Synthesis and Application of Locust Bean Gum Grafted Polyaniline in Removal of Methyl Orange Dye

E. Fosso-Kankeu, L. van der Merwe, S. Pandey, F. Waanders and S.K. Ntwampe

***Abstract*—** Nowadays, the use of natural and modified polymers for the removal of dyes from wastewater is becoming more common. We briefly summarize some of the results in this article. The present study focuses mainly on the synthesis of locust bean gum grafted polyaniline (LGP) via in situ oxidative polymerization using ammonium persulfate (APS) as an oxidant in an acidic medium. The LGP adsorbent was characterized by using Fourier Transfer Infrared spectroscopy (FT-IR). The adsorption efficiency and the adsorption capacity of the prepared adsorbent was evaluated by observing the adsorption of methyl orange (MO) as an anionic dye from aqueous solutions. Batch-sorption experiments were carried out to evaluate the influence of adsorbent dose on the adsorption of MO dye. It can be observed the optimized condition of 120 minutes, a dosage of 1.6 g/L LGP adsorbent showed the best results for the adsorption capacity (mg/g) and dye removal efficiency (%) of 20.58, and 66, respectively.

***Index Terms*—**Biopolymer; Polyaniline; locust bean gum, methyl orange, Adsorption

I. Introduction

Industrial activities like the manufacturing of leather, plastic, paper, and the processing of food produce wastewater that contains organic pollutants that have several environmental concerns [1-3]. When an organic dye of synthetic origin is dispersed in water, it can be classified as one of these pollutants since it decreases the quality of the water, making it difficult to treat due to its synthetic origin and complex molecular structure which makes it non-biodegradable [4]. These non-biodegradable dyes can cause the formation of cancer and genetic mutations in humans [1], as well as decrease the photosynthetic activity of aquatic organisms [5]. Dyes can be classified based on their particle charge after they have been dissolved in an aquatic medium. The classes include cationic, anionic, and non-ionic [6]. Methyl orange (MO) is classified as an anionic dye [2].

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There are a lot of techniques available to remove organic dyes from aqueous solutions. Some of these techniques include filtration, coagulation-flocculation, photo- and catalytic degradation, oxidation, biological treatment, and adsorption [1,7-13]. Among these, adsorption is probably the most environmentally friendly technique available to remove organic dyes from aqueous solutions as it has the benefit of completely removing the dye molecule as compared to other techniques that leave behind harmful portions of the dye [14,15]. Furthermore, the adsorption method has advantages like its simple design, effectiveness, efficiency, easy operation, economic viability, and the fact that it is insensitive to toxic pollutants [1,6,16]. In recent years, the demand for low-cost, highly effective, and environmentally friendly adsorbents have increased substantially [1,5,7].

Polyaniline (PANI) is a conducting polymer and is used in a variety of applications like antistatic and anticorrosion coating, batteries, and sensors [17-22]. Reference [20] mentions that polyaniline is also applied to adsorption processes for the removal of organic pollutants or dyes. There are several reasons why this conducting polymer has recently gained much attention. It's a low cost, simple preparation methods, well-defined electrochemistry, environmental and chemical stability, high conductivity, non-toxic nature, unique redox properties, and tunable properties are a few of them [5, 9-12]. Polyaniline as an adsorbent has limitations like its surface area and crystalline nature of its polymeric chain which can lead to the aggregation of said chains [5,23,24]. It, however, has been determined that when polyaniline is synthesized in the presence of other materials, its properties can be improved.

Natural biopolymer are eco-friendly and non-toxic [25]. The utilization of various types of natural and modified biopolymers for wastewater treatment was reported in literatures [26-29]. Locus bean gum is among the natural biopolymers, which very very rarely exploited for wastewater treatment. Locust bean gum is a galactomannan polysaccharide with a linear chain of (1 →4)-linked β-D-mannopyranosyl units with (1 →6)-linked α-D-galactopyranosyl residues as side chains [30,31]. According to [32], it was the first galactomannan to be utilized in industries like textiles, paper, cosmetics, as well as food products. It is used as a thickener, stabilizer, or gelling agent in food applications like baked goods, beverages, dairy, and processed fruit [30,33]. Its ability to form a viscous solution at low concentration, stabilize

dispersion and emulsion, and to replace fat in dairy products are some of the reasons why this polysaccharide is so widely applied [32]. Locust bean gum is natural, biodegradable, non-toxic, and has a relatively low cost. It is a polydisperse, non-ionic molecule, and therefore not affected by ionic strength, pH, or heat processing [32]. Furthermore, it has low solubility in water at ambient temperature and heat treatment is needed for it to reach its maximum solubility and viscosity [1]. Locust bean gum has proven to be a viable adsorbent in the removal of dyes from aqueous solutions whether it was used without modification [7], as a locust bean gum-based hydrogel [1], terpolymer gel composite [34], or a cryogel [33]. It was observed from literature that the adsorption performance of locust bean gum is mainly based on van der Waals forces and hydrogen bonding [7].

To the best of the author's knowledge, a locust bean gum grafted polyaniline composite has not yet been synthesized via in-situ oxidative polymerization and it will also be the first time that this composite will be used for the adsorption of methyl orange from an aqueous solution.

Hence, the present work will include the synthesis of the composite via in-situ oxidative polymerization. In addition, the adsorptive capacity for the removal of methyl orange (MO) was analyzed using a UV-visible spectrophotometer with different dosages of the adsorbent.

II. Experimental Method

A. Materials

Aniline (Rochelle Chemicals, 99%); ammonium peroxydisulfate, APS (Ace, 98%); hydrochloric acid, HCl (Ace, 32%); dimethyl sulfoxide, DMSO (Merck, ≥95%); locust bean gum, LBG (Sigma Aldrich); and methyl orange (Ace). All materials were used without any further purification. The chemical formula and structure of methyl orange is provided in Table.1

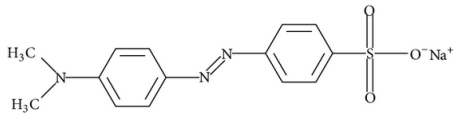
Methyl orange (Structure)	
	
Chemical formula	$C_{14}H_{14}N_3NaO_3S$
Molar mass	327.33 g·mol^{-1}
Appearance	Orange solid
Density	1.28 g/cm^3
wavelength of maximum absorbance (λmax)	470 nm

TABLE. I Structure and composition of Methyl orange

B. Synthesis of Locust Bean Gum Grafted Polyaniline (LGP)

Locust bean gum grafted polyaniline (LGP) was synthesized as previously reported by [24], with a few adjustments. 2 g LBG was dissolved in 75 mL deionized water. This solution was then heated to 70°C to completely dissolve the locust bean gum. The solution was kept at this temperature for 30 minutes under vigorous stirring. After cooling to room temperature, aniline (20.7 mmol) in 1M HCl solution was added to the LBG solution under constant stirring. The reaction mixture was stirred for 2 hours while cooling it down to below 5°C. After 2 hours, 0.6 g of APS (2.6 mmol) was added to the mixture under vigorous stirring. The reaction mixture was continuously stirred overnight. A large amount of dimethyl sulfoxide (DMSO) was added to the reaction mixture to remove the PANi homopolymer and subsequently centrifuged. The sample was then washed with DMSO until the supernatant was colorless and subsequently dried in an oven at 60°C overnight.

C. Characterization

The Fourier-transform infrared (FTIR) spectrum of the synthesized adsorbent was obtained using the IRAffinity-1 spectrophotometer of Shimadzu.

D. Batch Adsorption Experiments

The adsorption study was carried out using methyl orange (MO) as the model dye in a water solution to investigate the adsorption capacity of the LGP adsorbent. The batch experiments were carried out at 25°C in a set of Erlenmeyer flasks to study the effect of the varied adsorbent dosage (20, 40, 60, and 80 mg). 50 mg of the dye was added to 1 L of distilled water and the solution pH was adjusted to seven by adding HCl (0.1N) or NaOH (0.1N). Thereafter, the required amount of adsorbent was added to 50 mL of the dye solution and was stirred at 160 rpm. After 120 minutes, 20 mL of the samples were collected and centrifuged. The ultraviolet-visible (UV-vis) spectra of the supernatant were analyzed using a GENESYS™ 10S UV-vis spectrophotometer. The percentage removal of the dye was calculated using (1), where C_0 is the initial dye concentration (mg/L), C_t is the dye concentration at time t [35].

$$\%\ Removal = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (1)$$

The amount of dye adsorbed per unit mass of adsorbent at equilibrium was calculated using (2), where q_t is the adsorption capacity at time t, C_0 is the initial dye concentration (mg/L), C_t the dye concentration at time t, V the volume of the solution (L), and m the mass of the adsorbent (g).

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad (2)$$

III. Results and Discussion

A. FTIR Characterization

Fig. 1 illustrates the FTIR spectrum of LGP. The broad band stretching from 3540-3200 cm^{-1} can be ascribed to the hydrogen-bonded O-H stretch. In addition, the peaks at

881 cm^{-1} and 949 cm^{-1} corresponds with the out of plane hydrogen-bonded O-H. Moreover, the band at 1034 cm^{-1} can be ascribed to O-H bending and the bands between 1154 cm^{-1} and 1052 cm^{-1} are due to the C-O bond stretching which is characteristic of saccharides. The medium band stretching from 3500-3300 cm^{-1} is due to the N-H stretching of the amine group; whereas the peaks between 1250 cm^{-1} and 1020 cm^{-1} are ascribed to the C-N stretching of the aliphatic amine group. Furthermore, the band at 2927 cm^{-1} is due to the stretch vibration in reference to C-H and C-H_2, more commonly known as sp^3 C-H stretching. Also, the C=O stretching of the carbonyl group is attributed to a band of 1635 cm^{-1}, and the band at 1685 cm^{-1} can be ascribed to C=C stretching. The peak at 1306 cm^{-1} can be ascribed to the C-N and C=N stretching which is characteristic of polyaniline. Moreover, the bands at 1553 cm^{-1} and 1475 cm^{-1} are the characteristic C-C stretching of the quinoid and benzenoid rings, respectively. These bands are typically found in PANi. Lastly, the band at 811 cm^{-1} can be attributed to the out of plane bending of C-H.

Taken the above-mentioned into account, it can be concluded that polyaniline was indeed grafted onto locust bean gum.

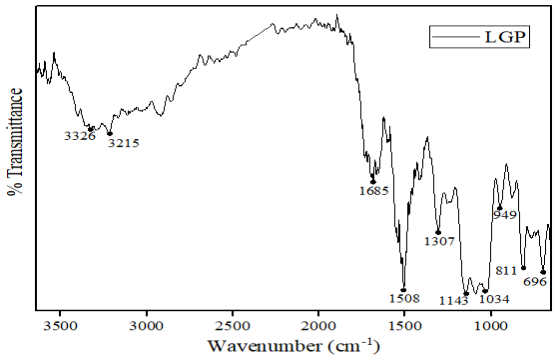


Fig 1: FTIR spectra of LGP

B. Effect of Adsorbent Dosage on the Adsorption Capacity

The adsorbent dosage is an important parameter to consider during the adsorption process as it affects the total amount of active sites available as well as the total specific surface area. This parameter was investigated by varying the adsorbent dosage from 20 mg to 80 mg (0.4 g/L to 1.6 g/L), with an initial MO concentration at 50 mg/L, pH 7, and at a temperature of 25°C. The contact time was kept constant at 120 minutes. The adsorption capacity increases with the increase in adsorbent dosage (Fig. 2) where a dosage of 1.6 g/L showed the best capacity of 20.58 mg/g. Furthermore, the percentage MO removal also increased with an increase of adsorbent dosage (Fig. 3) reaching a maximum of 66% with an LGP dosage of 1.6 g/L. Both these increases might be due to the increase in the total number of adsorption sites on the surface as the dose increases. Another reason might be that the total specific area of the surface increases with the increase in dosage.

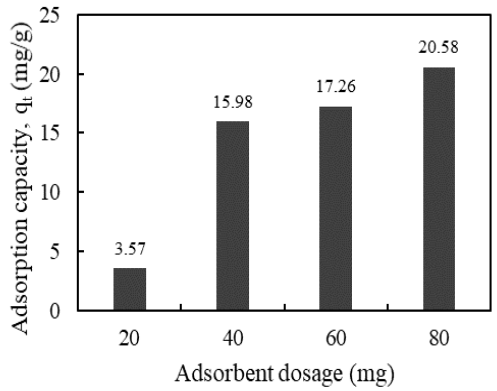


Fig 2: Effect of adsorbent (LGP) dosage on the adsorption capacity (Initial MO concentration: 50 mg/L; pH 7; T: 25°C; time: 120 min; V: 50 mL)

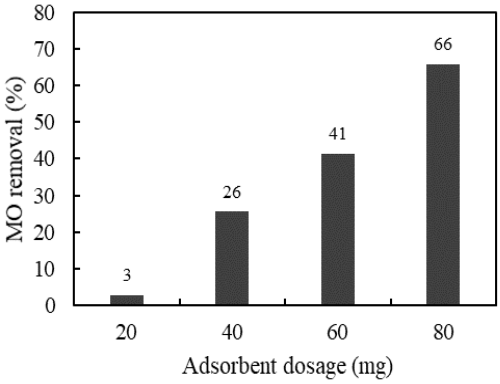


Fig 3: Effect of adsorbent (LGP) dosage on percentage removal of MO (Initial MO concentration: 50 mg/L; pH 7; T: 25°C; time: 120 min; V: 50 mL)

IV. Conclusion

In this study locust bean gum grafted polyaniline (LGP) via in situ oxidative polymerization has been successfully prepared. FTIR characterizations confirm that graft copolymerization took place. In addition, the LGP dosage showing the best results with regards to adsorption capacity and percentage removal was a dosage of 1.6 g/L, for both instances. A maximum of 20.58 mg/g and 66% was obtained for the adsorption capacity and percentage removal, respectively. Thus, LGP is an effective adsorbent to improve water quality. LGP could replace commercial polymers, with an additional incentive of reduced costs.

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