

Kinetic studies and grafting mechanism for methyl aniline derivatives onto chitosan: Highly adsorptive copolymers for dye removal from aqueous solutions



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ABSTRACT

A polysaccharide, chitosan received vast attention because of its non-toxic, low cost and biodegradable properties. In this study, three promise grafted chitosan copolymers using methyl polyaniline conducting polymeric isomers were successfully synthesized through oxidative-radical copolymerization using ammonium persulphate as initiator in acidic medium. The kinetic behaviors of graft copolymerization were extensively studied under various parameters. Moreover, the rate of grafting copolymerization is affected by concentrations of monomer, initiator, and HCl in addition to temperature. The activation energy (E_a), enthalpy of activation (ΔH^\ddagger) and negative value of entropy (ΔS^\ddagger) support the progress of copolymerization. Environmental impacts of the grafted polymers in water detoxification were manifested. A comparison study for adsorption of remazol red dye from aqueous solutions onto Ch-g-PMeANIs was investigated.

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1. Introduction

Among all conducting polymers, polyaniline (PANI) and its derivatives are the most promising polymeric materials which can be frequently used because of its easy synthesis, flexibility, high electrical conductivity and environmental stability [1–3], as well as its potential applications in many areas including: sensors, actuators, rechargeable batteries, and anticorrosion coatings [4–6]. In addition, polyaniline is efficient for selective adsorption of the dyes through chemical interaction [7,8].

Chitosan is essentially the N-deacetylated derivative of chitin. Next to cellulose, chitin is considered to be the second most abundant natural organic resource on earth. Chitin can be found in marine invertebrates, fungi, insects and yeasts. Chitin can be deacetylated to form chitosan by using NaOH solution at high temperature [9,10]. Chitin and chitosan have been of interest in the past few decades due to their potential broad range of use from industrial applications to biomedicine and food applications [11,12]. Chitosan has drawn considerable attention because it has excellent properties of biocompatibility, biodegradability and reactive surface functional groups for easy surface modification [13–16]. Chitosan is a brittle material and tends to absorb a quantity of moisture; it is also a low cost, high molecular weight, with unique physicochemical properties [17].

Among the various methods used for chitosan modification, graft copolymerization has been the most used. Grafting of chitosan allows

the formation of functional derivatives by covalent binding of a molecule grafted onto the chitosan backbone. Chitosan has two types of reactive groups that can be grafted. First, the free amine groups on deacetylated units and secondly, the hydroxyl groups on the C3 and C6 carbons on acetylated or deacetylated units [18,19]. Moreover, the use of a given initiator, catalyst or other agent affecting kinetics of the polymerization enable to obtain polymers having well defined geometry, better physical, chemical properties and narrow polydispersity [20]. Grafting of chitosan is a common way to improve its properties such as increasing chelation [21], antibacterial effect [22] and enhancing adsorption properties [23]. Furthermore, grafted chitosan composites were recently, proceeded as highly efficient membranes for dehydration of isopropanol, biosensor for sialic acid and potential surfaces for Cr(IV) uptake [24–26].

Adsorption techniques are being widely used to remove certain classes of pollutants from waters, especially those that are not easily biodegradable. Adsorption has a specific advantage of removing the complete dye molecule, unlike certain removal techniques, which destroy only the dye chromophore leaving the harmful residual moieties in the effluent [27]. In recent years, the use of biopolymer/conducting polymeric composite materials as adsorbent has gained a substantial attention due to their outstanding adsorption performance, low cost, wide availability and the presence of various functional groups. Moreover, these materials have been demonstrated as effective adsorbent for the removal of dyes, heavy metals and fluoride ions from aqueous solution [28]. Chitosan is one of biopolymer that has adsorption properties, and grafting of chitosan has been reported in literature to create additional adsorption site, thereby improving its adsorption performance [29].

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The kinetic study of grafting chitosan with substituted polyaniline at different parameters contributes to develop our understanding about grafting mechanism and optimizing the synthesis method. Furthermore, the yield and rate constants which are obtained at different parameters for this chemical graft copolymerization would benefit both laboratory and industrial applications. However, the kinetics of chemical graft copolymerization of chitosan with methyl aniline isomers has never been studied to our knowledge. Moreover, research on rate constants, activation energy, activation entropy and enthalpy of such copolymerization process is also still very infrequent and unique.

Therefore, the aims of this work are: firstly to provide an insight into the kinetic studies of three novel Ch-g-PMeANIs and to determine the relationship between the rates of grafting with concentrations of monomer, initiator and HCl at different temperatures, as well as correlating some kinetic parameters to the grafting reaction. Secondly, present desired environmental impacts by investigating the boosted adsorption properties of Ch-g-PMeANIs as eco-friendly copolymer for the removal of remazol red RB-133 dye from aqueous solutions. Adsorption isotherms and kinetics were discussed.

2. Experimental

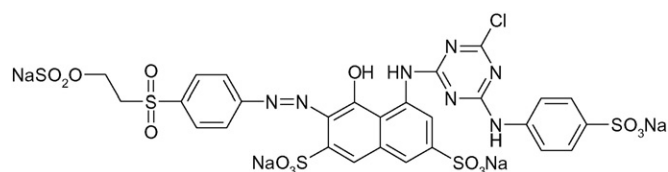
2.1. Materials

Chitosan was extracted from the shrimp shells as described in the literature [30,31] (M. Wt. ~109,000; degree of deacetylation >85%), N-Methylaniline (NMANI), 2-Methylaniline (2MANI) and 3-Methylaniline (3MANI) were provided from Sigma Aldrich. Ammonium persulphate and N-Methyl-2-pyrrolidone (NMP) were purchased from Loba Chemie (India). Hydrochloric acid, acetic acid and acetone of AR grade were provided from El-Nasr Chemical Co. (Egypt) and were used as received. The commercially available water-soluble reactive dye remazol red RB-133 (RR RB-133, Scheme 1) is obtained from DyStar and used as received without further purification.

2.2. Synthesis of Ch-g-PMeANIs

Aqueous solution of chitosan was prepared by dissolving calculated amount of the chitosan in acetic acid (2 wt.%) and stirring for 2 h on a magnetic stirrer at room temperature ($25 \text{ }^\circ\text{C} \pm 2$). The resulting solution was filtered to remove undissolved particles before proceeding grafting reaction. After that, appropriate amount of substituted aniline monomer in HCl was added to chitosan solution at $5 \text{ }^\circ\text{C}$, under constant stirring for 20 min. to form a homogeneous solution.

A definite amount of ammonium persulfate in HCl was added drop wise into the above solution and stirring was continued in an ice bath at temperature $5 \text{ }^\circ\text{C}$ for 5 h. After that, the solution was centrifuged, and the separated precipitate was washed firstly with bidistilled water and again separated from the washing solution by centrifugation. The water washed precipitate was secondly washed with N-methyl-2-pyrrolidone (NMP) for several times followed by final treatment with acetone to separate sPANI (homopolymer) and sPANI (oligomers) from Ch-g-sPANI. The final pure Ch-g-PMeANIs copolymers were dried at $50 \text{ }^\circ\text{C}$ for 24 h. Scheme 2 shows an example of the general synthetic route of chitosan-graft-substituted polyaniline.



Scheme 1. Structural formula of Remazol red RB-133 (RR RB-133).

2.3. Methods

The grafting and efficiency percentages were calculated by:

$$\text{Graft yield(G)\%} = (W_1 - W_0 / W_0) \times 100 \quad (1)$$

where, W_1 , and W_0 are the weights of Ch-g-PMeANIs and pristine chitosan.

The rate of grafting (Ri) was calculated as follows:

$$\text{Rate of grafting (Ri)} = (G\% \times W_0 \times 1000) / (100 \times V \times t \times M) \quad (2)$$

where G% is percent graft yield, W_0 is weight of original chitosan, V is the total volume of reaction mixture (mL), t is reaction time (seconds), and M is molecular weight of monomer.

Moreover, the rate kinetics of Ch-g-PMeANIs grafting copolymerization has been investigated by correlating function of monomer, initiator and HCl concentration. Eq. (3) shows the relation of grafting rate with the monomer, initiator and acid concentrations:

$$Ri = K[\text{Monomer}]^m \times [\text{Initiator}]^n \times [\text{HCl}]^a \quad (3)$$

Here m, n and a can be experimentally determined by the logarithmic form of the Eq. (3):

$$\text{Log Ri} = \text{Log K} + \text{Log}[\text{Monomer}]^m + \text{Log}[\text{Initiator}]^n + \text{Log}[\text{HCl}]^a \quad (4)$$

2.4. Instrumental

Infrared measurements were performed using a Shimadzu FT-IR spectrometer. UV-Vis diffuse reflectance of grafting copolymer samples was obtained using a Shimadzu Japan 3101 p spectrophotometer. The differential scanning calorimetric (DSC) measurements were carried out using a Netzsch DSC 204 (Germany). The UV-vis absorption spectra of RB-133 during the adsorption process were recorded by an UV-vis. Agilent Cary 60 spectrophotometer.

2.5. Adsorption experiments

The adsorption studies for dye removal from aqueous solution either by Ch-g-PMeANIs or grinded flakes of ungrafted chitosan as adsorbents were carried out in a batch process. 40 mL dye solution of desired concentration was taken into a conical flask then 0.04 g of adsorbent was added and shaken at $25 \pm 2 \text{ }^\circ\text{C}$ on a horizontal rotary shaker. Adsorbent was then separated and the filtrate was analyzed for residue using an UV-vis. Agilent Cary 60 spectrophotometer. At maximum absorbance wavelength ($\lambda_{\text{max}} = 522 \text{ nm}$), the specific amount of dye adsorbed was calculated using the equation:

$$q_e = [(C_0 - C_e) \times V] / W \quad (5)$$

where q_e is the adsorption capacity at equilibrium (mmol/g); C_0 and C_e are the initial dye concentration in contact with the adsorbent and the dye concentration after the batch adsorption proceeds (mmol/L), respectively; V is the volume of aqueous solution (L), and W is the mass (g) of adsorbent used in the experiments.

The preparation conditions of graft-copolymer which employed in adsorption studies are monomer concentrations ($1.0 \times 10^{-2} \text{ mol L}^{-1}$), Initiator concentration ($7.5 \times 10^{-2} \text{ mol L}^{-1}$), HCl concentration (0.2 mol L^{-1}) and at temperature $5 \text{ }^\circ\text{C}$ as described in Section 2.2. that give graft yield as clarified in Section 3.1.

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