

# A feasibility study on the green synthesis of iron oxide nanoparticles using *Chlorella vulgaris* extract for photocatalytic degradation of crystal violet

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**Abstract.** Iron oxide nanoparticles have recently been proposed as an efficient and environmentally friendly material for wastewater treatment. In comparison to chemical and physical approaches, green nanoparticles synthesis method that employs microalgae or plant extract is regarded as more cost-effective and environmentally friendly. In this study, iron oxide nanoparticles were synthesised using *Chlorella vulgaris* extract, and their feasibility in removing crystal violet dye from wastewater via photocatalytic degradation was investigated. Iron oxide nanoparticles was synthesized by adding *C. vulgaris* extract to 0.1 M iron (III) chloride solution. The X-ray diffraction (XRD) peaks revealed that the iron oxide nanoparticles were crystalline in nature. The nanoparticles were also analysed using Field Emission Scanning Electron Microscope (FESEM), revealing a sphere with cylindrical shape of about 109 nm in size, with the Energy Dispersive X-ray (EDX) elemental analysis showing the highest proportion of O followed by Fe. The ability of iron oxide nanoparticles to remove crystal violet dye in the dark and in the presence of ultraviolet (UV) light was investigated. The percentage removal was consistently higher under the presence of UV lamp at all durations tested (30 – 90 minutes), indicating the feasibility of iron oxide nanoparticles to photodegrade crystal violet dye.

**Keywords:** Iron oxide nanoparticles; *Chlorella vulgaris* extract; Photodegradation; Crystal violet.

## 1. Introduction

Crystal violet (CV) is a synthetic basic dye that is widely used, and it enters aquatic systems through the effluent of textile, paint, medical and biotechnology industries. CV is well known for being mutagenic, teratogenic, and mitotically poisonous. It could have a severe negative impact on both the ecosystem and human health. The improper management and frequent discharge of CV-containing wastewater into the environment pose a potential risk to ecosystems and populations, including significant damage to aquatic systems. The accumulation of CV in the human body cause severe illness, and in extreme cases, cancer and death [1]. As a result, the removal of CV from wastewater prior to discharge is of great interest from both an environmental and economic standpoint.

Rapid and significant advances in wastewater treatment have been made in an effort to alleviate the global water pollution issues. Nanomaterials such as iron oxide nanoparticles have recently been



proposed as an efficient, cost-effective, and environmentally friendly wastewater treatment material, particularly for the removal of heavy metals and dyes [2]. Nano-sized materials with particle sizes within the range of 1 to 100 nm have large surface areas, high reactivity, easy dispersion, and excellent adsorption performance, making them appealing for wastewater treatment [3]. Due to a growing need to develop environmentally benign technologies for the synthesis of nanoparticles, it has become a topic of immense interest for researchers worldwide to identify the green synthesis route which allows for better control of the size and shape of the nanoparticles. On the contrary to chemical and physical approaches to synthesis nanoparticles, the innovative biological technique using bacteria, fungi, actinomycetes, yeast, algae or extract from plants is deemed as a more economical and environmental-friendly method in this context [4]. The interesting characteristics exhibited by plant extract and microorganisms to hyper-accumulate and biologically reduce metallic ions make them a promising candidate to produce metallic nanoparticles for detoxification and antimicrobial applications [5].

In recent years, microalgae which are non-pathogenic and ubiquitous in nature, are explored for biofuel production and synthesis of nanoparticles [6]. According to Dayel et al. [7], bioactive components such as proteins, polysaccharides, tannins and steroids in microalgae could reduce metal salts into metal nanoparticles. In the work of Arsiya et al. [8], stable palladium nanoparticles were successfully produced from the extract of *Chlorella vulgaris* through a simple, low cost, environmental-friendly route without the need for high temperature, pressure and hazardous chemicals. To date, green production of microalgae-based silver nanoparticles has become more popular for its antimicrobial activities [6-7]. However, the reports on the synthesis of other metallic microalgae-based nanoparticles such as iron oxide remain scarce in the literature. Furthermore, the use of microalgae-based nanoparticles for CV removal via photocatalytic degradation has yet to be investigated.

The viability of producing iron oxide nanoparticles using *C. vulgaris* extract was examined in the present paper. The morphology and crystallinity of the iron oxide nanoparticles produced were characterized using Field Emission Scanning Electron Microscopy (FESEM) equipped with the Energy Dispersive Spectroscopy (EDS) and X-Ray Diffraction (XRD). Subsequently, the potential of using the synthesized microalgae-based nanoparticles to photodegrade CV was explored. The present research promotes dye removal processes supporting sustainable development beyond pollution reduction. The use of green nanoparticle synthesis to reduce the use of harsh chemical and process conditions, as well as energy consumption, portrays an economically viable and environmentally friendly strategy for combating the negative effects of dye-contaminated wastewater.

## 2. Materials and Methodology

### 2.1. Synthesis of iron oxide nanoparticles

The iron oxide nanoparticles were synthesized according to the procedures reported by Mishra et al. [9] with slight modifications. 40 ml of *C. vulgaris* extract (culture medium) was added to 360 ml of 0.1 M iron (III) chloride solution. After two hours of stirring at 70°C, the solution changed colour to dark brown, suggesting the production of the nanoparticles. The mixture was then centrifuged at 20,000 x g and 25°C for approximately 30 minutes to isolate the nanoparticles. The nanoparticles were kept in an airtight container for future usage.

### 2.2. Characterization of iron oxide nanoparticles

The surface morphology of the iron oxide nanoparticles was examined using Field Emission Scanning Electron Microscopy (FESEM) equipped with the Energy Dispersive Spectroscopy (EDS) (JEOL, JSM-7800F), and the crystallinity was characterized using X-Ray Diffraction (XRD) (PHILIPS, PW 3040/60 MPD X'PERT HIGH PRO PANALYTICAL).

### 2.3 Photodegradation of crystal violet using iron oxide nanoparticles

The ability of iron oxide nanoparticles to photodegrade crystal violet was investigated using ultraviolet (UV) light (with wavelength of 395 nm). 50 mg of nanoparticles were mixed with 100 ml of 10 mg/L

CV solution. The mixture was stirred at room temperature and in the presence of UV light for 30 mins, 50 mins, 70 mins and 90 mins to determine the percentage removal. The final concentration of crystal violet was measured using UV-Vis spectrophotometry (PerkinElmer) at a wavelength of 582 nm after the stirring. The percentage removal of crystal violet was calculated using equation (1).

$$\text{Removal Percentage (\%)} = \frac{C_o - C_f}{C_o} \times 100\% \quad (1)$$

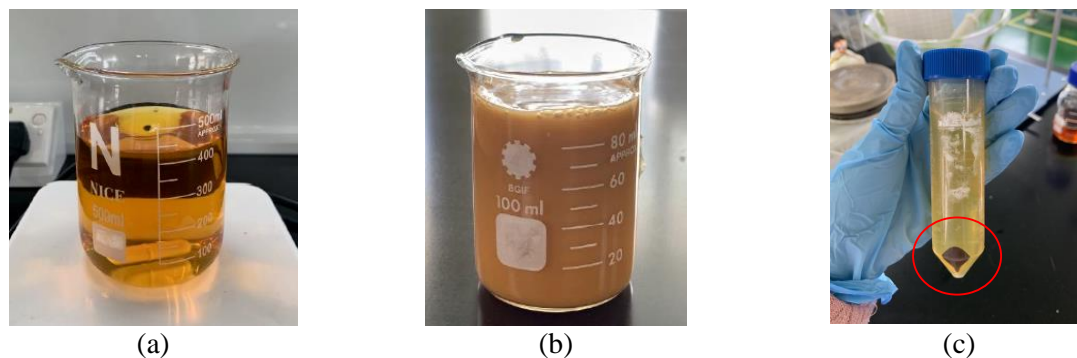
Where  $C_o$  was the initial concentration of crystal violet (10 mg/L) and  $C_f$  was the final concentration of crystal violet in mg/L.

The stirring of iron oxide nanoparticles with crystal violet dye solution was repeated in the dark. The removal percentage was compared to the results obtained when UV light was present.

### 3. Results and Discussions

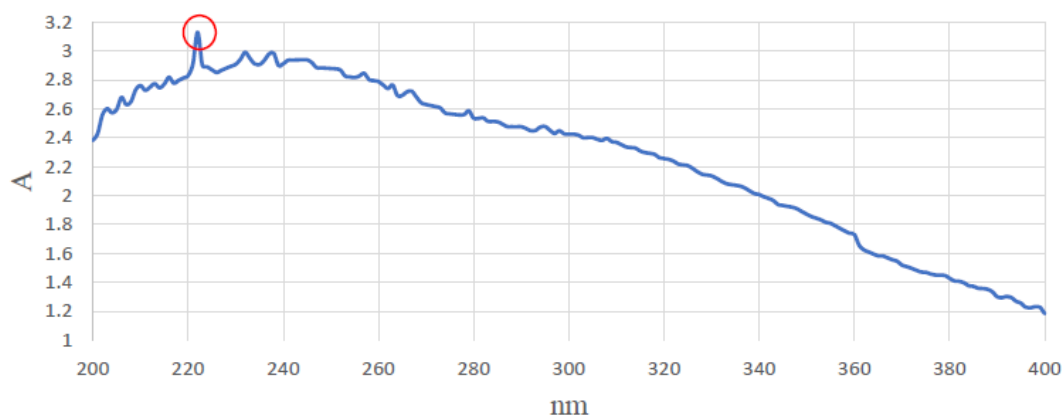
#### 3.1. Formation of iron oxide nanoparticles

The colour change of the iron (III) chloride and *C. vulgaris* mixture before and after heating is depicted in Figure 1 (a) and (b), respectively. The colour of the solution changed to dark brown, indicating the formation of iron oxide nanoparticles [10]. Figure 1(c) shows the iron oxide nanoparticles obtained after the centrifugation process.



**Figure 1.** Colour change of solution (a) before heating and (b) after heating; (c) iron oxide nanoparticles synthesized (circled in red)

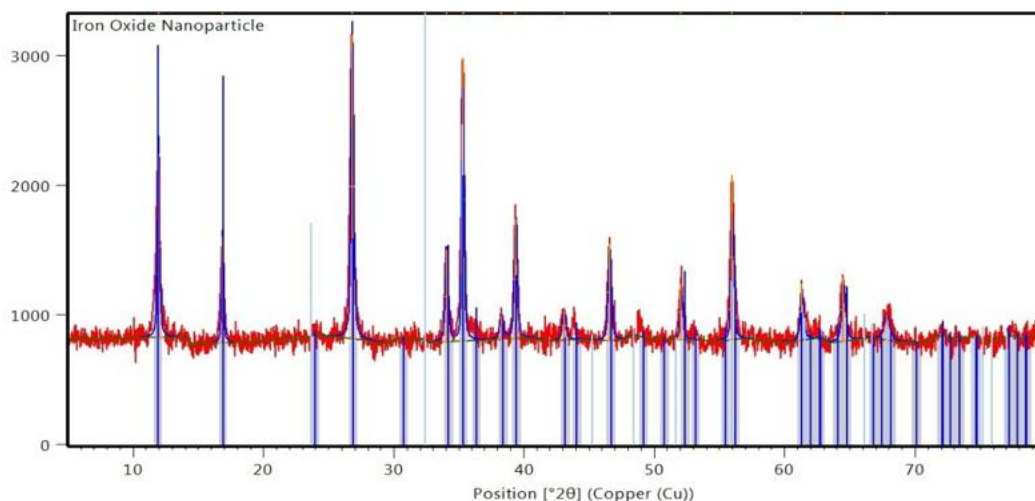
The iron oxide nanoparticles were then subjected to UV-vis wavelength scanning within the range of 200 – 600 nm (Figure 2). The presence of iron oxide nanoparticles was indicated by a sharp peak in the spectra at 223 nm. The result agreed with the findings of Pattanayak and Nayak [11], who discovered that the UV-vis spectroscopy of iron nanoparticles produced using curry leaves extract was within the range of 216 – 265 nm.



**Figure 2.** UV-vis spectroscopy of microalgae-based iron oxide nanoparticles

### 3.2. Characterization of iron oxide nanoparticles

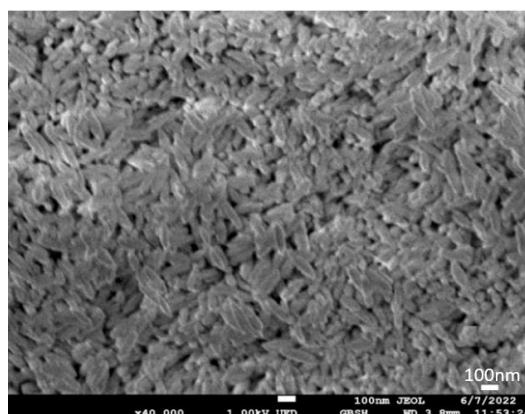
The peaks of the XRD spectra are critical for identifying the phases and properties of nanoparticles. In this context, the breadth of the peak indicates the average crystalline size of a nanoparticle, where sharp peaks indicate large crystallites and broad peaks indicate small crystallites. Figure 3 shows the XRD spectrum of the synthesized iron oxide nanoparticles in the present study.



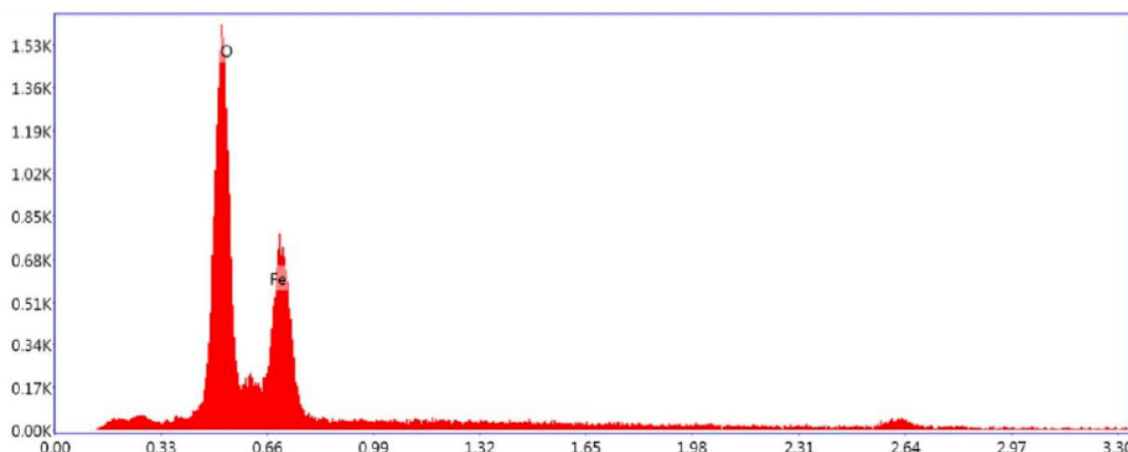
**Figure 3.** XRD spectrum of microalgae-based iron oxide nanoparticles

The XRD pattern showed diffraction peaks at  $11.96^\circ$ ,  $16.88^\circ$ ,  $26.81^\circ$ ,  $34.04^\circ$ ,  $35.29^\circ$ ,  $39.33^\circ$ ,  $46.53^\circ$ ,  $52.02^\circ$  and  $55.95^\circ$  assigned to the planes (1 1 0), (0 2 0), (1 3 0), (2 1 1), and (6 2 0), respectively. This was similar to the peaks of gamma-Fe<sub>2</sub>O<sub>3</sub> crystal with the tetragonal structure reported by Mishra et al. [9] that confirmed the synthesized iron oxide nanoparticles were crystalline in nature (correlated to ICDD data card no. 00-034-1266).

The surface morphology of the iron oxide nanoparticles was examined using FESEM and EDX was used to determine its composition. The results are presented in Figure 4 and 5, respectively. The nanoparticles were visible in FESEM images as cylindrical spheres that were about 109 nm in size. Despite the fact that the size is slightly larger than the typical range of 1 - 100 nm for nanoparticles used in wastewater treatment, the current synthesis process has yet to be optimized. In terms of EDX analysis (Figure 5), the main components found in the sample were Fe and O, which were the expected iron oxide nanoparticles.



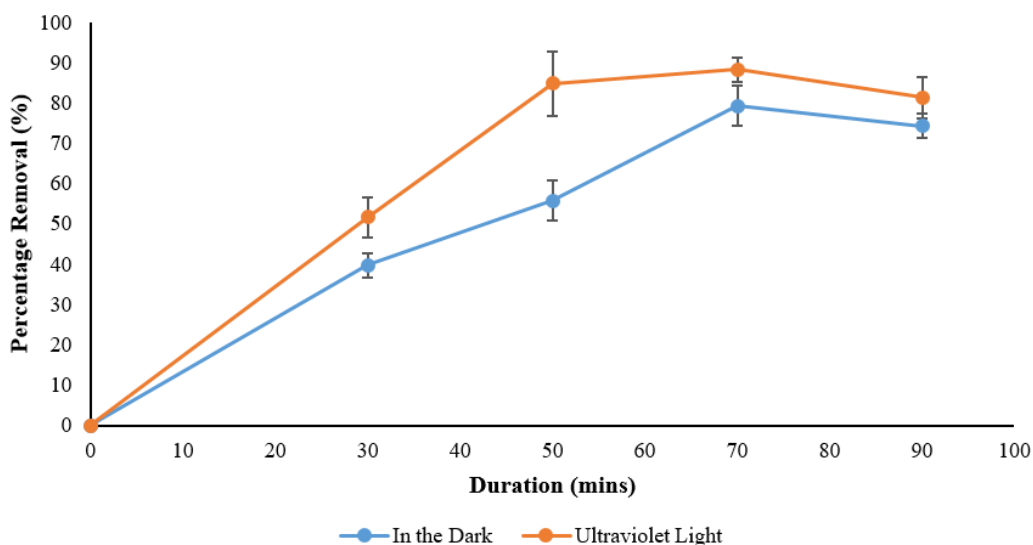
**Figure 4.** FESEM image of the synthesized iron oxide nanoparticles



**Figure 5.** EDX analysis of the synthesized iron oxide nanoparticles

### 3.3. Photodegradation of crystal violet using iron oxide nanoparticles

The performance of iron oxide nanoparticles to photodegrade crystal violet dye was evaluated. The degradation process was carried out under two conditions: first, in the presence of UV light and second, in the dark. The degradation test was performed in the dark to determine whether or not an adsorption process is taking place. In both conditions, the colour of the CV solution changed from purple to nearly colourless, indicating that the CV dye was removed from the solution. Figure 6 depicts the percentage of CV dye removed using iron oxide nanoparticles in the presence of UV light and in the dark at different time intervals up to 90 minutes.



**Figure 6.** The effect of time on the percentage removal of CV dye in the absence and presence of ultraviolet light

Figure 6 shows that the percentage of CV removed was consistently higher in the presence of UV light than in the absence of light throughout the 90-minute stirring time. When the stirring was done in the dark, the iron oxide nanoparticles acted as an adsorbent to remove the CV dye, and the CV particles became attached to the surface of the nanoparticles due to their high surface area [12]. As the stirring time increased, more CV dye particles were attached to the surface of iron oxide nanoparticles. Therefore, rapid removal of CV dye was observed within the first 70 minutes. Following that, the removal percentage was found to be slightly lower, most likely due to desorption of CV dye from the surface of the nanoparticles. This must be confirmed by measuring the pH of the CV dye solution, which

was not recorded in the current study. Contrarily, the performance of the iron oxide nanoparticles in removing CV dye in the presence of UV light was noticeably better than the dark despite the similar percentage removal trend.

Bhuiyan et al. [13] explained that hydroxyl radical will be produced by the iron oxide nanoparticles when they are irradiated by the ultraviolet light. This results in the formation of hole ( $h^+$ ) and electron ( $e^-$ ) pair. Water is transformed into a hydroxyl radical by this hole ( $h^+$ ), which causes the dye to oxidise and degrade. On the other hand, an electron forms a superoxide radical when it combines with a molecule of oxygen. The superoxide radical is further transformed into the powerful oxidising agent hydroxyl radical, which breaks down the dye into harmless by-products. These results explained the results shown in Figure 6, which showed that the synergetic adsorption-photocatalytic degradation of CV dye occurred when the CV dye solution and iron oxide nanoparticles were stirred in the presence of ultraviolet light. The present study revealed that the synthesized microalgae-based iron nanoparticles could be used as an adsorbent without the presence of light and could be potentially explored for its ability to photodegrade CV dye when UV light is available.

#### 4. Conclusions

Effective green synthesis of the microalga-based iron oxide nanoparticle was accomplished by using the *C. vulgaris* extract. Green synthesis in this research is more environmentally friendly and safer than traditional methods because no toxic chemicals are used. It is also more cost-effective because the process requires lesser resources and energy than traditional physical and chemical methods. Characterization of the iron oxide nanoparticles using FESEM and XRD analysis revealed that the nanoparticles' properties were acceptable, though optimization of the synthesis procedures may be required to achieve particle sizes less than 100 nm. The experimental results showed a significant difference in the percentage removal of CV dye from the solution when experiments were performed in the dark versus in the presence of ultraviolet light. The percentage removal of the CV dye performed under ultraviolet light irradiation was found to be greater than the percentage removal performed in the dark. The findings of the current study demonstrated that it was feasible synthesising iron oxide nanoparticles using *C. vulgaris* extract and using it to photodegrade crystal violet dye. Detailed and in-depth research on the optimization of iron oxide nanoparticle preparation as well as the photodegradation reaction is suggested to further investigate the effectiveness of green iron oxide nanoparticles in removing CV dye from aqueous solution.

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