



# Effect of functionalization on the adsorption capacity of cellulose for the removal of methyl violet



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## ABSTRACT

In this research paper a comparative study has been carried out for the removal of methyl violet dye using unfunctionalized and functionalized cellulose. The functionalization was achieved through esterification of cellulose with furan-2,5-dione. The functionalization of the cellulose was evidenced using BET, FT-IR, SEM and TGA. The adsorption isotherm data was fitted using different isotherm models like Langmuir, Freundlich, Temkin, Flory–Huggins and Dubinin–Kaganer–Radushkevich models and found to follow Langmuir and Temkin isotherm models with high value of correlation coefficients. Functionalized cellulose ( $106.38 \text{ mg g}^{-1}$ ) showed higher dye removal capability than unfunctionalized cellulose ( $43.668 \text{ mg g}^{-1}$ ). The kinetics of adsorption was investigated using pseudo first order, second order, Elovich, liquid film diffusion and intra-particle diffusion models. The mechanism of adsorption was found to follow pseudo second order rate equation. Thermodynamic studies showed that the adsorption process was endothermic and spontaneous.

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## 1. Introduction

The quest for clean water has been greatly hampered by pollution emanating from waste product being disposed in water bodies. The surging population growth and their demand for brightly coloured textiles, foodstuffs and other materials increased the production of dyes and consequently led to the release of dyes and dyestuff into water bodies due to ineffective wastewater treatment methods. It is estimated that over 200 kilotonnes of dye are released as effluent into streams from textile industries annually. Dyes are generally made up of highly toxic and carcinogenic chemicals which have adverse effects on human health as well as aquatic life [1,2]. Moreover, remediation of dye effluent is challenging because of their high solubility, non-degradable nature, diversity and often changing composition in water [3]. In most of the countries, it is a legislative requirement that industries should eliminate colours from their dye-containing effluents before disposal to water bodies. However, the removal of dyes in the effluents is one of the major problems because of the persisting nature of the colour,

stability and fastness, difficulty in the degradation and toxicity [4]. Moreover, these effluents are aesthetically highly displeasing since the dye contaminated water is highly coloured [5,6]. Many physical and chemical methods including adsorption, coagulation, precipitation, filtration and oxidation have been used for the treatment of dye-containing effluent [7,8]. Use of surfactants such as cetylpyridinium chloride (CPC), a cationic surfactant, has been reported to remove dissolved organic compound from wastewater [9]. Oxidative degradation agents like fenton reagent and ultraviolet photolysis have also been employed to mitigate dye pollution. Advanced oxidative processes such as titanium dioxide ( $\text{TiO}_2$ ), iron sulphide and zerovalent iron, have emerged as powerful degradation reagents due to their redox capabilities [10,11]. However, these agents have the drawback of producing some undesirable by-products, complete mineralization is not possible and their effectiveness is very much pH dependent. Adsorption appears to offer the best prospects over other methods of wastewater treatment. This is particularly so with regard to initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants [12,13]. Moreover, adsorption leaves behind no by-product and the adsorbents can be easily separated from the water after the treatment process. The adsorbent of choice and which is recognized by US Environmental Protection Agency (US EPA) is activated carbon since it has high adsorptive surface area. However, its use has been limited due to its high cost [9,14]. Research into the design of cheaper, environment friendly and more efficient adsorbents has been stepped up with a view of addressing dye pollution. Biopolymers, in the last decade, have been explored as highly potential

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candidates for the adsorption of textile dyes from aqueous waste [12]. These biopolymers have the advantage of easy availability, biodegradable nature, biocompatibility and low cost [15,16].

Biopolymers such as cellulose, chitin and chitosan, the two abundant resources, have been reported as emerging sorption materials for the removal of dyes. Chitin, chitosan and chitosan composites have been reported to have a very high affinity for the majority of dye groups such as reactive, direct, and disperse but they show lack of affinity for basic dyes [12,13,6]. Several polysaccharides were evaluated as adsorbents to remove dyes from synthetic dyeing effluents [17–20]. Elevated degrees of colour removal were recorded using locust bean gum (85%) and cassia gum (81%) [21]. Zhi et al. [22] utilized the films of carboxymethyl- $\beta$ -cyclodextrin and diazoresin for the removal of methylene blue. Rakhshae and Panahandeh also adsorbed methylene blue using the crosslinked products of pectin with glutaraldehyde and adipic acid [23].

Composites of clay minerals and cellulose acetate (CA) were found to possess the peculiar physical and chemical properties, although they lacked adsorptive properties [24]. The hydroxyl groups in the cellulose backbone form hydrogen bonding leading to low adsorption capacities. To improve the adsorption capacity, chemical functionalization of cellulose has been carried out through direct modification of cellulose or introduction of functional groups of active polymer into the weak cellulose polymer backbone during polymerization process [25].

In this research work, a comparison was made on the adsorption affinity for methyl violet by functionalized and unfunctionalized cellulose. Cellulose fibres were functionalized with furan-2,5-dione and the functionalization was confirmed using FT-IR and other characterization techniques. The adsorption process was monitored by varying the polymer dose and pH of the dyes solution. Adsorption isotherm and kinetic data was analyzed using different kinetic models.

## 2. Experimental

### 2.1. Materials and methods

Methyl violet, toluene, furan-2,5-dione, nitric acid, pyridine and ethanol were supplied by Sigma Aldrich, South Africa. Cellulose was supplied by a generous donation by CSIR, Forestry and Forest Products Research Centre, Durban. All the chemicals were of analytical grade and used as received.

### 2.2. Functionalization of cellulose with furan-2,5-dione

Cellulose, 5.0 g, was cleaned by soaking in 0.1% nitric acid followed by cleansing twice with double distilled water. The excess water was extracted by vacuum filtration and the dry cellulose was soaked in absolute ethanol. The mixture was then exchanged with toluene to remove water. It was then placed in a three-necked flask and 200 mL of toluene added followed by 12.5 mL pyridine. This mixture was placed in an oil bath at 65 °C and stirred mechanically for 2 h. Furan-2,5-dione, 10 g, was added and the mixture stirred for 18 h. The mixture was filtered while hot. The functionalized cellulose was purified through soxhlet extraction using ethanol, where solvent and unreacted reagents were removed. The final product was dried in a desiccator.

#### 2.2.1. Characterization

The functionalized and unfunctionalized cellulose materials were characterized using different techniques like FTIR-ATR, BET, SEM and TGA. The grafting of furan-2,5-dione onto cellulose was monitored by comparison of the FT-IR spectra of the unfunctionalized and functionalized cellulose. Perkin Elmer spectrum 100 FTIR

spectrometer with attached diamond attenuated total reflectance (ATR) in the spectral range of 600–4000  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ . Surface textural properties of the cellulose samples were determined by Surface Area and Porosity Analyzer (ASAP2020 V3.00H, Micromeritics Instrument Corporation, Norcross, USA). All the gases used for analysis were of instrument grade. Changes in the morphology of the cellulose after functionalization were evaluated using scanning electron microscope (TESCAN, VEGA SEM) under a 20 kV electron acceleration voltage. The samples were carbon coated using graphite since the materials were non-conducting. Stability of the material to thermal change was investigated using thermogravimetric analysis (Perkin Elmer TGA 4000, thermogravimetric analyzer). A mass of 10 mg was placed in platinum crucible and heated in a temperature range of 30–600 °C at a heating rate of 10 °C  $\text{min}^{-1}$ .

### 2.3. Adsorption studies

#### 2.3.1. Preparation of dye solutions

The stock solution of methyl violet of 1000  $\text{mg L}^{-1}$  was prepared by dissolving appropriate amount of dye in 1000 mL of the distilled water. The stock solution was further diluted with appropriate amount of distilled water to prepare the working dye solutions of desired concentrations.

#### 2.3.2. Adsorption of methyl violet using unfunctionalized and functionalized cellulose

The adsorption of basic dye, i.e. methyl violet from the aqueous solution using unfunctionalized and functionalized cellulose was carried out in batch mode. The adsorption experiments were done in 100 mL glass bottles. In a typical adsorption experiment 40 mg of the adsorbent was added in 50 mL of the 50  $\text{mg L}^{-1}$  dye solution. The bottles of the dye solutions were placed in a temperature controller water bath shaker and shaken for 24 h at 140 rpm. After the desired time interval, the glass bottles were taken out of the water bath shaker and the dye solution was filtered out using 0.45  $\mu\text{m}$  syringe filter. The remaining concentration of dye in the solution was analyzed using UV-vis spectrophotometer (Shimadzu, UV-2450, UV-Vis spectrophotometer) at 586 nm as  $\lambda_{\text{max}}$  for the adsorption of methyl violet. The percentage dye removal or the adsorption efficiency was calculated using the following equation:

$$\% \text{ removal} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where  $C_0$  is the initial concentration ( $\text{mg L}^{-1}$ ) and  $C_e$  is the equilibrium concentration ( $\text{mg L}^{-1}$ ) of methyl violet.

Optimization of the polymer dose was carried out with the varied amount of the adsorbents (30, 40, 50, 60, 70, 80, 90 and 100 mg) under the same experimental conditions described earlier in neutral medium. Percentage removal of dye was calculated using Eq. (1).

After the optimization of polymer dose, the optimization of pH was carried out at pre-optimized polymer dose in the dye solutions of the different pH (2.0–12.0) under the similar experimental conditions. Percentage removal of dye was calculated using Eq. (1).

Adsorption isotherm experiments were carried out at 25 °C by adding the optimized polymer dose (100 mg) in 50 ml dye solutions of different concentrations (100–500  $\text{mg L}^{-1}$ ) at pH 7.0. The bottles were placed in the water bath and shaken for 24 h. The equilibrium adsorption ( $q_e$ ) was calculated using the following equation:

$$q_e = \frac{C_0 - C_e}{m} \times V \quad (2)$$

where  $q_e$  is the equilibrium adsorption of the dye per unit mass of the adsorbent ( $\text{mg g}^{-1}$ ),  $m$  is the weight of the adsorbent (g) and  $V$  is the volume of the dye taken (L).

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