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Optimizing the Surface Features of Chitosan/TiO_2 Hydrogel for Smart Nutrient Release

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ABSTRACT

In this work chitosan/ TiO_2 nanocomposites hydrogels were synthesized and characterized in order to fabricate nanocomposites hydrogels based on low cost, biological safe and eco-friendly materials. The effects of TiO_2 concentration on the structural, optical, and swelling ratio properties were investigated. The developed nanocomposites hydrogels reveal that TiO_2 nanoparticles concentration play a key role in enhancing the hydrophilic nature and structural characteristics of the obtained hydrogels. Higher TiO_2 concentrations make the hydrogel less hydrophilic and more hydrophobic. The presence of TiO_2 nanoparticles in the chitosan matrix likely modifies the hydrogel's physical structure, making it less hydrophilic and more rigid as TiO_2 concentration increases. The prepared chitosan/ TiO_2 nanocomposites hydrogels properties show that they can help in maintaining water retention for a longer duration, possibly by strengthening the gel structure and reducing the rate of water loss, which confirms their suitability for slow-release fertilizers and precision agriculture applications.

KEYWORDS: Chitosan/ TiO_2 hydrogel, nanocomposites, XRD, UV, swelling.

1. Introduction

Hydrogels have extensive industrial applications, therefore, research on the development of new class of hydrogels and the modification of already existing are significantly increasing. Hydrogels have intermediate properties of solid and liquid materials and most of their applications are related to their ability to respond with a little change in different external stimuli such as temperature, pH, salt, electrical and magnetic fields [1-4]. Some characteristic properties of hydrogels such as ability to swell in water without changing shape, inert nature towards most of the chemicals, higher loading capacity and non-toxicity make them a suitable material to use extensively in a large number of industrial applications such as slow and restricted release of various drugs and agrochemicals [5], soft tissue engineering [6, 7], making of contact lenses [8], wound dressing [9] and water purification [10]. For agriculture, water conservation is a method to increase the production and preserve the environment [11]. Water conservation and efficiency can play an important role in solving water management challenges, more efficient and more reliable improvements have been implemented over the past years [12]. Investments in agricultural water can contribute in several ways to ensuring environmental sustainability. To maximize the soil water retention is the key for yield improvement under drought stress in arid area [13]. A common method for water retention is the application of super absorbent hydrogel, which is 3D network polymers, absorbing a large amount of water compared with its weight and not dissolving in water [14]. Synthetic polymer are very important from industrial view point but the same time they are constantly increasing solid waste because majority of them are very difficult to degrade [15, 16]. Therefore, the polymers which are biodegradable can be used as an alternative of synthetic polymers. Nowadays a special attention has been paid to natural polymers. Natural polymer hydrogels are generally non-toxic, biocompatible, and biodegradable [17]. Accordingly, this study focuses on utilizing a natural and environmentally benign polymer, chitosan, to develop nanocomposite hydrogels aimed at enhancing water retention capabilities. Chitosan/ TiO_2 nanocomposites hydrogel had been taken in mind in this work to present an attempt for fabrication and characterization of hydrogel based on low cost, biological safe and environmental stable materials.

2. Materials and Methods

2.1 Synthesis of Titanium dioxide TiO_2

Titanium dioxide (TiO_2) nanoparticles were produced using a chemical coprecipitation technique. First, a solvent mixture of distilled water and ethanol at a volume ratio of 50:1 was prepared. Titanium isopropoxide (TTIP), amounting to 5 ml, was gradually added dropwise into this solvent under continuous stirring at room temperature for a duration of two hours. The resulting white TiO_2 precipitate was collected and repeatedly washed three times with distilled water and ethanol to remove impurities effectively. Subsequently, the purified nanoparticles were dried at 100 °C for 12 hours and then sintered at 400 °C for 3 hours to enhance their crystallinity.

2.2 Preparation of chitosan/TiO_2 nanocomposites hydrogels

In the preparation of the nanocomposite, 2 grams of chitosan were dissolved in 50 ml of 2% acetic acid solution, subjected to vigorous stirring and high-speed mixing. After 30 minutes, the TiO_2 nanoparticles were added to the chitosan solution. The mixture was then maintained under magnetic stirring at room temperature for 24 hours, followed by sonication at 35 °C for 4 hours to achieve a homogeneous dispersion. The resulting media was poured into Petri dishes and dried overnight at 50 °C in an electric oven. Hydrogel formation was achieved by coagulating the chitosan films in a sodium hydroxide (NaOH) bath for 24 hours. The hydrogels were then thoroughly rinsed with distilled water to eliminate residual NaOH and byproducts. Cross-linking was performed by immersing the membranes in 200 ml of a 2% (v/v) glutaraldehyde solution, with continuous magnetic stirring for 24 hours. Finally, the hydrogels were extensively washed with distilled water to remove any residual glutaraldehyde.

2.3 Characterization

The structural characteristics of the samples were further investigated through X-ray diffraction (XRD) utilizing a Shimadzu XRD-6000 diffractometer, also manufactured in Japan. The optical properties of the obtained materials were performed by a computerized double beam UV- 2300 spectrophotometer (SPECORD 200 PLUS, Analytik Jena, Germany) with 5 nm steps, at normal incidence at room temperature in the wavelength range 200 – 900 nm.

3. Results and Discussions

3.1 X-ray diffraction (XRD)

The XRD patterns for Chitosan, TiO_2, and the obtained chitosan/TiO_2 nanocomposite hydrogels are shown in fig. 1. The XRD pattern of pure TiO_2 nanoparticles (NPs) displays sharp, well-defined peaks characteristic of the anatase phase, specifically at the (101), (004), (200), (204), and (220) planes, consistent with JPDF card 01-089-4921, confirming their high crystallinity. In contrast, pure chitosan exhibits a broad, diffuse peak around 20°, indicative of its amorphous nature and disordered polymer chain arrangement. Upon incorporation of TiO_2 NPs into the chitosan matrix, the intensity of TiO_2 diffraction peaks progressively increases with TiO_2 concentration, demonstrating successful dispersion within the polymer network. Consequently, the composite hydrogel exhibits a mixed crystalline–amorphous configuration, in which the crystalline TiO_2 phase enhances overall crystallinity and contributes to a more ordered and robust nanocomposite architecture.

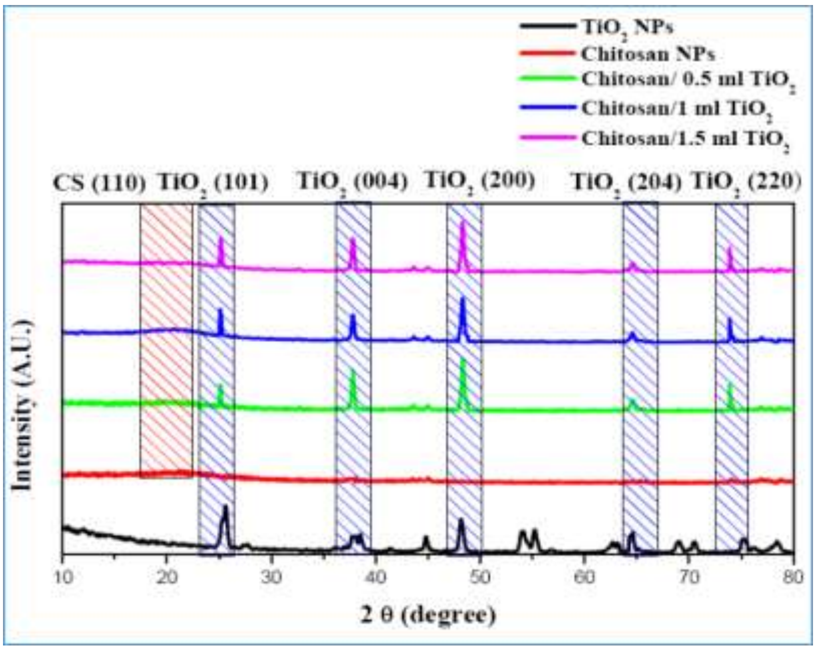

Fig. 1 XRD patterns of chitosan, TiO_2, and Chitosan/TiO_2 hydrogels with varying TiO_2 concentrations (0%, 0.5%, 1%, and 1.5%).

3.2 Optical properties

Fig. 2 depicts the absorbance as a function of wavelength for chitosan/TiO_2 nanocomposites hydrogels. The spectra of pure TiO_2 NPs reveal strong absorption in the UV region, a characteristic feature of TiO_2 due to its wide bandgap of approximately 3.2 eV. This bandgap corresponds to the energy required for electron excitation from the valence band to the conduction band, making TiO_2 an effective material for UV absorption and photocatalytic applications. While pure chitosan exhibits minimal absorption across the UV-visible range. This is attributed to the absence of significant chromophores in its molecular structure, which limits its ability to interact with UV or visible light. Consequently, chitosan's optical behavior is largely inactive in this spectral range.

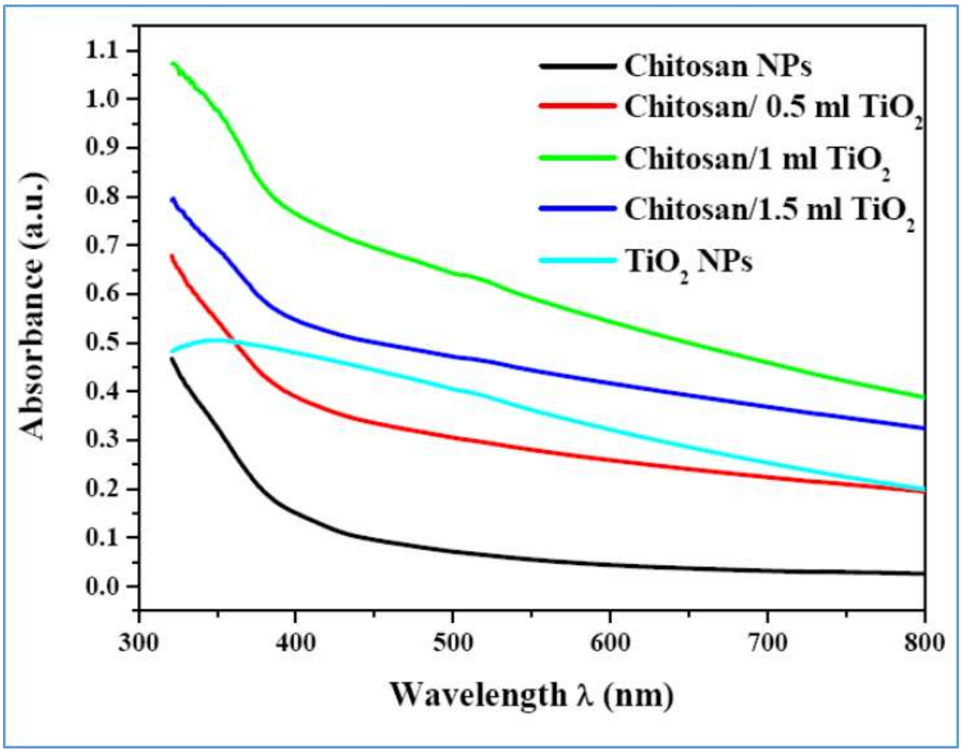

Fig. 2 UV-vis spectra of chitosan, TiO_2, and chitosan/TiO_2 hydrogels with varying TiO_2 concentrations (0%, 0.5%, 1%, and 1.5%).

Upon incorporating TiO_2 into the chitosan matrix, the UV-Vis spectra show a marked enhancement in UV absorption. This increase is directly proportional to the TiO_2 content in the composite, with higher TiO_2 concentrations leading to stronger UV absorption. This behavior indicates that the TiO_2 NPs are effectively dispersed within the chitosan matrix, contributing their optical properties to the composite. At higher TiO_2 loadings, the UV-Vis spectra reveal a noticeable red shift in the absorption edge. This shift suggests improved electronic interactions between the chitosan polymer matrix and the TiO_2 NPs. Such interactions may arise from charge transfer between the polymer and the NPs, potentially reducing the effective band gap of the composite material.

3.3 Swelling behavior of chitosan/TiO_2 nanocomposites hydrogels

The swelling behavior of chitosan/TiO_2 nanocomposites hydrogels with varying TiO_2 concentrations (0%, 0.5%, 1%, and 1.5%) was investigated over time to understand the influence of TiO_2 on the hydrogel's water absorption properties, Fig. 3. The results demonstrate a direct relationship between the TiO_2 content and the swelling ratio, highlighting the role of TiO_2 nanoparticles in enhancing the hydrophilic nature and structural characteristics of the hydrogels. Hydrogels with higher TiO_2 content (1.5%) showed the highest swelling ratio across all time points. For each TiO_2 concentration, swelling increases over time, but the rate of swelling slows as equilibrium is approached. The difference in swelling ratios becomes more pronounced with time, indicating that TiO_2 significantly influences water absorption capacity.

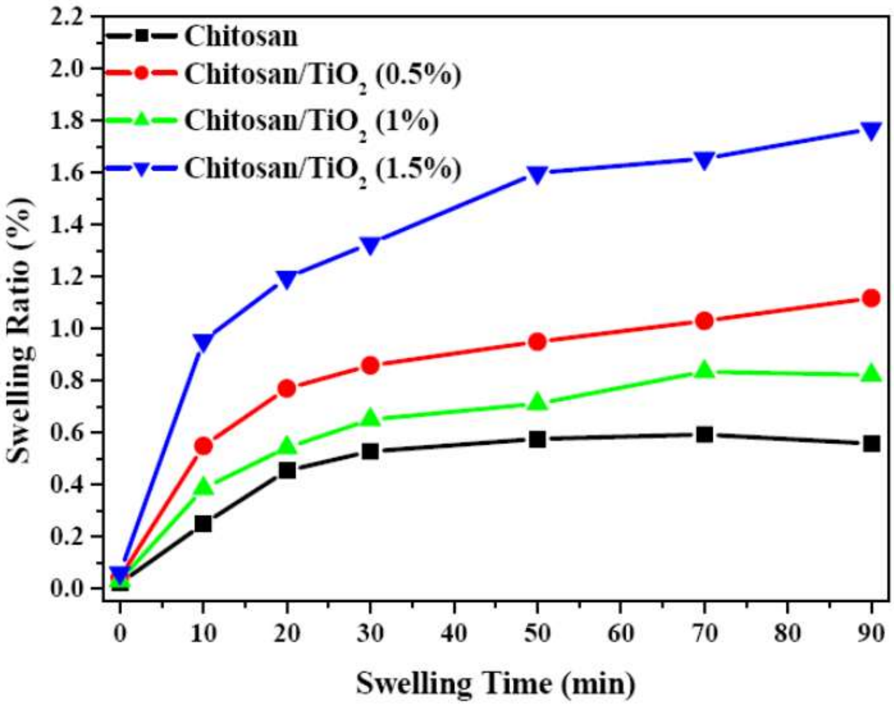

Fig. 3 Swelling behavior of chitosan and chitosan/TiO_2 hydrogels with varying TiO_2 concentrations (0%, 0.5%, 1%, and 1.5%) over time.

Hydrogels with a higher TiO_2 content exhibited a greater swelling ratio at all-time intervals. This can be attributed to the hydrophilic nature of TiO_2 nanoparticles, which promotes water retention within the hydrogel matrix. TiO_2 likely improves the porosity of the hydrogels, enabling more water molecules to be absorbed and retained within the polymer network. The results suggest that the addition of TiO_2 enhances the hydrogel's cross-linked network structure, likely due to the interaction between TiO_2 and the chitosan matrix. The improved network facilitates water absorption while maintaining structural integrity, as reflected in the consistent increase in swelling ratio with TiO_2 concentration.

Conclusion

In conclusion, the XRD and UV analyses demonstrated a synergistic interaction between chitosan matrices and TiO_2 nanoparticles. The TiO_2 nanoparticle concentration critically influenced the physicochemical properties of the chitosan/TiO_2 nanocomposite hydrogels. Hydrogels with lower TiO_2 loading exhibited enhanced rapid swelling kinetics and sustained moisture retention capacity, rendering them optimal for applications in soil conditioning and drought mitigation. In contrast, hydrogels with higher TiO_2 content provided controlled release profiles for water and nutrients, indicating their potential as slow-release fertilizer carriers in precision agriculture systems.

Authors' contributions

Hager Obeid did the experimental part wrote the original manuscript. Alaa Hassan Said analyzed the data and wrote the original manuscript. A. M. Mansour, A. A. Ebnalwaled revised the original manuscript. All authors read and approved the final manuscript.

Availability of data and materials

All the data used to support the findings of this study are included within the article. Other data are available from the corresponding author upon request

Competing interests

The authors declare that they have no competing interests.

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