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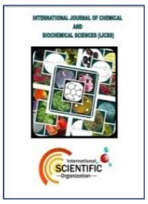

Novel Cellulose-Based Photocatalysts for Environmental Remediation: Synthesis, Characterization, and Application in Dye Degradation

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Abstract

Dye degradation photocatalysts packed with stable tin sulfide (SnS) are synthesized and characterized in this investigation. The photocatalysts are produced by incorporating SnS nanostructures into a cellulose matrix and then subjecting the mixture to a hydrothermal processing. Structure, morphology, and optical examinations were performed to evaluate the specimens. Orthorhombic form is assigned for every rise that appears in x-ray diffractograms. The SEM analyses verify the development of the discovered orthorhombic formations. The SnS nanoparticles' composition has been verified using EDS. Visible-range optical analysis reveals strong luminosity. The spectrum gaps (directly and indirectly) in optics both shift to the blue as a result of the significant quantum phenomenon. Eliminating 93 percent of the methylene red dye in the wastewater.

Keywords: Stable tin sulfide (SnS), photocatalyst, dye degradation, nanostructure, orthorhombic

Full length article

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1. Introduction

Sustainable solutions are urgently needed to address pollution issues because of the negative effects that human activity has on the ecosystem. A photocatalytic (PC) collects light energy and uses it to start chemical processes that break down contaminants into harmless chemicals. PC is a new technique that has showed significant promise for environmental rehabilitation. A possible choice among the different substances employed as PC is cellulose, a naturally plentiful and renewable polymer [1]. Plants main structural element is cellulose, a long-chain polysaccharide formed of repeating glucose units. It has numerous outstanding qualities, such as a large surface area, porosity, and biodegradability. These characteristics make cellulose a desirable material for a variety of uses, including as a catalyst support material. Significant advancements have been made recently in the creation of new cellulose-based PC for environmental cleanup [2]. The addition of metal nanoparticles (NP) is one method for enhancing the PC activity of cellulose. As electron sinks, metal NP can collect the electrons produced during the PC reaction and keep them from recombining with holes. As a result, PC activity increases and electron-hole separation becomes more effective. Metals with varied band gap energies and redox potentials, such as gold, silver, copper, and titanium, have all been employed as NP. The effectiveness and selectivity of the PC reaction can be affected by the metal used. Doping with heteroatoms is a different method to increase the PC activity of cellulose. Doping is the process of purposefully introducing impurities into a material in order to alter its electrical properties [3].

The band gap of cellulose can be expanded with new energy levels by doping it with heteroatoms like nitrogen, sulfur, or boron. Increased efficiency may result from the separation of photogenerated charge carriers made easier by these energy levels. Additionally, cellulose's electronic structure and interaction with pollutants can be impacted by the kind and quantity of heteroatoms, which can also have an impact on the selectivity and stability of the PC. Another way to increase cellulose's PC activity is by functionalizing it with organic compounds. Porphyrins and dyes are examples of organic compounds that can function as sensitizers, absorbing light energy and transferring it to the cellulose to promote electron-hole separation and boost PC activity [4, 5].

The nanostructure of tin sulfide (SnS) is amphoteric in nature. SnS semiconductor (SC) is a p-type SC with direct bandgap values between 1.39 and 2.33 eV and an indirect bandgap values between 1 and 1.5 eV. The resulting bandgap of SnS SC depends on the manufacturing process and the heat treatment temperature. SnS has a wide range of scientific interests due to its peculiar characteristics, including “low toxicity, earth abundance, and excellent chemical stability”. SnS has excellent photo-response ability and, during photodegradation, completely absorbs visible light. They were researching SnS NP' pH factor. They discussed how pH levels affect or are essential to SnS NP's PC activity. They will be able to see how the pH value concentration affects the PC activity of the SnS NP.

Study [8] discussed about the PC uses of bismuth oxyhalide-based PC in the production of hydrogen, oxygen, and other gases, the reduction of carbon dioxide (CO2), nitrogen fixation, organic synthesis, and pollution removal. But few reviews have focused on BiOBr among bismuth oxyhalides. The performance of the PC process is dominated by the PC function of the PC. The optimal PC must possess “high visible-light effectiveness, a narrow band gap energy, inexpensiveness, low recombination rate, protection, improved charge separation, and excellent stability” [9].

Light and SC are used in the PC technology. It is highly stable, non-toxic, resistant to corrosion, and does not produce secondary contamination [10]. Due to its efficient use of solar energy that is both naturally occurring and unrenewable, one of the environmentally friendly strategies for tackling the world's energy and environmental concerns is SC's PC. As such, it is a great option for removing organic contaminants from wastewater [11]. For sustainability in various energy and environmental areas, PC materials must be more accessible, affordable, and safe and using metal oxides as catalysts fit well within these qualities [12]. The most effective methods for cleaning up the environment right now, particularly when it comes to the degradation of organic contaminants in wastewater, are PC materials based on metal oxide NP. PC oxidizes and degrades organic pollutants to create SC with broad band gaps and favorable properties such as non-toxicity and stability in water by using metal oxide-based nanomaterials (NM) that have "carefully controlled structural, crystalline, and surface features." These NM are produced using carefully controlled structural, and surface, features crystalline [13]. Study [14] describes that NM as having a minimum length of 1 nm and a maximum length of 1000 nm; but, in practice, they are typically seen of as having a diameter between 1 and 100 nm. However, there is no universally recognized definition of a NM, and each organization has its own definition. For example, the International Organization for Standardization (ISO) defines NM as supplies with any external nanoscale dimension or internal nanoscale surface structure, whereas the European Union (EU) Commission defines NM as manufactured or naturally occurring supplies with particles that are either loosely bound, aggregated, or gathered and have an external dimension that ranges in size from 1 to 100 nm. Through procedures like the elimination of impurities and metals, the catalytic breakdown of toxic substances into less hazardous molecules, and the deactivation of pathogens, NM are used to purify water. Nanotechnology's recent advancements have opened up new avenues for environmental remediation, particularly in the treatment of wastewater [15].

A highly conventional, environmentally friendly, and economically effective co-precipitation process has been used to create a dual functional ZnO/CuO gas sensor and PC for use in environmental remediation. The synthesized ZnO/CuO nanocomposite showed improved PC activity, which was primarily caused by the catalyst's effective redox potential to produce h^+ and O_2^- species [16].

In order to produce Ni-doped 2D/2D layered MoS_2/g-C_3N_4 heterostructures with varying Ni concentrations, a two-step approach including hydrothermal sulfurization and liquid-phase exfoliation was carried out. The PC reduction of Cr(VI) by these materials is highly effective and stable [17]. The efficient creation of WO3-Fe_2O_3-rGO ternary nanocomposites with good photostability and recyclability using a straightforward hydrothermal process. The resulting WFG nanocomposites provide more adsorption and reaction sites, alter the valence band potential in a favorable direction, and improve the effectiveness of charge transit and separation. When exposed to solar radiation, WFG nanocomposites exhibit stronger PC activity for the dyes MB and RhB than pure and binary nanocomposites [18]. Article [19] described that “Ag_3PO_4/PDIsm” is a potential inorganic-organic Z-scheme PC with applications in PC. The photoactivity and photostability of the Ag_3PO_4/PDIsm Z-scheme PC were enhanced in comparison to those of pure Ag3PO4.

The numerous techniques that can be used to successfully create PSCs with diverse morphologies and controlled pore sizes. It has been established that the same synthetic processes can be used to make 124 semiconducting salts, in addition to a wide variety of other materials, with only small modifications, notably in the case of metal oxides. This is particularly true when it comes to the generation of materials that are conductive. As a result, metal sulfides can likewise be converted into PSCs [20].

2. Materials and methods

2.1 Materials

Experimental Ethylene Glycol (EG), Tin (II) chloride ($SnCl_2.2H_2O$), and sodium sulfide (Na2S)” were used as solvents, sulfur sources, and, tin respectively, and were not purified. These substances were of the analytical variety. 0.1M of $SnC_{l2}2H_2O$ was dissolved in 90ml of EG, and 0.1M of Na_2S was dissolved in 80ml of EG. This mixture was continuously agitated for three hours, and then it was held in an ultra-sonicator at 60 degrees Celsius for another half an hour.

A solution of 0.1M Na_2S has been added to the solution of $SnCl_2$ and $2H_2O$ in a dropwise manner. Then, the solution is stored in a vessel that has a Teflon coating and is placed in an oven at a temperature of 180 degrees Celsius. The particles that had precipitated were centrifuged and repeatedly cleaned with ethanol and distilled water. The non-woven cellulose paper fillers have been treated with SnS NP to create the reusable PC fillers. The PC degradation activity of SnS NP was investigated in the visible portion of the spectrum between wavelengths of 400 and 700 nm using anionic methylene red dye.

MR is an anionic dye, and the wavelength at which it absorbs the most light is approximately 464 nm. A solution of MR dye at a concentration of 4 ppm was made. The maximum wavelength at which MR absorbs is 464 nm, and constant UV-Vis spectroscopy measurements are made at this wavelength to determine various absorption value. The reaction was conducted in a sealed chamber that was lit by a 36 watt white LED. A UV-Vis spectrophotometer was used to measure the absorption at regular intervals while the

PC samples were submerged in the solution. With passing time, the dye's hue fades.

We assess the performance of SnS NP based on the estimated value of the rate constant (k) and photo degradation%. Under similar conditions of experimentation, the PC activity of SnS NP reduced when the pH of SnS increased from 2 to 10.

2.2 Characterization

By employing Cu Kα as a radiation source and performing scans between 2° and 90°, X-ray diffraction (XRD) data were used to study the structural properties of SnS NP. LS55 Perkin Elmer instruments were used to measure the photoluminescence. UV-VIS spectrometer readings were taken between 300 nm and 800 nm to determine transmittance and absorption across the spectrum.

3. Results and Discussions

3.1 Structural

It pertains to the physical arrangement of the cellulose-based photo catalyst, including its morphology, surface area, porosity, and particle size distribution. These structural features can significantly influence the photo catalytic performance of the material. It involves the study of the crystalline structure of cellulose-based photocatalysts. Cellulose itself has a semi-crystalline structure, and when it is modified or combined with other materials to form photocatalysts, the resulting crystalline arrangement can impact its photo catalytic efficiency. This refers to the interfaces between the cellulose-based photocatalyst and other materials, such as semiconductor nanoparticles or metal oxides. The interaction at these interfaces plays a crucial role in promoting charge separation and enhancing photocatalytic activity. Figure 1 displays the hydrothermally produced SnS's obtained X-ray diffraction peaks. All peak patterns confirm the SnS peaks, which closely resemble orthorhombic ones. The diffraction peaks for SnS is "(16.5°, [1, 1, 0]); (21.15°, [1, 2, 0]); (25.91°, [0, 2, 1]); (26.94°, [1, 0, 1]); (30.09°, [1, 1, 1]); (31.42°, [1, 3, 1]); (38.91°, [0, 0, 2]); (45.09°, [1, 1, 2]) and 50.41°". Equation (1) Of the Debye-Scherer formula was used to determine the size of the SnS crystallite. SnS NP come in a range of sizes, including 12nm, 10nm, 24nm, and 26nm.

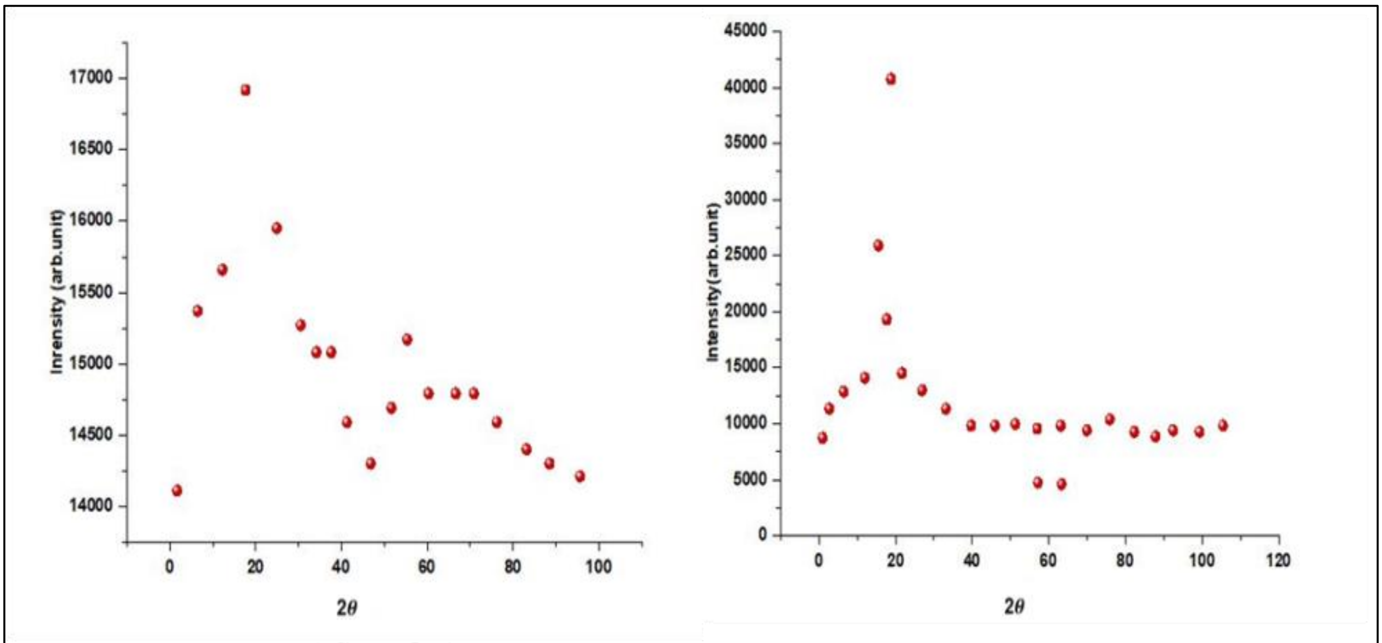
$$D = K\lambda / \beta Cos\theta \qquad (1)$$

3.2 Methyl red dye degradation using PC

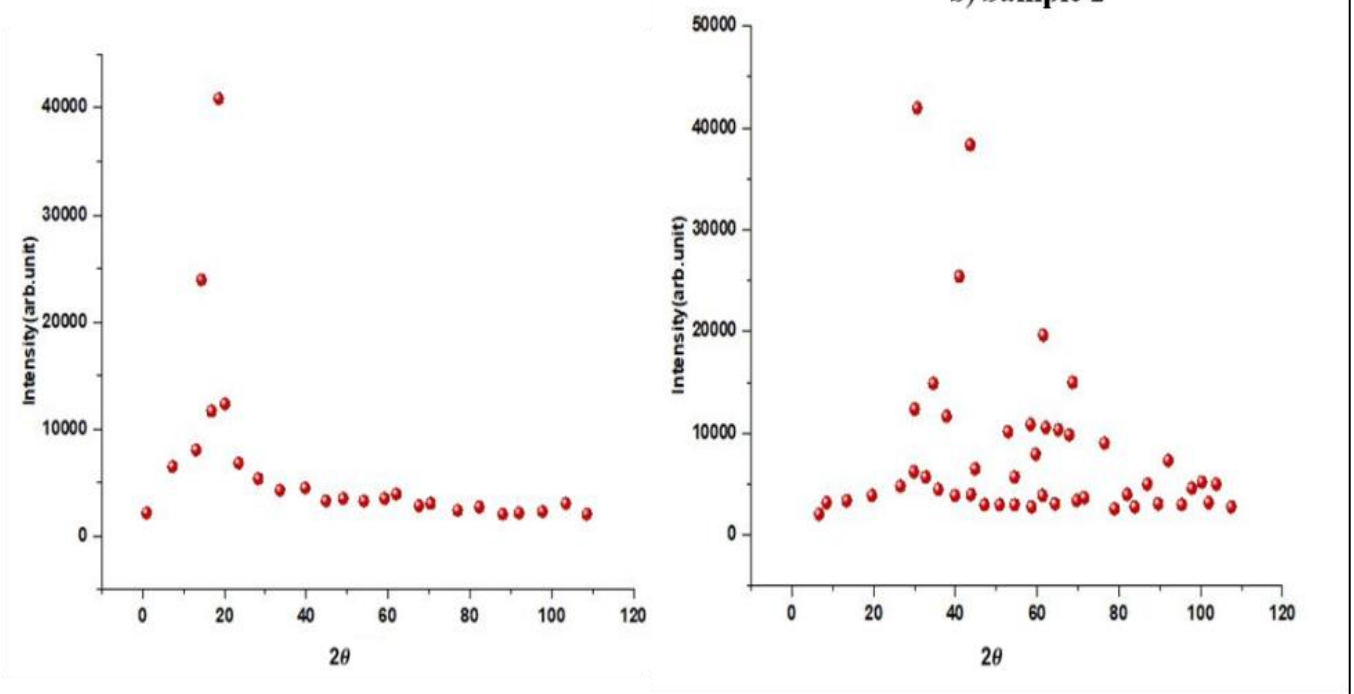
Methyl red is a commonly used dye in various industries, and its degradation is of interest due to its potential environmental impact. Photocatalysis (PC) offers a promising method to degrade organic pollutants like methyl red efficiently. Photocatalysis involves the use of a photo catalyst to facilitate the degradation of pollutants through photochemical reactions induced by light energy. The generated reactive species attack and break down the adsorbed methyl red molecules on the photo catalyst surface. This process results in the cleavage of the dye molecules into smaller, less harmful compounds or complete mineralization to CO_2, H_2O, and inorganic ions. Methyl red dye molecules adsorb onto the surface of the photocatalyst. This step allows the dye molecules to come into close proximity to the photocatalyst's active sites, enhancing the chances of interaction during the degradation process. Photocatalysis has shown promise as an environmentally friendly method for degrading various organic dyes, including methyl red. It utilizes solar energy and produces non-toxic end products, making it a potential solution for wastewater treatment and environmental remediation. However, successful degradation relies on the selection of an appropriate photocatalyst and the optimization of reaction parameters to achieve efficient and cost-effective dye removal. In Figure 2, the anionic dye's absorption is greater at sporadic pH2 values and decreases as the pH rises because the MR dye contains more charged sulfonate groups. Within 60 minutes, almost 93% of the damage has already happened.

3.3 Morphological

"Morphological" refers to anything related to the form, shape, structure, or appearance of an object, organism, or system. It involves the study, description, and analysis of the physical characteristics and external features of a subject. In biology, morphology is the study of the form and structure of living organisms, including plants, animals, and microorganisms. It involves observing and classifying their external features, such as size, shape, color, and texture. In the context of materials science, morphological changes refer to alterations in the shape, size, or distribution of particles or structures within a material. These changes can occur during various processes, such as crystallization, solidification, or phase transitions. In any scientific or technical field, "morphological characteristics" describe the physical attributes, properties, and features that are used to distinguish and classify objects or entities. Overall, "morphological" is a term widely used across different disciplines to refer to the external or physical aspects of a subject and how these aspects can be analyzed, understood, or influenced. It plays a crucial role in categorization, identification, and comprehension of various phenomena and objects in the natural and artificial world. Figure 3 depicts the SnS NP samples. Particles created with the aid of image j software are incredibly small, yet they have a surface. In Figure 3, the surface is uniformly covered in grains sized particles.

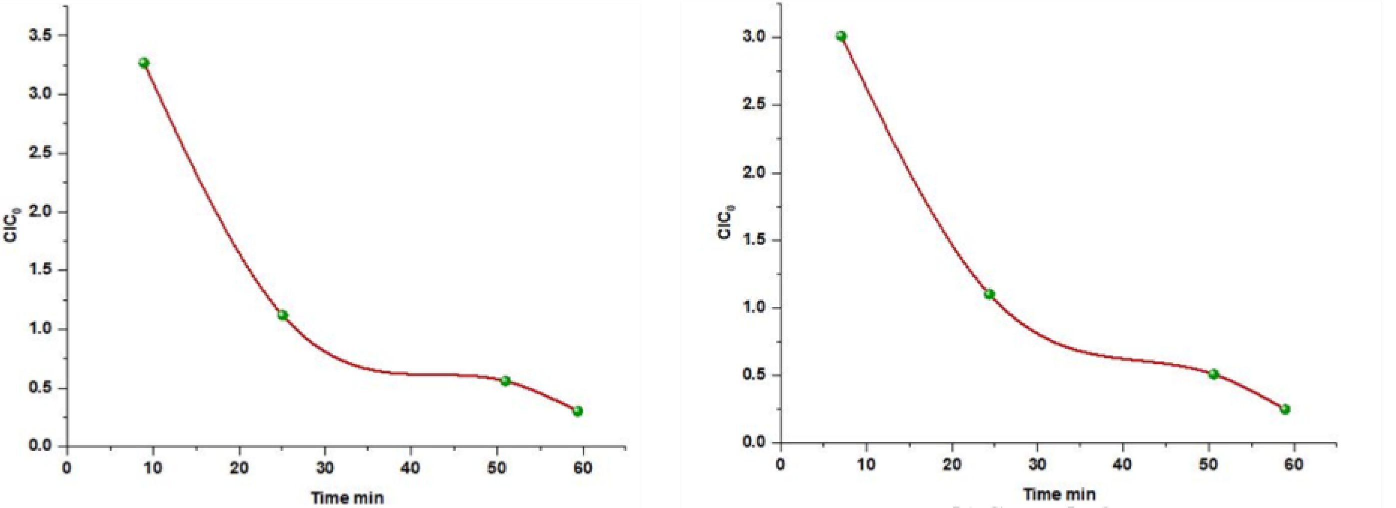


a) Sample 1 **b) Sample 2**



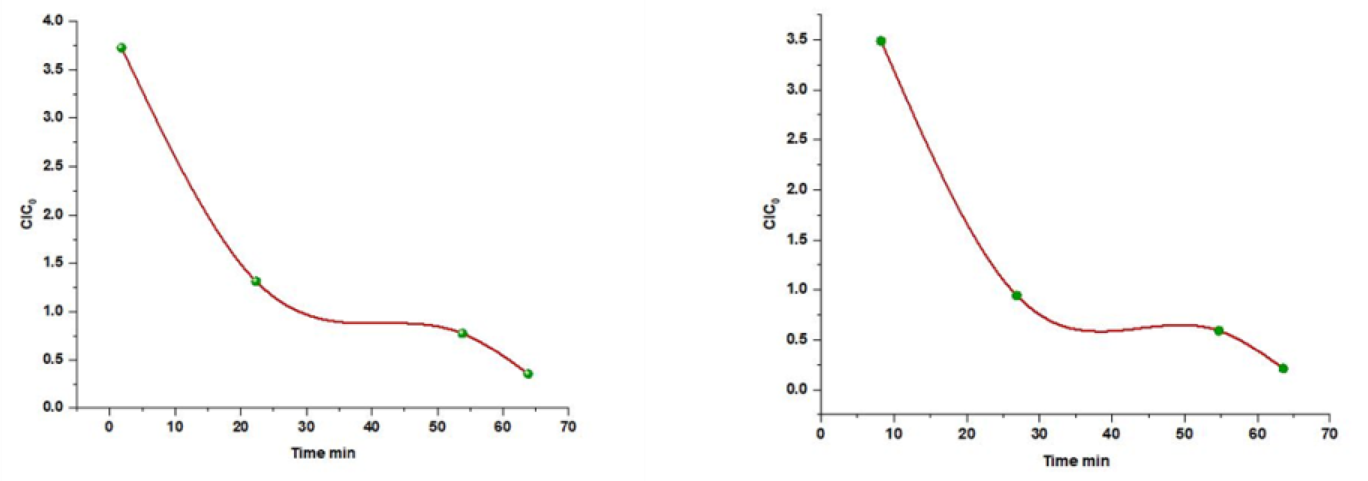
c)Sample 3 **d) Sample 4**

Figure 1: Diffraction patterns of X-ray of SnS NP



a) Sample 1

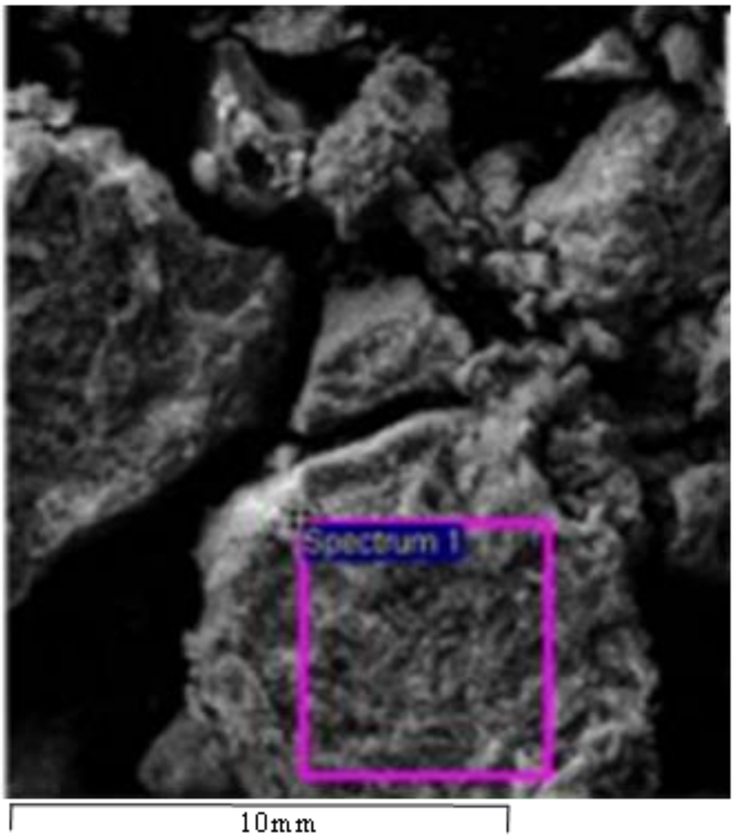
b) Sample 2



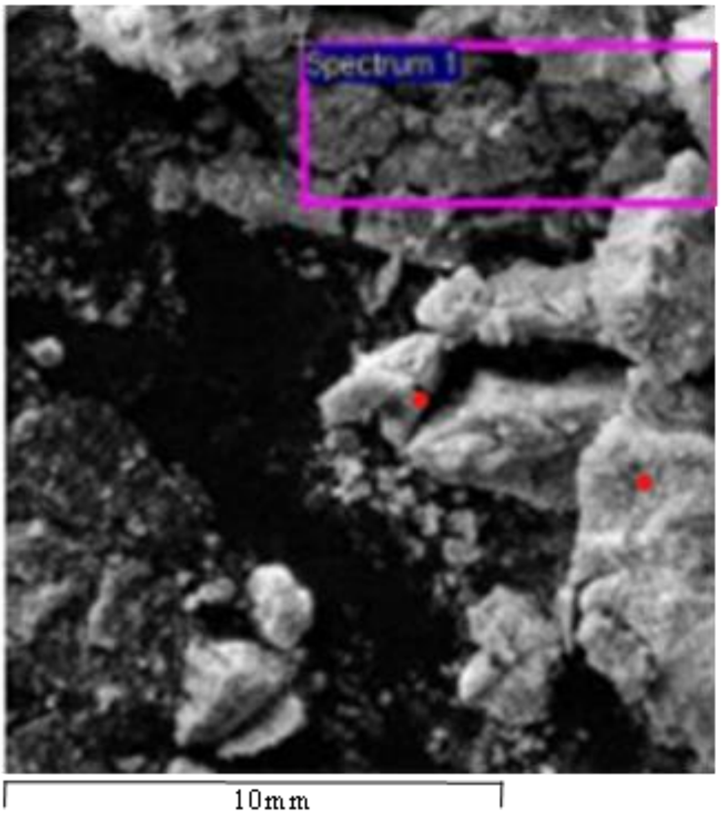
c) Sample 3

d) Sample 4

Figure 2: The amount of MR dye that is being degraded in 60 minutes during the first cycle



a) sample 1



b) sample 2

Figure 3: SEM analyses SnS NP samples

4. Conclusions

The hydrothermal development of SnS NP and inclusion in cellulose fibers for use as a PC is demonstrated in this work. As the pH values rise, the crystallinity falls. The SnS material exhibits good 93% dye degradation and stability as a PC for up to three cycles.

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