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ORIGINAL RESEARCH ARTICLE

Efficiency of chitosan catalyst in removing malachite green from their aqueous solutions

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ABSTRACT

This paper describes a green method for treating chemical contamination caused by malachite green from their aqueous solutions using chitosan as a solid catalyst under suitable reaction conditions, including dye concentrations, reaction time, catalyst amounts, and pH. Using UV-Visible measurements, complete removal (99%) was achieved under reaction conditions (80 ppm, 2 hr., 0.08 g, and pH = 11), respectively.

The removal reaction was caused by chemical adsorption on the chitosan surface by using Fourier transform infrared (FT-IR) spectroscopy. The chitosan spectrum was clearly changed after treatment as well as exhibiting absorption bands was appeared and vanished in the fingerprint region (400–1400 cm-1). Additionally, new bands were seen in the broad band of (O-H) groups at (3415.93-3462.22 cm-1) and secondary imine groups at (1604.77 cm-1) and at double-bond region (1500-2000 cm-1).

Accordingly, changes in the catalyst surface were observed both before and after the removal reaction using atomic force microscopy (AFM). Furthermore; the Nano scale characteristics, surface roughness, particle size, and topography parameters were examined. The surface area increased dramatically from (953.9 to 5224 nm²) and the mean diameter of the surface particles increased significantly from (23.70 to 54.94 nm), these changes were resulted from the malachite green adsorption on the surface.

With the arithmetic mean height increasing from (18.65 to 45.01 nm) and the root-mean-square height increasing from (20.49 to 50.27 nm), the topological parameters of the chitosan surface also showed a significant increase in roughness. The results clearly indicated that the removal reaction occurred on the chitosan surface through its high chemisorption capacity and catalytic oxidation of malachite green.

Keywords: Chitosan; malachite green dye; green treatment; solid catalyst; water environment

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1. Introduction

Despite the growing public awareness of environmental issues, especially drought and desertification caused by climate change, and conversely, the pollution of water resources through the release of various chemical wastes from industrial facilities. River water is still widely used for various activities such as water purification, and use in various vital sectors such as industry and agriculture [1].

The use of green treatment technologies is essential to address the increasing global pollution by using naturally occurring solid catalysts to remove organic pollutants of dyes and antibiotics that introduced by humans into aquatic systems, as shown in Figure (1) [2,3].

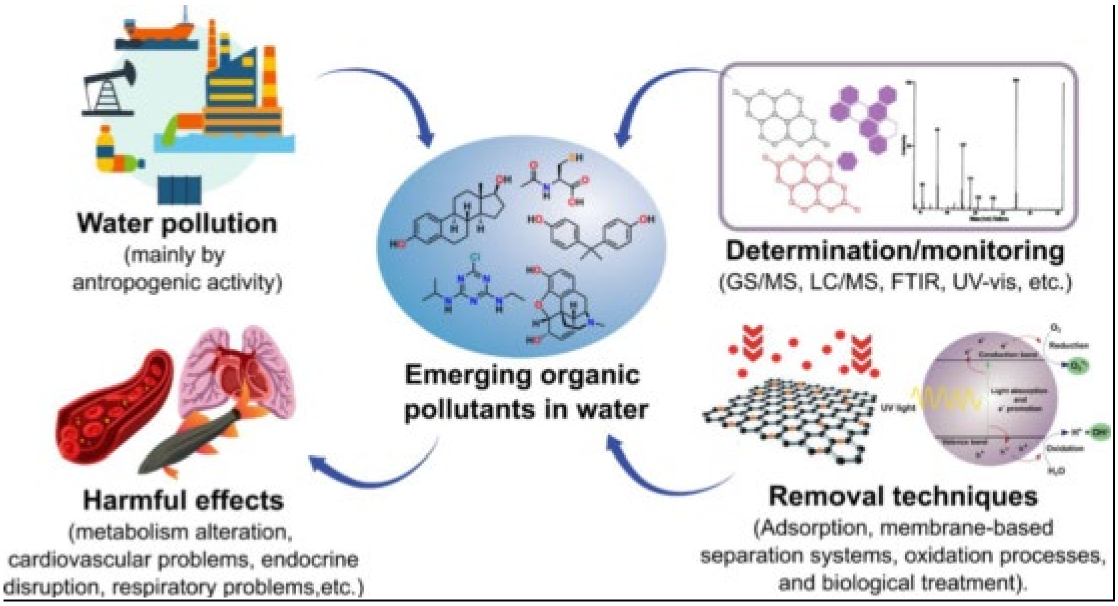

Figure 1. Describe the organic pollutants found in aquatic environment

Sustainable water management is desperately needed in this process because rivers can generally be defended as systems for transporting pollutants between their source and depositional areas [4].

Wastewater containing dyes, such as malachite green, is a byproduct of the printing and dyeing industries. The increased production of these industries has led to increased levels of dyes in wastewater. Wastewater can be treated using a variety of techniques: chemical, biological, and physical. The most effective and sustainable solutions are those that are environmentally friendly [5].

Moreover, malachite green is a synthetic, crystalline and basic dye that has unique qualities for the textile sector. It is extensively utilized in processing industries which include food, paints and dyes, leather dyeing, wool, silk, and as an ingredient in food coloring [6].

The classification of synthetic dyes is based on the fiber type from which cellulose, protein, and synthetic fibers are derived, as in fig.(2) [7].

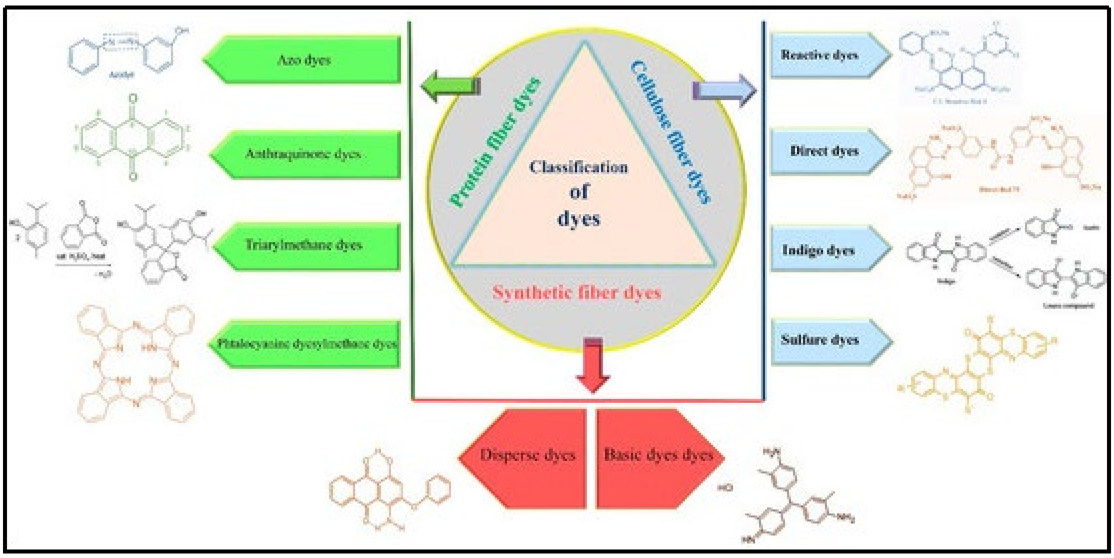

Figure 2. Classification of synthetic dyes

Chitosan is produced from chitin structurally. One of its many uses is the adsorption of dyes onto the chitosan surface by forming chemical bonds, which is the first step in the treatment reaction, followed by the catalytic degradation of dyes. It is worth mentioning that chitin is widely used as a major component in insects, fungi, and bacteria [8,9]. Compared to other polymers, chitosan has attracted considerable interest in water treatment owing to its substantial number of ($-NH_2$) and (-OH) groups as in fig (3). Chitosan and chitosan-based composites like ZnO can sequester toxic pollutants from water [10].

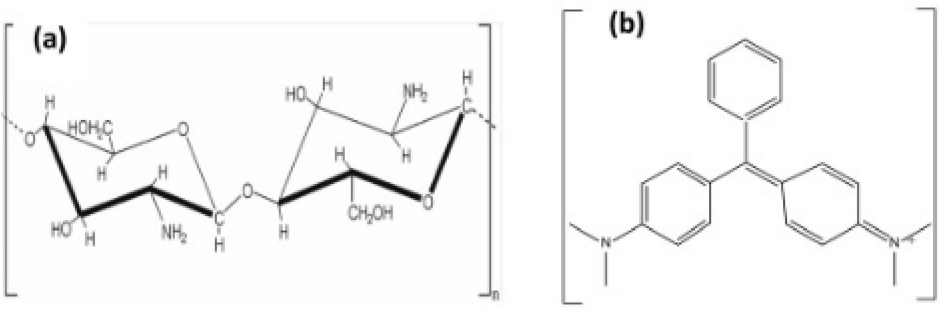

Figure 3. Chemical structure of (a) Chitosan and (b) Malachite green dye

The manuscript aimed to use a chitosan catalyst to remove malachite green from aqueous solutions. Techniques such as UV-Visible, FT-IR, and AFM were used to demonstrate the chemical adsorption and catalytic degradation on surface of catalyst.

2. Materials and methods

2.1. Preparation methods and techniques

Malachite Green (MG) is basic dye bought from Sigma-Aldrich (M) Malaysia. Deionized water that used to prepare solutions was supplied by USF ELGA water treatment system. Five known concentrations (20, 40, 60, 80 and 100 ppm) of Stock's malachite green solution were obtained. For each known concentration, 50 milliliters were taken and combined with varying amounts of chitosan (0.02, 0.04, 0.06, 0.08 and 0.1 g) as recommended by previous studies mentioned above. By using a magnetic stirrer, the solution was mixed to record the removal process. During each experiment, the concentration differences were measured and documented the color change over predetermined time periods (0.5, 1, 1.5, 2 and 2.5 hours). Additionally, the effect of pH (3-11) on the rate of removal was investigated by using HCl/ NaOH for control. Solution absorbance was measured at 620 nm. Following equation was adopted for calculate the removal (%):

$$\textit{Removal \%} = (C_o - C_t)/C_o \times 100\%$$

C_o and C_t refer to the initial and final concentrations (ppm) for the colorant MG that was removed by the adsorbent chitosan [10,11].

2.2. UV-Visible Spectroscopy

The ultraviolet-visible spectrum is responsible for the electronic transitions. These transitions occur when electrons are excited from a lower to a higher energy level, this happens in chemical bonds when molecules absorb these radiations. This spectrum exhibits bands of electron transitions ($\pi \rightarrow \pi^*$) due to the presence of π-bond in the chemical structure. Accordingly, the visible spectrum extends (400-800) nm and colored transitions ($n \rightarrow \pi^*$) are found on heteroatoms (O, N and S), when they bonded to carbon in single, double and triple bonds in aliphatic or aromatic compounds. This technique uses the Beers-Lambert law, which shows the relationship between absorbance and the concentration of the dye solution, to calculate the difference in concentrations before and after treatment with the chitosan [12].

2.3. Fourier Transform Infrared spectroscopy (FT-IR)

In FT-IR spectroscopy, the spectrum (400-4000) cm^{-1} represents a set of molecular absorption bands for a group of chemical bonds of functional groups. Moreover, it creates a unique molecular fingerprint at region from (400-1400 cm^{-1}) [13].

2.4. Atomic Force Microscope (AFM)

AFM is an important tool for examining the surface topology of solid catalyst. By allowing a computer-aided topographic map of the surface to be created as well as its various dimensions and parameters to be measured. In order to give a more comprehensive and efficient explanation of what truly transpired during the dye adsorption process on the catalyst surface, samples were examined using (AFM) both before and after malachite green treatment with chitosan catalyst.

3. Results and discussion

3.1. Effect of concentration, time, and pH of Malachite green MG over Chitosan

The efficiency of MG removal was investigated through a series of experiments using different doses of chitosan with various MG concentrations. From the results, the best removal of MG was at (20 ppm), due to increased number of binding sites surface of catalyst while the contact time plays a vital role in adsorption process kinetically where the maximum removal was at (0.5 hr.) and after that the adsorption rate lowers down to attain equilibrium state at (1.5 hr.) and after this very slight removal was observed due to saturation of binding sites [14].

Table 1. Results of Removal Experiments of Malachite Green over Chitosan [a]

MG (ppm)	R%	Chitosan (mg)	R %	Time Hrs.	R %	Ph
20	**76**	0.02	30	0.5	20	3
40	58	0.04	45.6	1.0	60	**5**
60	42.9	0.06	51	1.5	74.3	7
80	43.09	0.08	58	**2**	**99**	**9**
100	32.9	**0.1**	**64**	**2.5**	**98**	**11**

[a] ***R % =(C_o-C_t)/C_o × 100 % ;*** *C_o and C_t refer to the initial and final concentrations (ppm) for the MG.*

The best removal rate, with increasing dosage, reached (64%). The kinetic effect of chitosan on removal is now insignificant in this instance, despite the fact that the surface active sites are used less during dye adsorption. This is most likely because of its aggregation across the catalyst surface folds [15]. At lower pH values, it showed low adsorption of MG, due to presence of amino groups in chitosan which gets protonated at low pH values due to repulsion of MG molecules in acidic solution. However, when higher pH values showed basic, it showed high MG uptake due to negatively charged surface of chitosan [11].

In an alkaline (pH>7), a decrease in positive charge of chitosan amine groups occur owing to excess of (-OH) which may result in deprotonating and hence the surface charge of chitosan becomes negative [16].

3.2. FT-IR spectra for malachite green and chitosan

The stretching of (-OH) group caused an absorption peak at 3417 cm^{-1} in the spectrum, the (C-H) group underwent symmetric bending. The primary distinctive peaks were found in the fingerprint region of the absorption band 794.67 cm^{-1} which is attributed to stretching of (C=O). Aldehydes, ketones, carboxylic acids, esters 1583,56 cm^{-1}, that showed the functional groups of malachite green [17].

After adsorption of MG over chitosan. It was assigned to the stretching vibration of (OH) groups at 3415.93-3462.22 cm^{-1}, peak represented (CH) stretching vibration at 808.17 cm^{-1}, peak was for secondary imine group's at 1604.77 cm^{-1} and the stretching vibration of (C=C) groups at 1085.92 cm^{-1} as in figures (4 and 5) that a prove of chemical adsorption was happened.

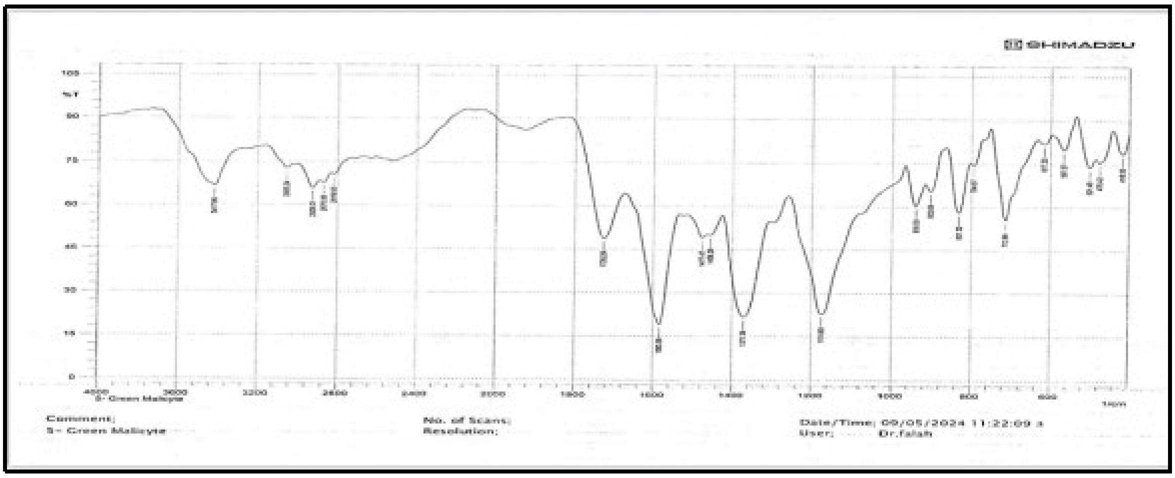

Figure 4. FT-IR spectra for Malachite Green

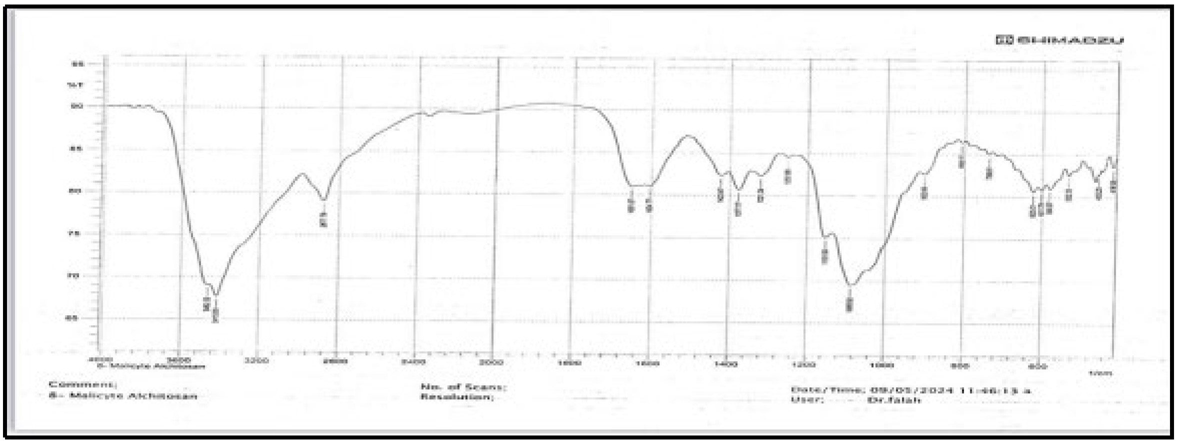

Figure 5. FT-IR spectra for Malachite Green over Chitosan

3.3. Atomic Force Microscope (AFM)

The AFM technique illustrated by analyzing catalyst particle characteristics (mean diameter and surface area) and surface roughness topology (root mean square height and mean height arithmetic).

Table 2. Particle analysis and surface roughness of Malachite Green (MG) and Chitosan before and after treatment

Chitosan and MG	Particle analysis parameters (nm)		Surface roughness analysis parameters(nm)	
	Mean Diameter	Surface Area	Root mean square height	Mean height arithmetic
MG dye	42.62	3253	53.61	46.28
Chitosan catalyst	**23.70**	**953.9**	**20.49**	**18.65**
MG over Chitosan	**54.94**	**5224**	**50.27**	**45.01**

Following treatment on the chitosan surface, malachite green adsorption caused the mean diameter of the surface particles to significantly increase from 23.70 to 54.94 nm and the surface area to dramatically increase from 953.9 to 5224 nm^2. The chitosan surface topological parameters also showed a notable increase in roughness, with the arithmetic mean height rising from 18.65 to 45.01 nm and the root-mean-square height rising from 20.49 to 50.27 nm, as taken from figures (6-13).

These results showed that chemical adsorption occurred on the catalyst surface rapidly. It is the beginning of the removal treatment through the degradation of malachite green due to the high catalytic oxidation activity of the surface.

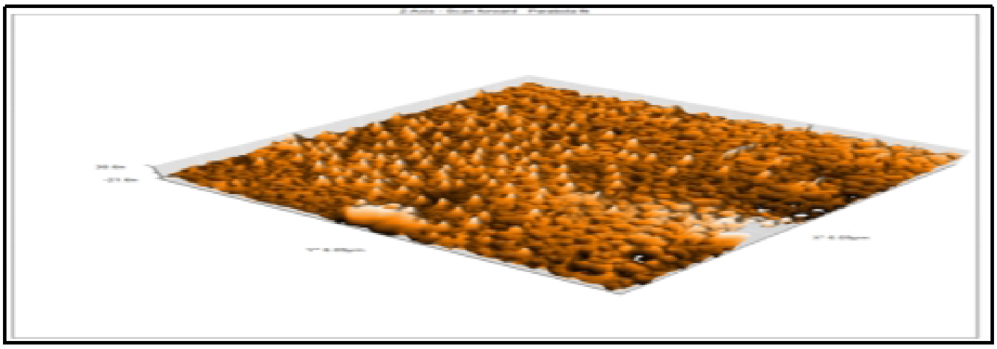

Figure 6. 3D Image of MG surface before treatment

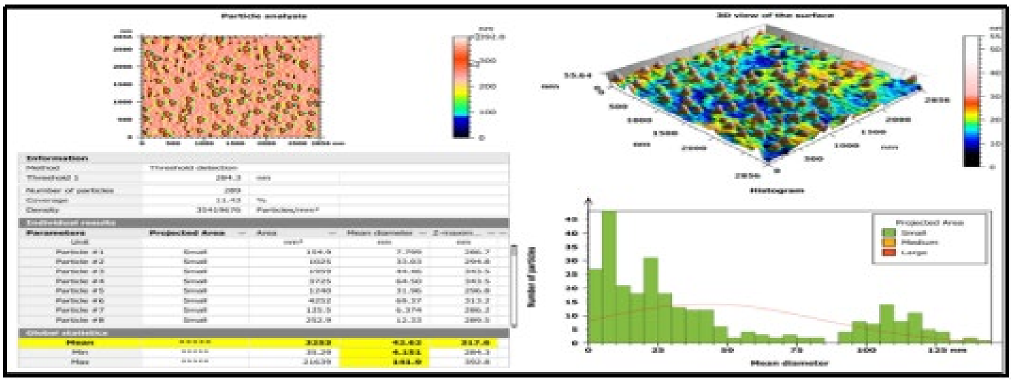

Figure 7. Particle analysis of MG before treatment

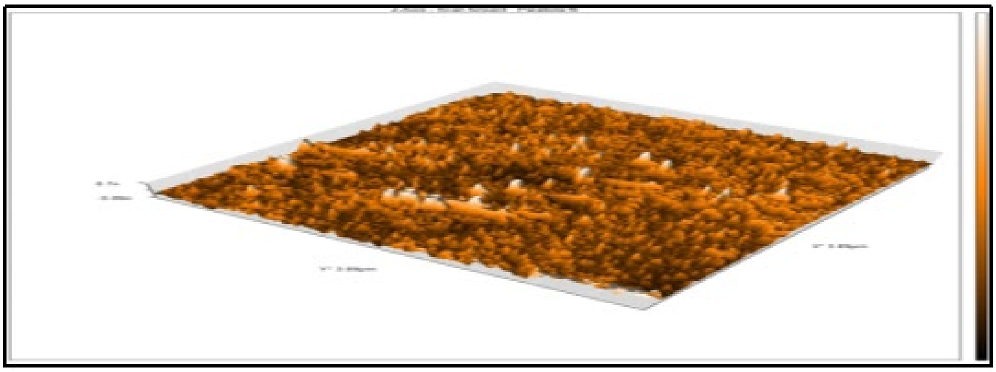

Figure 8. 3D Image of chitosan surface before treatment

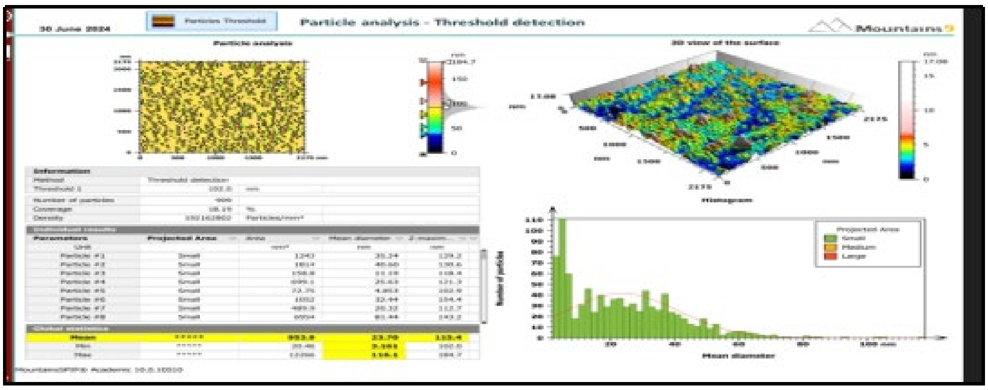

Figure 9. Particle analysis of chitosan before treatment

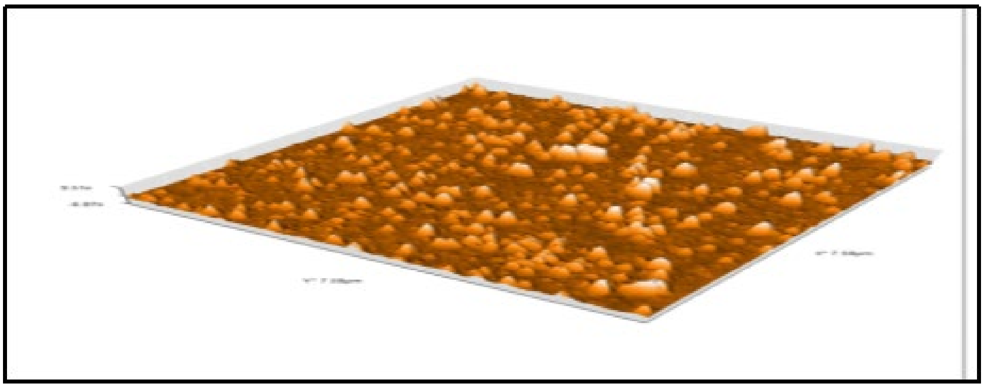

Figure 10. 3D Image of surface for MG over Chitosan after treatment

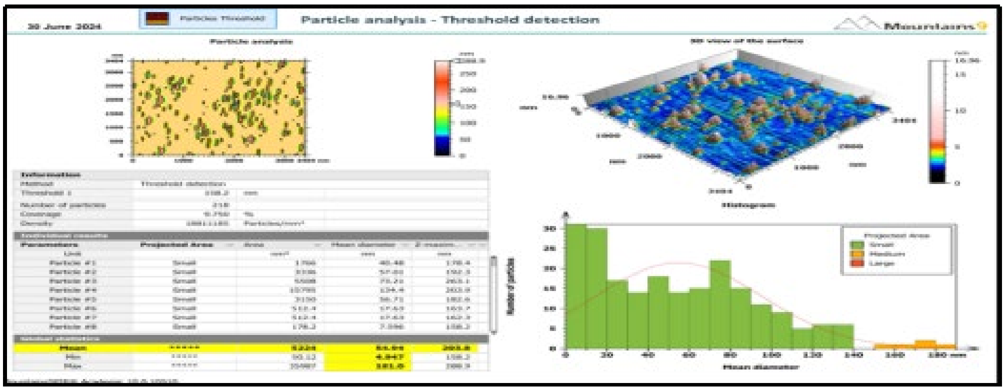

Figure 11. Particle analysis of MG over Chitosan after treatment

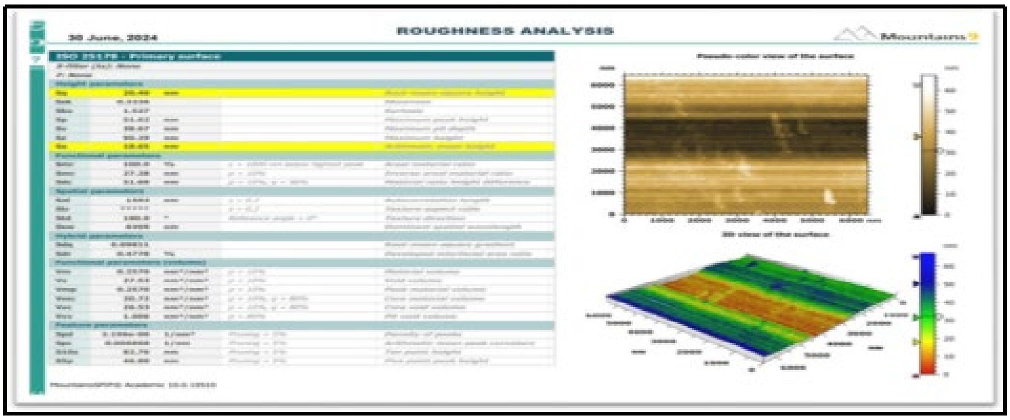

Figure 12. Surface roughness analysis of Chitosan before treatment

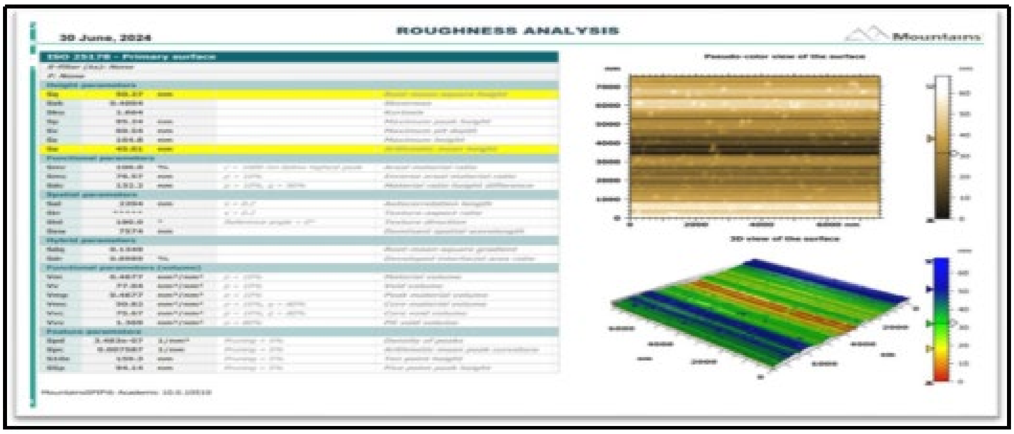

Figure 13. Surface roughness analysis of MG over Chitosan after treatment

Because of their small nanoscale size, high surface area, good crystallinity, surface homogeneity as shown from figures (6-13), these characteristics and parameters of surface topology are helpful tools. They are also used in a variety of environmental processes, such as the chemical adsorption and degradation of toxic organic compounds in contaminated water [3].

4. Conclusion

According to the results, the chitosan catalyst surface demonstrated high efficiency in removing malachite green dye under optimal reaction parameters, including catalyst dosage, pH, treatment duration, and dye concentration.

FT-IR spectra showed the appearance and disappearance of absorption bands of active groups after the removal treatment, indicating that the treatment was accomplished by chemical adsorption on the surface. AFM was used to track changes in the catalyst surface before and after the removal reaction. Significant changes in topography, particle size, surface roughness, and nanoscale properties were found to support the catalyst's treating speed. All of these results indicate that during the treatment and after chemical adsorption, oxidative catalytic degradation of the dye on the catalyst surface will occur.

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Conflict of interest

The authors declare no conflict of interest

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