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Microwave Assisted Synthesis of Poly(Diallyldimethylammonium Chloride) Grafted Locust Bean Gum: Swelling and Dye Adsorption Studies

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ABSTRACT

Poly(diallyldimethylammonium chloride) grafted locust bean gum was made by microwave irradiation technique using ammonium peroxydisulfate as initiator and N,N-methylene-bis-acrylamide as a crosslinker. The grafting conditions were optimized. The grafted gum was characterized using Fourier transform infrared, thermogravimetric analysis, and scanning electron microscope techniques. Swelling behavior of the gel was studied under different pH conditions. The grafted gum was evaluated for the removal of anionic dye "indigo carmine" from aqueous solution. The maximum adsorption was found to be 35.12 mg/g gel, and the adsorption data was observed to fit into Langmuir isotherm model.

Key words: *Locust bean gum, Poly(diallyldimethylammonium chloride), Microwave irradiation, Dye adsorption, Swelling.*

1. INTRODUCTION

Locust bean gum (LBG) is a polysaccharide of high molecular weight that is extracted from the seed of carob tree *Ceratonia siliqua* [1]. LBG has a wide range of applications such as in drug delivery [2], adsorption [3], emulsification, and gelation [4]. Diallyldimethylammonium chloride (DADMAC) is one of the water-soluble quaternary cationic monomers [5].

The presence of colored pollutant such as dye becomes increasingly a major treat to water bodies [6]. The removal of these pollutants from wastewater using cheaper and environmentally friendly techniques is a major challenge. Hence, the use of materials such as polymeric hydrogels became increasingly adapted for the removal of dyes from wastewater.

2. EXPERIMENTAL

2.1. Materials

LBG and DADMAC were purchased from Aldrich Chemical Company, India. Ammonium peroxydisulfate (APS) and N,N-methylene-bis-acrylamide (MBA) were obtained from Spectro Chem Pvt. Ltd., Mumbai, India. The dye indigo carmine (IC) was obtained from S. D. Fine Chemicals Ltd., Mumbai, India. Acetone was obtained from Nice Chemicals Pvt. Ltd., Kerala, India. Methanol was obtained from Himedia Laboratories Pvt., Ltd., Mumbai, India. All the reagents were of the analytical grade used as obtained.

2.2. Methods

2.2.1. Preparation of polyDADMAC-grafted LBG (PDADMAC-g-LBG) hydrogel

The grafting of DADMAC on to LBG was carried out based on the reported literature [7]. A fixed amount of LBG (0.1 g) was dispersed in 20 ml distilled water and stirred overnight followed by addition of varying amount of APS (0.01-0.06 g) and stirred for an hour. A specified amount of DADMAC (0.15-0.40 g) was added to the above solutions followed by MBA at varying amount (0.01-0.06 g) and stirred for 5 h. The solution was irradiated in a microwave oven under different conditions (0-100 w, 60-160 s) with alternate heating and cooling. The solution was left overnight to complete the grafting process and precipitated out using acetone followed by washing with methanol 2-3 times to remove the un-reacted monomers. The products were dried in an oven overnight at 50°C. The grafting efficiency and percentage grafting (GP) were calculated using the below equations as follows:

$$GP = \frac{(w_1 - w_0)}{w_0} \times 100 \quad (1)$$

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$$GE = \frac{(w_1 - w_0)}{w_2} \times 100 \quad (2)$$

Where, W_0, W_1 and W_2 are the weight of LBG, grafted LBG and DADMAC, respectively; the grafting conditions were optimized under different conditions.

2.2.2. Characterization

Fourier transform infrared (FTIR) spectroscopy was recorded using FTIR (prestige-21, Shimadzu, Japan) in the range of 4000-400 cm^{-1} wavenumber during 40 scans, with a resolution of 2 cm^{-1}.

Surface morphology was examined using JEOL JSM-6380LA analytical scanning electron microscope (SEM) and micrographs were recorded at magnification of 5000 under 20 KVA after coating with gold film. Thermal stability of LBG and a representative sample of PDADMA-g-LBG was analyzed using standard differential scanning calorimetry-thermogravimetric analysis (TGA) (Q600 V20.9 model, Japan) in the temperature ranges of 10-700°C, under nitrogen atmosphere at the heating rate of 10°C min^{-1}.

2.2.3. Swelling studies

A known amount (g) of the grafted polymer sample (PDADMAC-g-LBG) was weighed (W_0) accurately and immersed in a solution of different pH (1.2, 7.0 and 9.0) and at different time intervals the grafted polymer was removed and wiped away the water content by blotting with tissue paper and re-weighed (W_1) until an equilibrium was reached. The swelling ratio (SR) in g/g was calculated from the relation below:

$$SR\ (g/g) = \frac{(w_1 - w_0)}{w_0} \quad (3)$$

2.2.4. Dye adsorption study

The adsorption study of the grafted gum was carried out in 100 mg/L of dye solution. The grafted gel was immersed in the dye solution, and at different time interval 1 ml of the solution were withdrawn and the absorbance was recorded using UV-visible spectrophotometer (UV-1800 SHIMADZU) at λ_{max} of 610 nm. Equilibrium adsorption studies were also carried out using different dye concentration (10-100 mg/L). The amounts of dye adsorbed at time t and at equilibrium were calculated from the following equations:

$$Q_t = \frac{(C_0 - C_t) \times V}{M} \quad (4)$$

$$Q_e = \frac{(C_0 - C_e) \times V}{M} \quad (5)$$

Where Q_t and Q_e are amount of dye adsorbed (mg/g) at time t=t and at equilibrium, respectively. C_0, C_t and C_e are dye concentration (mg/L) at time t =0, t=t and at equilibrium, respectively. M is the weight of the gel (g) and V is the volume (L) of the solution.

3. RESULTS AND DISCUSSION

3.1. FTIR Spectroscopy

The FTIR spectra of LBG (Figure 1a) showed a broad peak of 3311 cm^{-1} which is attributed to O-H group. The sharp peaks observed at 1004 cm^{-1} were due to C-O-H vibration. Similarly, the peaks observed at 1163 and 1138 cm^{-1} are for C-O-C stretching form glycosidic linkages and C-O-CH_2, which could be as results of grafting. The strong peaks observed at 2912 cm^{-1} are for C-H stretching. In additional to the characteristics peaks observed in LBG, a sharp peak of 1474 cm^{-1} for C-N stretching and a medium peak at 3022 cm^{-1} for quaternary N on Figure 1b was observed, which indicates the grafting of DADMAC on LBG successfully.

3.2. TGA Analysis

The thermal behavior of LBG (Figure 2a) shows three degradation steps with 12% weight loss between 50°C and 100°C due to the loss of water molecules. At 300-320°C, the major weight loss of 70% was observed

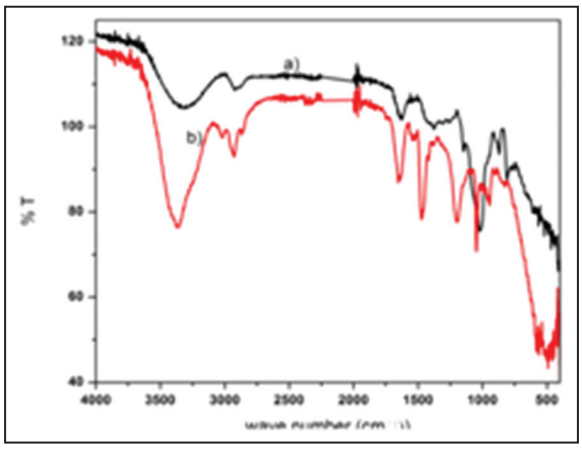

Figure 1: Fourier transform infrared spectra of (a) locust bean gum (LBG) and (b) poly(diallyldimethylammonium chloride) grafted-LBG.

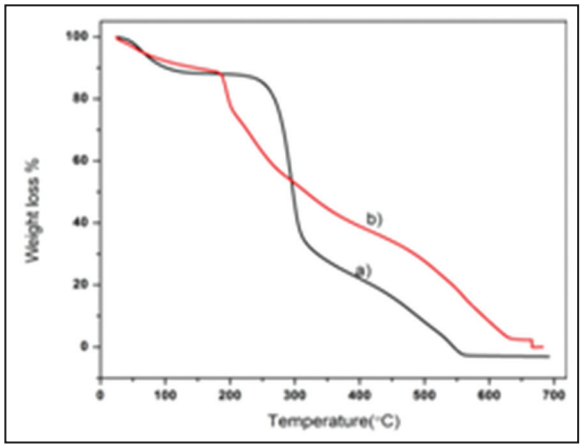

Figure 2: Thermogravimetric analysis curve for (a) locust bean gum (LBG) and (b) poly(diallyldimethylammonium chloride) grafted-LBG.

and is linked to breakage of the glycosidic linkage of LBG. At 560°C, the final decomposition of the gum occurs. For the grafted polymer (Figure 2b), the weight loss of 12% was observed at 100°C indicating the elimination of water molecule. There is 90% weight loss around 630°C on the representative sample. The final stage decomposition of the representative PDADMAC-g-LBG occurs around 670°C with almost 100% weight loss indicating greater thermal stability.

3.3. SEM Analysis

The morphology of LBG and the representative PDADMAC-g-LBG sample (Figure 3a and b) shows fibrous surface on LBG while grafted polymer is more homogeneous and smooth in shape.

3.4. Swelling Studies

The swelling behavior of the grafted polymer under different pH conditions is shown in Figure 4. The swelling pattern of the representative PDADMAC-g-LBG in different pH solution follows the order 1.2>9.0>7.0. This indicates that the gels swelled more in acidic (7.40-40.61 g/g) medium than in basic medium (16.42-29.54 g/g).

3.5. Dye Adsorption Studies and Isotherm

The adsorption of IC on PDADMAC-g-LBG with time is shown on Figure 5. The amount of dye (mg/g gel) adsorbed increases with time until equilibrium adsorption at around 600 minutes is reached. The amount of dye adsorbed at equilibrium was 42.36 mg/g of the gel. This is due to the interaction of the positive charge on the quaternary amino group of the grafted polymer and negative charge of the sulfate group of the dye molecule. The adsorption of 150 mg/g of IC was reported [8]. For equilibrium adsorption studies, a fixed amount (0.05g) of the grafted gel was used in 25 mL of the varied dye concentration (10-100 mg/L). The two most widely and commonly used isotherm models namely; Freundlich [8] and Langmuir models [9] were employed in this work to understand the adsorption behavior of the dye on PDADMAC-g-LBG. The Freundlich isotherm is represented by the equation below:

$$\ln Q_e = \ln K_f + \frac{1}{n}\ln C_e \qquad (6)$$

Where Q_e is the amount of dye adsorbed at equilibrium (mg/g), C_e is the concentration of dye solution at equilibrium (mg/L), K_f and n are Freundlich adsorption isotherm constants that represent the extent of adsorption and the degree of nonlinearity between the dye concentration and the adsorption, respectively. The values of K_f and n were calculated from the intercept and slope of the plot between ln Q_e and ln C_e and are presented in Table 1. The value of n indicates whether the adsorption is favorable or otherwise. If it lies within the range of 1 to 10 then, the adsorption is considered favorable. In this study, the value of n indicated favorable adsorption.

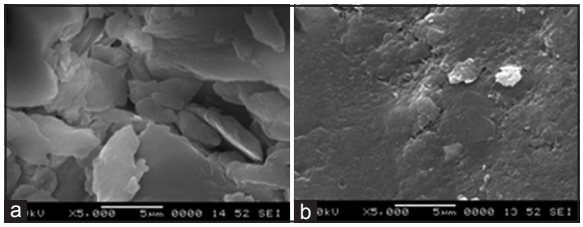

Figure 3: Scanning electron microscope images of (a) locust bean gum (LBG) and (b) representative poly(diallyldimethylammonium chloride) grafted-LBG.

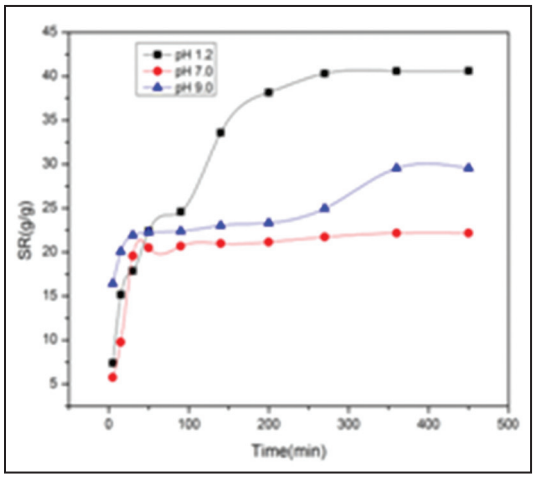

Figure 4: Swelling ratio (g/g) of the poly(diallyldimethylammonium chloride) grafted-locust bean gum under different pH.

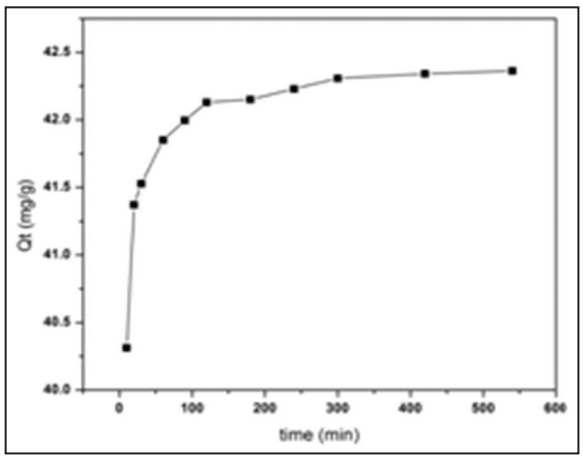

Figure 5: Dye adsorbed (g/g) on poly(diallyldimethylammonium chloride) grafted-locust bean gum under different.

The Langmuir adsorption model is expressed in the equation given below:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m}.C_e + \frac{1}{K_L Q_m} \qquad (7)$$

Where, C_e and Q_e are the concentration of dye (mg/L) and amount of dye adsorbed at equilibrium

Table 1: Adsorption parameters for IC on PDADMAC-g-LBG at ambient temperature.

Co (mg/L)	Freundlich model			Langmuir model			
	K_f	n	R^2	R_L	K_L	Q_m	R^2
10-100	1.169	2.35	0.956	0.25-0.77	0.0296	4.63	0.995

PDADMAC-g-LBG=Poly (diallyldimethylammonium chloride) grafted locust bean gum, IC=Indigo carmine

(mg/g), respectively. Q_m is the maximum adsorption corresponding to complete monolayer coverage on the surface (mg/g), K_L is the Langmuir constant which is related to the energy of adsorption (L/mg). K_L and Q_m are determine from the intercept and slope of the linear plot of C_e/Q_e versus C_e) and presented in Table 1. The basic features of the Langmuir isotherm can be represented in terms of separation factor (dimensionless equilibrium parameter) R_L [10].

$$R_L = \frac{1}{1 + K_L C_o} \quad (8)$$

Where, C_o is the highest initial concentration of the dye (mg/L) and K_L is the Langmuir constant (L/mg). The value of R_L determined the nature of adsorption. Hence, the values of R_L (Table 1) obtained in this study showed favorable adsorption of IC on PDADMAC-g-LBG. The R^2 values of Freundlich and Langmuir isotherm models are 0.956 and 0.995, respectively, which indicated the equilibrium adsorption data best fit into Langmuir model.

4. CONCLUSION

PDADMAC-g-LBG was successfully prepared and characterized using FTIR, TGA, and SEM techniques. The grafted polymer was found to have pH-responsive swelling behavior. Adsorption capacity of the grafted polymer towards the dye IC was found to be moderate. The adsorption data of the polymer were observed to be fit into Langmuir model.

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Bibliographical Sketch

Prof. B. Vishalakshi received M.Sc. (Chemistry, 1986) from Mangalore University and Ph.D. (Polymer Chemistry, 1996) from Indian Institute of Science, Bangalore. She has been a Faculty Member in the Department of Chemistry, Mangalore University since 1996. Presently, she is the Chairperson of the Department of Chemistry, Mangalore University. Her research interests are in the field of polyelectrolytes and hydrogels. Prof. Vishalakshi has published over 40 papers in peer reviewed scientific journals on the modification of polysaccharides for development of polymer materials for pharmaceutical and industrial applications. Prof. Vishalakshi is a life member of Indian Council of Chemists, Society of Polymer Chemistry, Dharwad Chapter (Karnataka) and Society of Biomaterials and Artificial Organs (India). She received Dr. Kalpana Chawla State Award for Young Women Scientists – 2013 by the Karnataka State Council for Science and Technology, Government of Karnataka for her outstanding contribution for development of science and technology in the state.