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# Green synthesis of Xanthan gum/Methionine-bentonite nanocomposite for sequestering toxic anionic dye



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#### ABSTRACT

The present paper deals with the synthesis of a novel and ecofriendly Xanthan gum/Methionine-bentonite (XG/ Meth-bent) nanocomposite and was further explored for the removal of toxic congo red dye (85%) from aqueous solution. The nanocomposite was characterized by various techniques such as SEM, FTIR, XRD, TGA and zeta potential analysis. The surface area of bentonite and nanocomposite were found to be  $23 \text{ mg}^2\text{g}^{-1}$  and  $71 \text{ mg}^2\text{g}^{-1}$  respectively. The maximum adsorption was found at pH 3, contact time 60 min and temperature 323 K respectively. The point of zero charge was found to be 7. The adsorption isotherm and kinetic were best fitted by Langmuir isotherm and pseudo-second order kinetic model with Langmuir monolayer adsorption capacity 530.549 mgg<sup>-1</sup> at 323 K. Thermodynamic studies showed that the adsorption was endothermic, spontaneous with increased randomness at solid/solution interface. Desorption with regeneration (upto fifth cycle) was best observed by NaOH.

#### 1. Introduction

Dves being colored stuff discharged from dyeing, paper and pulp, textiles, plastics, leather, cosmetics and food industries poses serious health and environmental problems [1-4]. They imparts visible pollution and decreases the reaeration capacity of the streams. They are stable and difficult to biodegrade owing to its complex aromatic molecular structure [1]. They are toxic and have carcinogenic properties that causes acute and/or chronic effects on exposed organisms [1,5]. Congo red is an aromatic dye, known as a carcinogen agent that causes skin irritation and causes allergic side effects [6]. It is the sodium salt of benzidine diazo-bis-1-naphthylamine-4-sulfonic acid having  $\lambda_{max}$  497 nm [7]. Here, it has been chosen as model dye because of its biohazard nature, severe side effects, complex chemical structure, limited biodegradability and stability towards light as well as high solubility in aqueous solution [2]. Therefore, it has become a global environmental concern to remove this dye from wastewater. Various methods such as coagulation, flocculation, reverse osmosis, biological treatment, solvent extraction etc. have been adopted for removal of dyes from aqueous solution [8]. Among the numerous techniques, adsorption has been the most versatile and widely used because of its low cost, ease of operation, efficiency, simplicity of the equipment and mostly because the adsorbent can be chosen from a wide variety of natural materials [5,8]. Adsorbents based on natural polymers are preferred now-a-days because of their low cost, easy availability and biodegradable nature [2]. Certain limitations like low surface area, poor thermal stability and lower hydrodynamic volume and; its strong synergistic effect with inorganic nanofiller forces the use of these hybrid nanocomposite in the removal of dyes [2]. The bionanocomposites are prepared by incorporation of natural clay minerals with organic modifications as inorganic nanofillers which results in intercalation or exfoliation compounds [9]. Clay minerals and specially organoclays are commonly used for environmental applications for water treatment. The organophilic properties of these organoclays enhance the capability to adsorb dyes [9]. The association of clays with amino acid and biopolymers is the great move towards green nanocomposite.

In this context, it has been reported the use of present bionanocomposite in which xanthan gum (XG) is used as a biopolymer and methionine (Meth) as a modifier to ecofriendly nanofiller bentonite (bent) for sequestering Congo red dye. Xanthan gum is anionic polyelectrolyte consisting of a cellulosic backbone with two mannose and one glucuronic acid side chains on every second glucose residue. It is stable over a wide range of pH and temperature that provides many applications in various fields of research. Bentonite contains two silica tetrahedral sheets with central alumina octahedral sheets connected with common layer of hydroxyl sheets. It has swelling behavior as large amount of water can be adsorbed in the interlayer spacing of bentonite.

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Its hydrophilic nature that allows easy fixation to biopolymers elaborates its study to functionalized bentonite with L-Methionine and xanthan gum [10]. Bentonite clay offers an attractive, non-toxic, high surface area, hydrophilic nature to easily trap biomolecule and inexpensive option for the removal of dyes [11]. In view to explore the properties of the nanocomposite in remediation of toxic dye, we have evaluated their batch adsorption studies.

Various adsorbents in literature such as Apricot stone [3], Schiff base-chitosan grafted L-monoguluronic acid [5], chitosan/organo-montmorillonite nanocomposite [7], Cationic-starch/ clay bionanocomposite [9], bentonite [11], rice husk [12], activated carbon [13], etc. have been reported for the removal of congo red dye. Keeping in view of toxic effects of dye, this study highlights the application of the synthesized XG/Meth-bent nanocomposite for efficient removal of congo red dye from aqueous solution. The nanocomposite have also been characterized using various techniques.

#### 2. Experimental section

#### 2.1. Reagents and materials

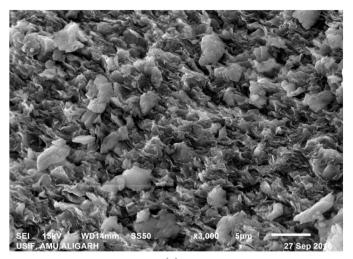
Xanthan gum and Bentonite were purchased from Sigma Aldrich, USA. L- Methionine and Congo red were obtained from CDH Laboratory Reagents, New Delhi. Sodium hydroxide (NaOH), Hydrochloric acid (HCl) and Potassium chloride (KCl) were of analytical reagent grade. All solutions were prepared with double distilled water.

#### 2.2. Synthesis of XG/Meth-bent nanocomposite

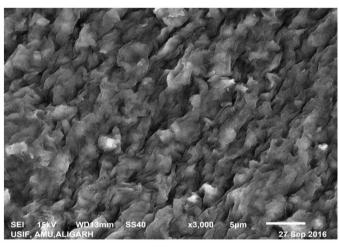
5 g of bentonite in 100 mL of distilled water was left for dispersion at 60 °C for 12 h at 420 rpm. Then, 0.1 M L-methionine solution (prepared in 100 mL of distilled water) was added to the bentonite solution and this solution was left for mixing at 700 rpm for 6 h. 3.5 g (in 150 mL of distilled water) of xanthan gum solution was added to the L-methionine modified bentonite solution and was left for subsequent mixing at 60 °C with vigorous stirring for 12 h. The nanocomposite was precipitated using 250 mL acetone. The solution was filtered, washed with water, dried in oven at 60 °C and powdered using mortar (Fig. 1).

#### 2.3. Preparation of stock solution

The stock solution of  $1000 \text{ mgL}^{-1}$  was prepared by dissolving the desired amount of congo red in double distilled water. The stock



(a)



(b)

Fig. 2. SEM images of a) Nanocomposite b) Congo red loaded nanocomposite.

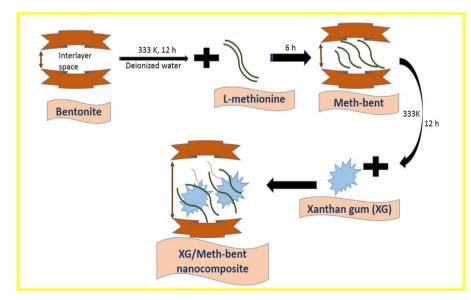


Fig. 1. Schematic illustration of the synthesis of the XG/Meth-bent nanocomposite.

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