ethanol and dried at room temperature for several days.

Adsorption experiments

All adsorption experiments were carried out in a series of 50 mL Erlenmeyer flasks contain 20 mL of dye solution (40 mg/L) with a various dosage adsorbent. The effects of pH and contact times (0 – 120 min) were investigated. The solutions were the shaken and at various contact time, then adsorbent (Epy-Chit-cin) was separated by centrifuged and the solution was analyzed by using UV-Vis spectrophotometer. The remove rate R (%) and adsorption capacity q (mg/g) were calculated based on the experiments using formulas are listed as follows:

$$R\,\% = \frac{Co - Ct}{Co} \times 100$$

Where C_o (mg/L) is the initial concentration of MG and C_t (mg/L) is the concentration of MG after adsorption.

Results And Discussions

Characterization of Epy-Chit-cin

The FT-IR spectrum of Epy-Chit-cin is shown in Fig. 1. As seen in Fig. 1, the peak appearing at 2861 cm^{-1} is assigned to the stretching of the C-H bond [3,11,18]. The sharp peak at about 1632 is assigned to the C=N iminic stretching band [3,11,18]. Two peaks appeared at about 1060 cm^{-1} is assigned to the C-O-C in the pyranose ring and the C-N stretching band [3, 4].

The UV-Vis spectrum of Epy-Chit-cin is shown in Fig. 2. The solubility of this compound is very low in all common organic solvents such as methanol, Ethanol, acetonitrile, chloroform, DMF and DMSO. As seen in Fig. 2, the UV-Vis spectrum has been recorded by dispersion of compound in the water by ultrasonic irradiation for 30 min. A broad peak at 282 nm is assigned to the n-π* and π-π* in the aromatic and iminic groups of Epy-Chit-cin [18].

TG-DTA curves of Epy-Chit-cin are presented in Fig. 3. Epy-Chit-cin shows three degradation stages. This compound is stable until 75 ºC. After that, in the first stage between temperature range 75 – 150 ºC, it show a little mass loss (< 5%) corresponds to moisture or ethanol molecules adsorbed on the surface of Epy-Chit-cin [19]. In the second stage, Epy-Chit-cin shows mass loss of ≈50% in the temperature range 150-400 ºC and is attributed to the thermal degradation of polymeric chain. This stage is exothermic and confirmed by DTA curve, while the first stage (evaporation of moisture or ethanol) is endothermic. In the third stage, there is a mass loss of ≈17 % from 400 to 825 ºC, due to the thermal degradation of residual crosslinked of the second stage [19].

DSC thermogram of Epy-Chit-cin shows in Fig. 4. There is a n endothermic peak around 84.5 ºC due to evaporation of moisture and ethanol molecules [18,20], while there is an exothermic peak at about 277.5 ºC assigned to the its thermal degradation of polymeric chain [18,20].

In the XRD pattern of Epy-Chit-cin (Fig. 5), there are two peaks at 11.29º and 20.48º. Chitosan reveals a peak at about 10º and 20º [4,14]. In this compound a peak appeared at about 11.29º may be confirm the changes on the modified chitosan using epichlorohydrine and trans-cinnamaldehyde.

Adsorption studies

Methyl green is a cationic triphenylmethane dye and used for dyeing nylon, wool, silk and cotton in the textile industry [21] and as indicator dyes due to their pH sensitivity [22]. Then the pH of solution is one of the most important parameter in the adsorption process [2,411,14]. The maximum methyl green removal (353.33 mg/g) was observed in the pH of 7 for activated bentonite [23] and 67.93 mg/g in the pH of 8 for activate carbon [24]. The effect of initial pH on the removal percentage of MG was studied by varying the initial pH from 2 to 10 by adding a solution of HCl (0.1 M) or NaOH (0.1 M) and shown in Fig. 6. The maximum methyl green removal (98.47%) was observed in the pH of 8, due to partial δ^- surface charge of Epy-Chit-cin. In this case, an electrostatic attraction occurs between this partial negative charge and the positive charge of methyl green. Therefore, the pH of 8 was used to investigate the effect of contact time and adsorbent amount on MG removal.

The percentage removal of MG solution at different contact times for various adsorbent dosages (0.05, 0.01 and 0.02 g) are shown in Fig. 7. As seen in Fig. 7, the percentage removal of MG increased by increasing the adsorbent dosage. It is also seen that the percentage removal is much faster at the beginning of the reaction, due to the increase in adsorbent active sites on the surface of Epy-Chit-cin. Also, the percentage removal has been increased by increasing the contact time [24].

Conclusions

In this paper, the Epy-Chit-cin absorbent based on the chitosan as natural polymer was successfully prepared by reaction of chitosan, epichlorohydrine and trans-cinnamaldehyde and characterized by various techniques. The adsorption performance of Epy-Chit-cin on removal of MG from aqueous solutions was investigated. Results show that the Epy-Chit-cin as adsorbent can removed the MG from aqueous solution and the removal rate achieved was 98.47%. These results show that the Epy-Chit-cin can be used as an environmentally friendly bio-adsorbent.

Declarations

Conflict of interest

The authors declare that there is no conflict of interest.

Acknowledgments

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Figures

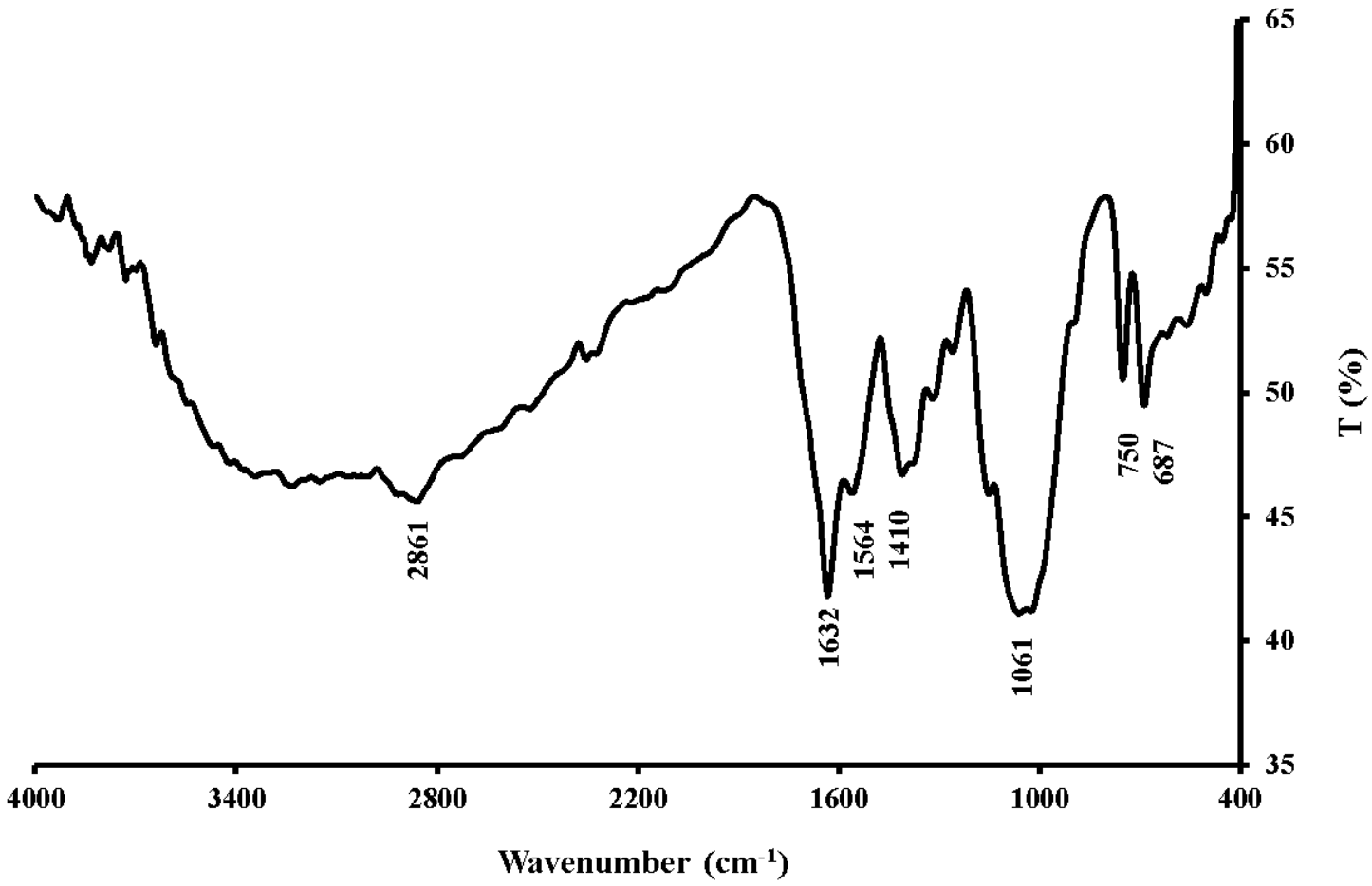

Figure 1

FT-IR spectrum of Epy-Chit-cin

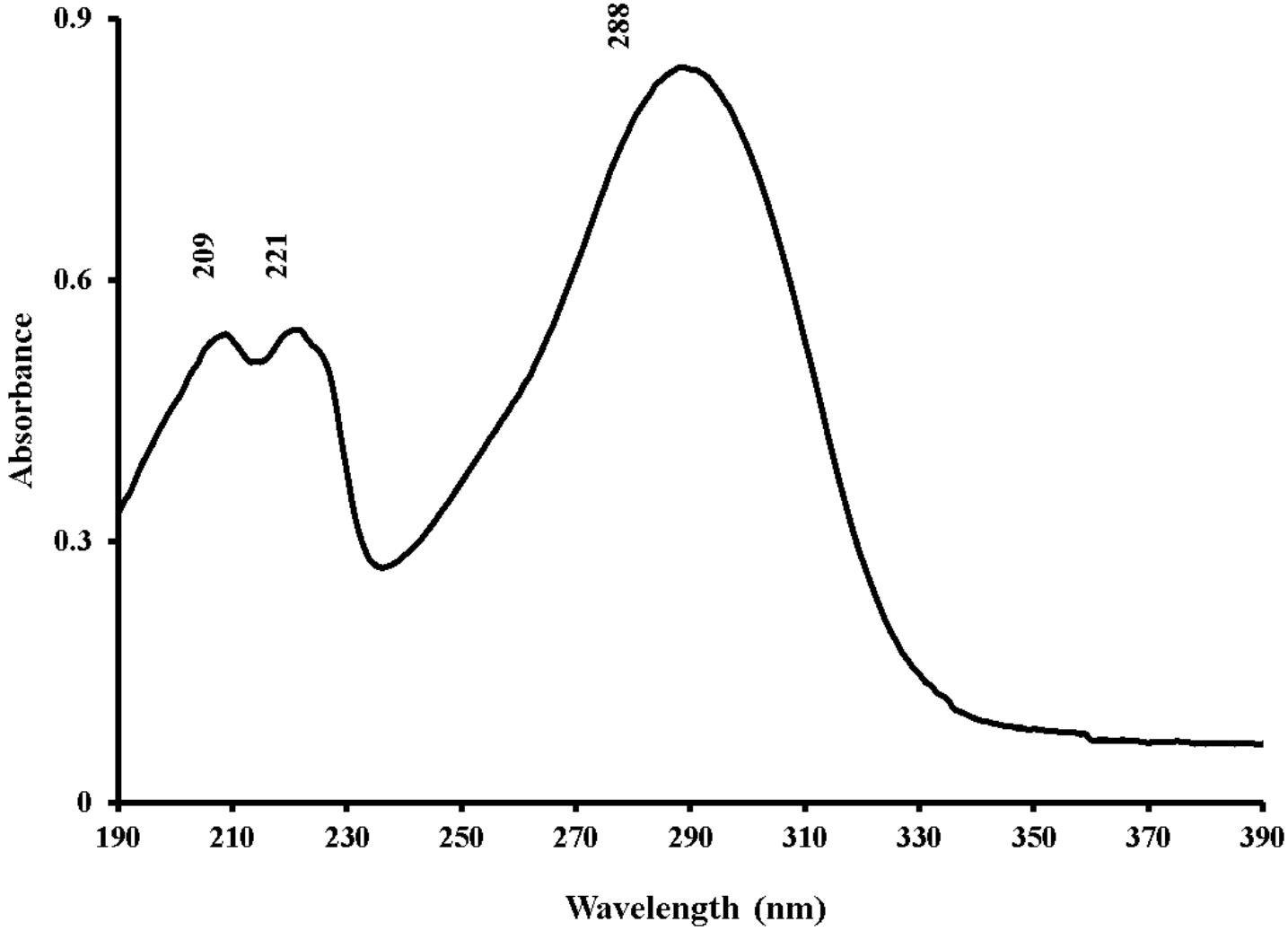

Figure 2

UV-Vis spectrum of Epy-Chit-cin

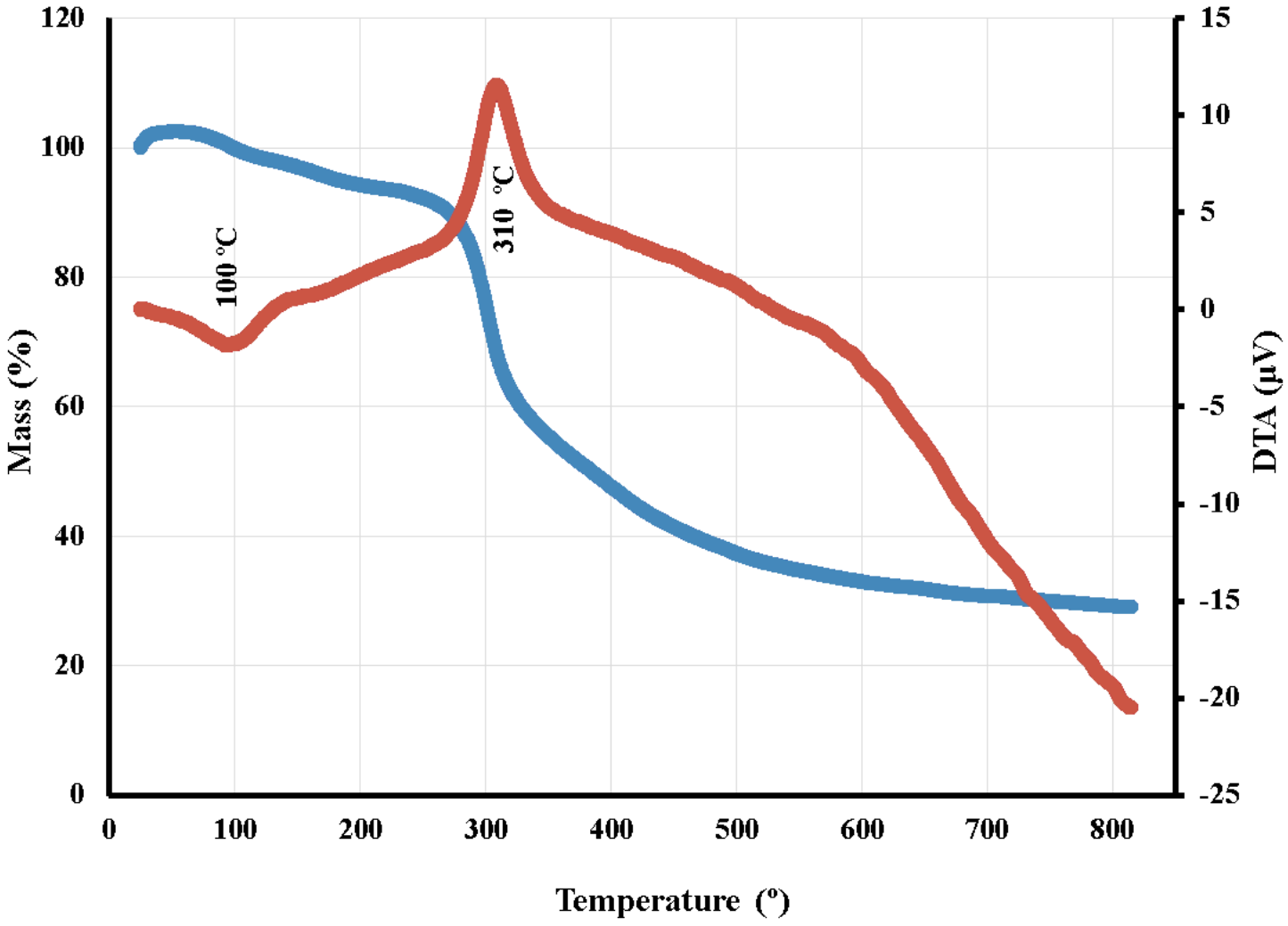

Figure 3

TG-DTA curves of Epy-Chit-cin

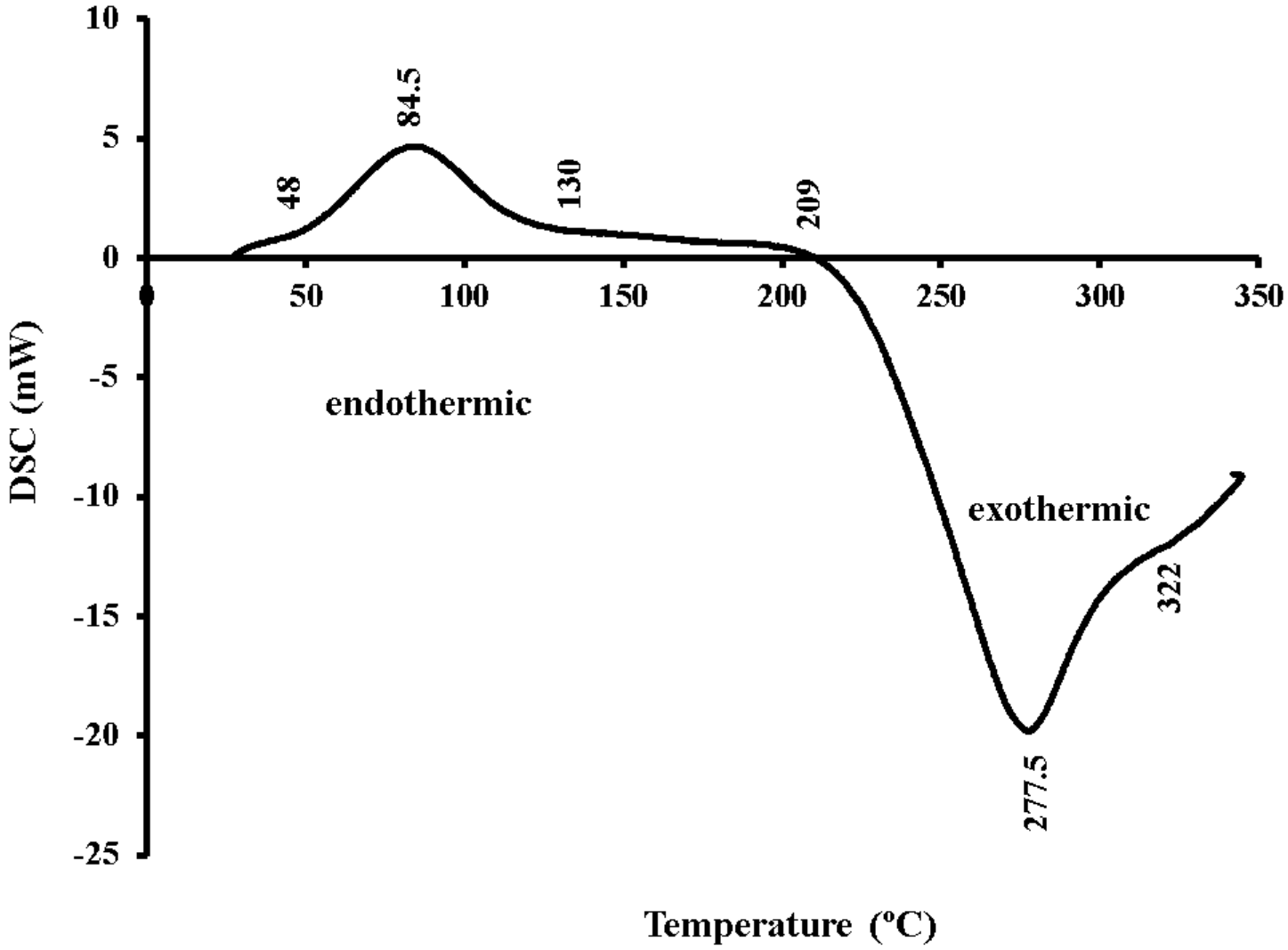

Figure 4

DSC thermogram of Epy-Chit-cin

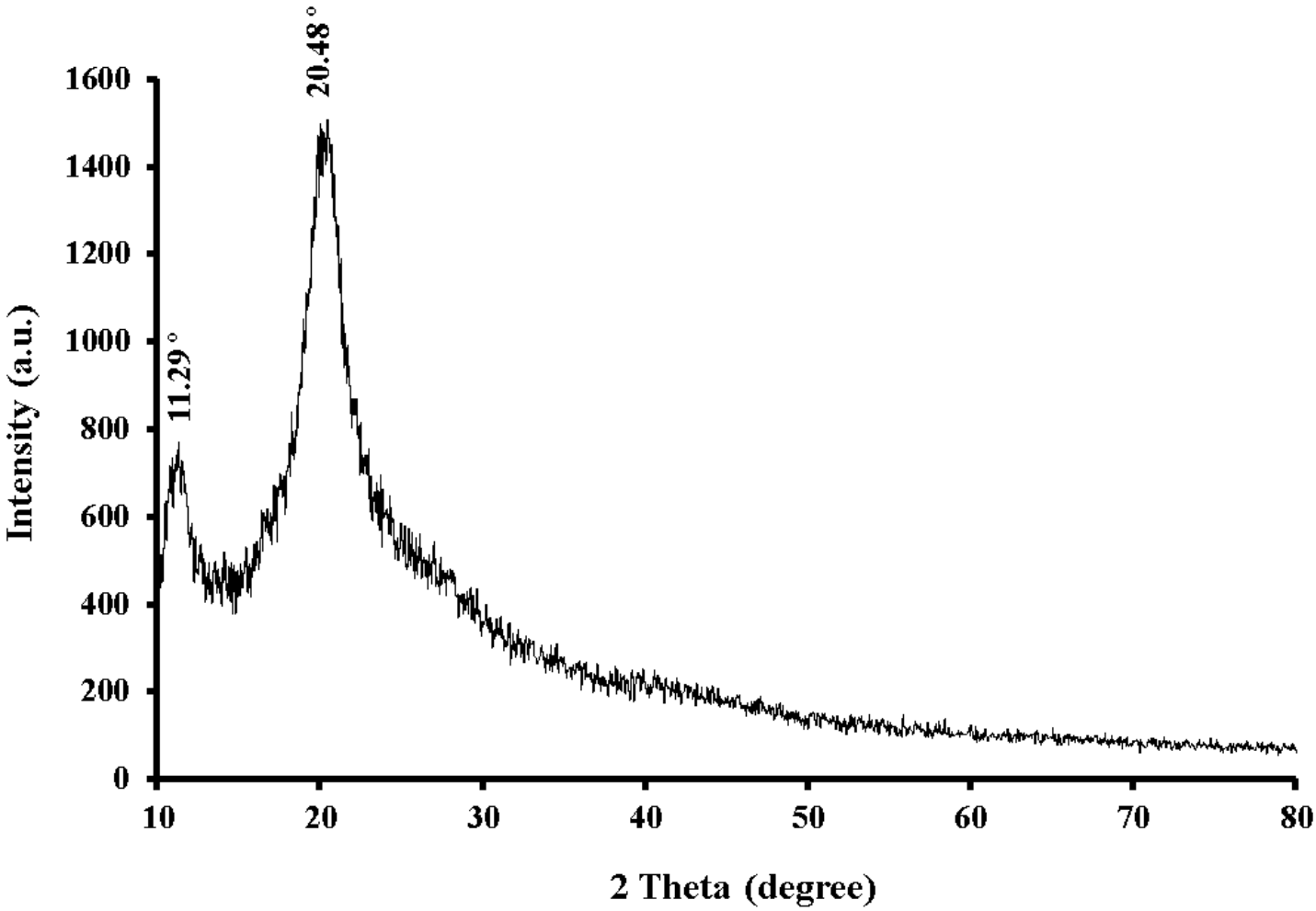

Figure 5

XRD pattern of Epy-Chit-cin

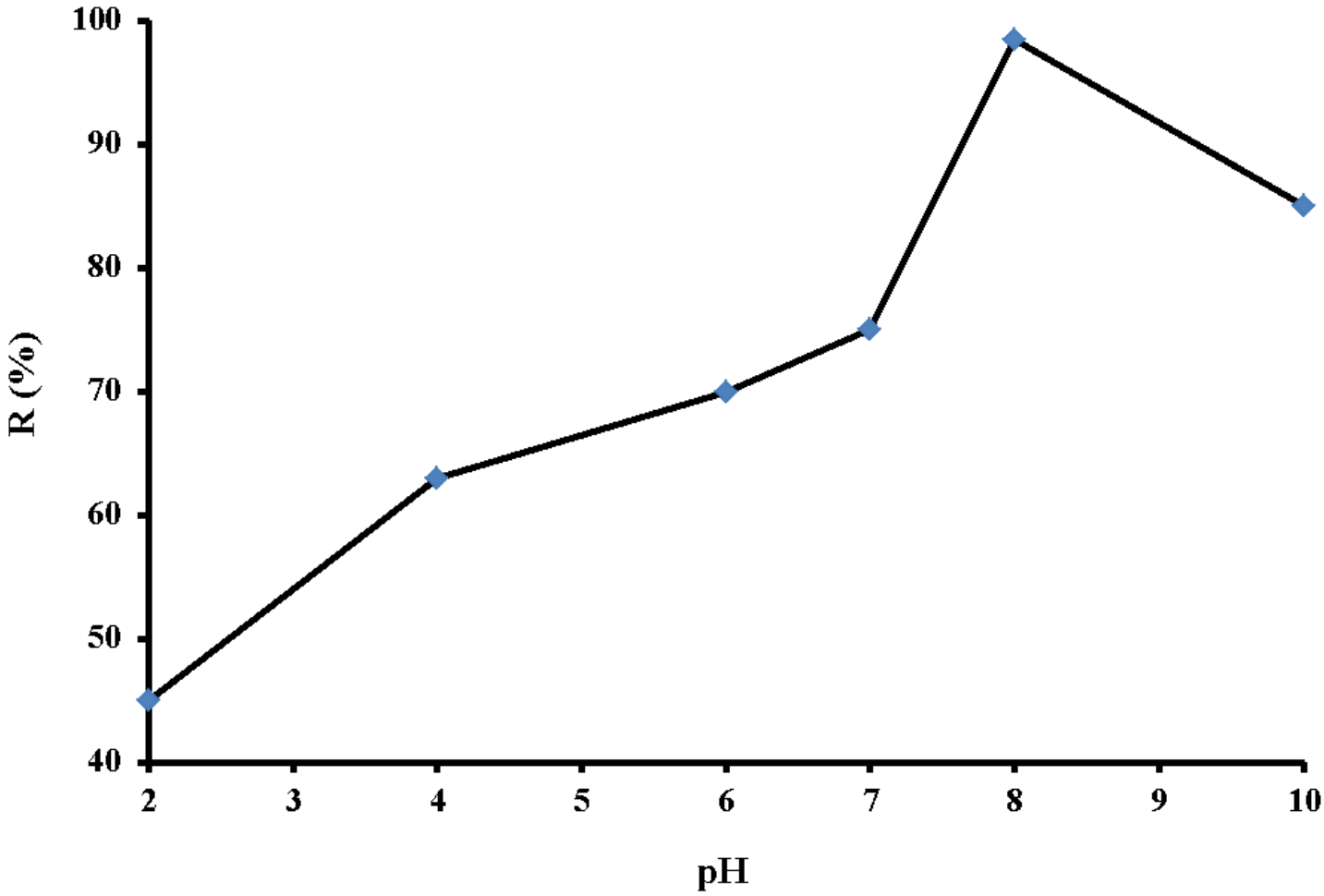

Figure 6

Effect of initial pH on removal percentage of MG

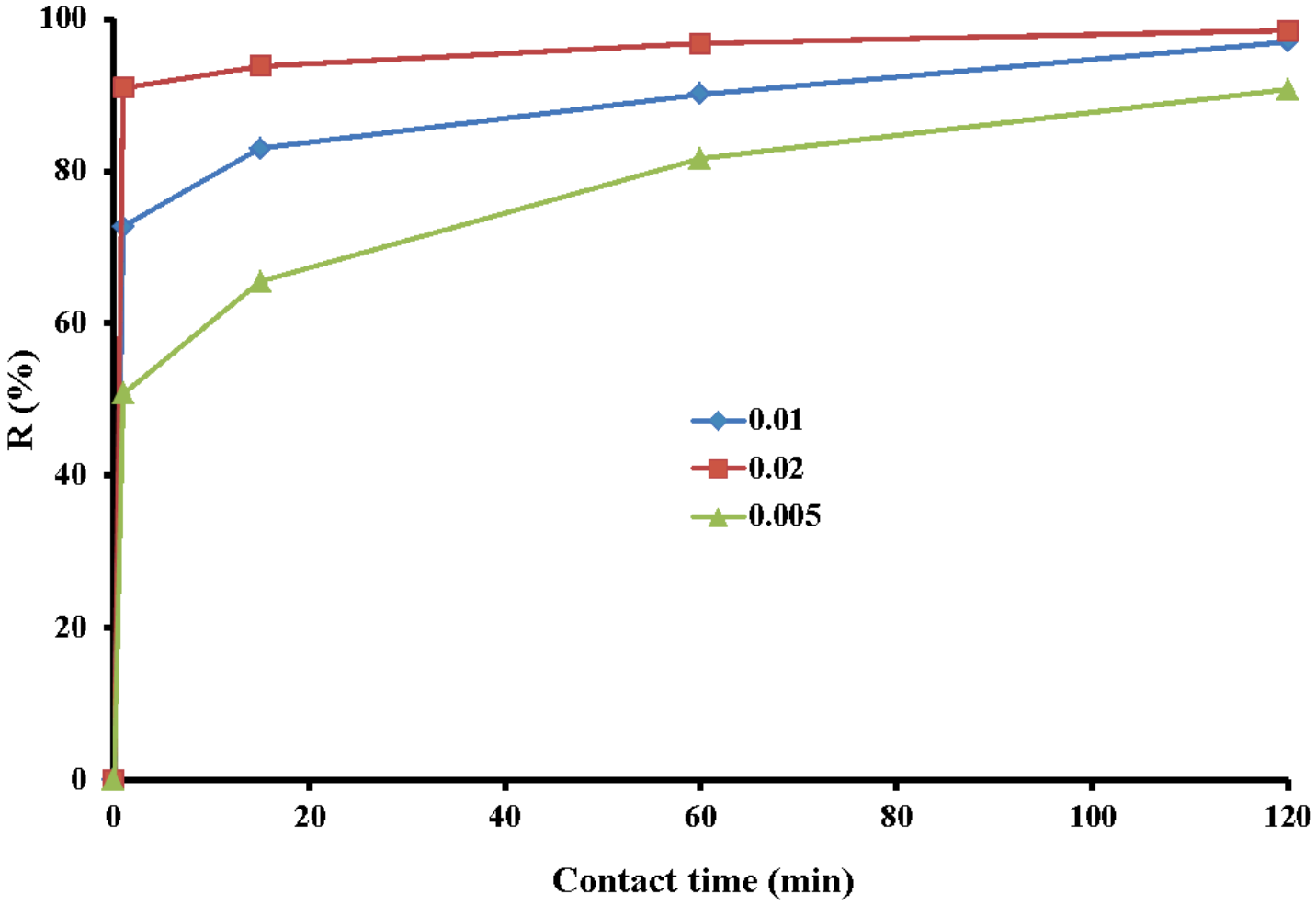

Figure 7

Effect of adsorbent dosage and contact time on the percentage removal of MG

Supplementary Files

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- Scheme1.png