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Methyl Orange Degradation by Green Synthesized Iron Oxide Nanoparticles by *Syzygium aromaticum*

[1]Kuruppu Achchige Pasan Gaminda, [2*]Thelma Abeysinghe, [3]Chanika Jayasinghe, [4]Rajendram Senthilnithy
[1,2,4] Department of Chemistry, The Open University of Sri Lanka, Nugegoda, Sri Lanka
[3] Department of Zoology, The Open University of Sri Lanka, Nugegoda, Sri Lanka
E-mail of the Corresponding author: *dtabe@ou.ac.lk

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ABSTRACT

Water contamination due to textile dyes is considered carcinogenic to the environment and living organisms. Many textile dyes resist degradation, and the degradation by-products of the textile dye cause severe effects on the ecosystems. Iron oxide nanoparticles were synthesized using *Syzygium aromaticum* extract to address this issue. Herein, the azo dye methyl orange (MO) degradation by the green synthesized iron oxide nanoparticles (GINPs) was investigated. The synthesized GINPs were characterized by scanning electron microscope (SEM), X-ray diffraction (XRD), and Fourier-Transform Infrared (FT-IR) spectroscopy. The results showed a successful synthesis and fabrication of GINPs by the *S. aromaticum* extract with the size ranging from nano to micro-region. A 100 ppm of MO was degraded up to 43 ppm in the first 20 min and reached equilibrium at 120 min, and the dye was degraded up to 40 ppm by the GINPs. At the equilibrium stage, 50 % of MO was degraded with a dosage (~20 ± 1 mg) of the GINPs, indicating the capability of GINPs in MO degradation compared to chemically synthesized zero-valent iron nanoparticles (CINPs).

1. INTRODUCTION

Azo dyes are utilized in numerous industries around the globe, and around 20% of the azo dyes used in the dyeing operation processes end up in wastewater (Basturk & Karatas, 2015). The chromophore N=N, known as the azo bond, is responsible for the colour of the azo dye (Phukan, 2015)manganese oxides, pumice or sand. Only such hybrid systems are likely to be sustainable. The present work focuses on the characterization of the ion selective nature of Fe0-based filters using three azo dyes: methylene blue (cationic. From the discovery of the first azo dye by Sir William Henry Perkin in 1856 (Perkin, 1856) to the present, numerous types of azo dyes have been developed (Rahman et al., 2014). As a result of the increased rate of manufacturing different dyes, the percentage of the azo dyes in the wastewater has also increased. The effluent sources with azo dyes are associated with textile, dyeing and printing, paper and ink manufacturing industries, and cosmetics. Azo dyes are very harmful to the environment and living organisms.

Azo dyes can cause skin cancers, thus posing an occupational hazard for people working in cosmetic and other dye-related industries. For decades, strategies such as ozonation, UV degradation, nanofiltration, membrane filtration, oxidation, adsorption, and electrocoagulation were employed to treat dye-contaminated wastewater (Dutta et al., 2016). However, due to the resistivity of the azo dyes, those methods are found to be ineffective in degrading the azo dyes. Further, the biological treatment using the micro-organisms was ineffective due to the low degradation activity. Hence, scientists have developed novel strategies to treat azo dye contaminations for the past few decades (Gao et al., 2019; Kobya et al., 2014). Zero-valent iron nanoparticles (ZVINPs) are recognized as potential remediation to treat azo dye contamination among these methods (Iravani, 2011). Scientists discovered that zero-valent iron could reduce the azo bond (N=N) of the azo dye, causing discolouration (He et al., 2012). Over time, different strategies were developed to synthesize ZVINPs, including chemical and physical approaches. However, utilization of these methods to synthesize ZVINPs is limited due to the expense and toxicity of the chemicals. Therefore, green synthesis emerged as an alternative approach to synthesizing ZVINPs due to its cost-effectiveness, eco-friendliness, non-toxicity, and utilization of bio-renewable natural sources (Huang et al., 2014). In green synthesis, various parts of the plant, such as leaves, seeds, flowers, roots, *etc.,* are used to prepare the green extract. The polyphenolic compounds in the green extract could act as a reducing agent to reduce metal ions and minimize the aggregation of the nanomaterials by acting as a capping/stabilizing agent. Therefore, various green extracts have been utilized to develop novel nanomaterials for various applications over time, and the functional properties of the green synthesized nanomaterials depend on the compounds available in the green extract. Furthermore, the size of the green synthesized nanomaterials significantly depends on the capping/stabilizing agents in the green extract (Chen et al., 2011).

Herein, our primary objectives are i) synthesis of novel iron oxide nanoparticles (GINPs) using *Syzygium aromaticum* (clove) buds extract, ii) characterization of the GINPs by SEM, and FT-IR analysis, and iii) evaluation and comparison of the methyl orange degradation efficiency by the GINPs and CINPs. To the best of our knowledge, this is the first study that reports on the degradation effect of methyl orange in the presence of green synthesized iron nanoparticles using *Syzygium aromaticum* extract.

2. MATERIALS AND METHODS

2.1. MATERIALS

Ferric chloride hexahydrate (≥99 %, $FeCl_3.6H_2O$), Sodium borohydride ($NaBH_4$), and methyl orange

(85%, $C_{14}H_{14}N_3NaO_3S$) were purchased from sigma aldrich. Clove buds were collected from local farms. Distilled water was used to prepare all solvents required for the experiments.

2.2. GREEN SYNTHESIS OF GINPS

A weight of 1 g of purified clove buds was added to 300 mL of distilled water. The solution was heated to 80 °C and stirred till the volume was reduced to 100 mL. The solution was filtered using gravity filtration and allowed to cool down to room temperature. 0.1 moldm^{-3} $FeCl_3.6H_2O$ solution was mixed with clove bud extract at a volume ratio 1:2, and stirred for 30 min at 60 °C. The colour of the solution instantly changed from yellow to black. A 50 ml of 0.1 moldm^{-3} $FeCl_3$ solution was mixed with 25 ml of the black colour solution, and the pH was adjusted to pH 10 with NH_4OH. The solution

mixture was continuously stirred for another 30 min at 60 °C. Finally, the black colour iron oxide particles were collected by gravity filtration and washed with ethanol and distilled water to remove any residual compounds of the extract. The particles were dried using a vacuum oven for 12 hrs at 50 °C. Zero-valent iron particles (CINPs) were chemically synthesized using a method reported by Rahman et al., 2014 using $FeCl_3.6H_2O$, and $NaBH_4$.

2.3. BATCH EXPERIMENT - METHYL ORANGE (MO) DEGRADATION EFFICIENCY

A 100 ppm solution of MO was prepared by dissolving 25 mg in 250 mL of deionized water. Further, a calibration plot was developed using concentrations of 5, 25, 50, 75, and 100 ppm solutions from each dye to determine the unknown concentration of the MO solutions.

Batch experiments were conducted using GINPs and CINPs. A 25 mL of MO solution (100 ppm) was incubated with 20 mg of GINPs particles separately in 50 mL polypropylene plastic vials fitted with plastic caps. The solution was mixed using a thermo incubator at 150 rpm at 25 °C. One of the vials was withdrawn at a specific time interval (0, 20, 40, 60, 100, and 120 min) and the solution was filtered through Whatman filter papers (Grade 1) to remove the particles and measure the residual concentration of MO in the solution. Same procedure was followed using CINPs to evaluate the MO degradation efficiency.

3. RESULTS AND DISCUSSION

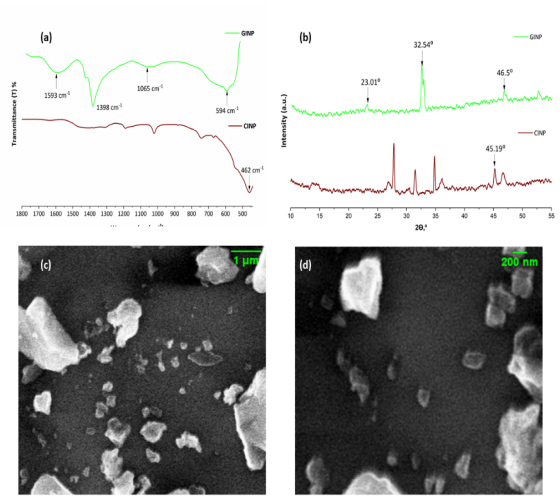

Figure 1. (a)FT-IR spectrums of the GINP and CINP, (b) XRD pattern of the GINP and CINP, SEM images of GINP (c) 10 KX, and (d) 25 KX magnification

The FT-IR analysis was carried out to determine the functional properties of the green synthesized iron nanoparticles (GINPs). According to Figure 1(a), the peak at 594 cm^{-1} corresponds to the Fe-O stretching vibrations, confirming the formation of GINPs by the components available in the clove extract. Further proving that the clove extract functions as a reducing and capping/stabilizing agent. The sharp peak at 1065 cm^{-1} and the peak at 1593 cm^{-1} are attributed to the C-N stretching vibrations of aliphatic amines and the C=C aromatic stretching vibration of the GINPs, respectively. The sharp peak at 1398 cm^{-1} corresponds to the -CH_2 groups (Parthipan et al., 2021; T. et al., 2020; Zhang et al., 2011)biocorrosion inhibition efficiency of Syzygium aromaticum (clove. The existing

findings confirm the fabrication of GINPs by the polyphenolic compounds in the clove extract. According to the Figure 1(a), the peak at 462 cm^{-1} corresponds to the Fe-O stretching vibration of the CINPs. The XRD pattern (Figure 1(b)) of the GNIPs exhibits a peak at 2Θ = 22.95°, which is a characteristic absorption peak for polyphenols in clove extract and value is in accordance with the reported data. The XRD pattern of the GNIPs shows characteristics peaks at 32.67°, and 45.75°, which correspond to magnetite (Fe_3O_4), and zero - valent iron (α-Fe), respectively. And the XRD pattern of the CINPs exhibits a peak at 45.31° which is attributed to α-Fe (Huang et al., 2014). Therefore, both XRD and FT-IR data confirm the GINPs' functionalization by the clove extract's polyphenolic compounds. The morphological characteristics and size of synthesized GINPs were analysed using SEM images as shown in Figure 1. Our findings indicated the successful synthesis of GINPs using the clove extract. The SEM images supported the FT-IR analysis data. SEM images of GINPs (Figure 1(c) and 1(d)) show that GINPs are irregular in shape with a size distribution from nano to micro-region due to aggregation (Smuleac et al., 2011). Further, the broad size distribution of the GINPs from nano to micro-region might occur due to the lower concentration of the capping agents in the clove extract.

3.1 BATCH EXPERIMENT - METHYL ORANGE (MO) DEGRADATION EFFICIENCY

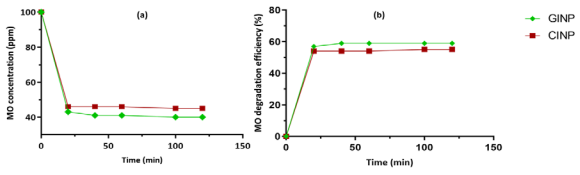

Figure 2. (a) MO concentration in the presence of GINPs and CINPs with time and (b) MO degradation ficiency of the GINPs and CINPs

MO degradation by GINPs can be separated into rapid removal and gradually slower stages until the equilibrium is achieved with time. According to Figure 2(a), the concentration of the MO declines with time and reaches an equilibrium stage at 120 min. Upon the 20 min incubation with GINPs, the initial concentration of the MO solution reached 43 ppm and 40 ppm at 120 min. Moreover, with the CINPs the initial concentration of the MO solution reached 46 ppm and reached 45 ppm at 120 min. Similarly, as shown in Figure 2(b), MO degradation efficiency by GINPs and CINPs reached 57 %, 54 % at the 20 min interval, and 59 % and 55 % at the equilibrium stage, respectively.

4. CONCLUSIONS

In summary, a novel synthesis of the iron oxide nanoparticles was achieved successfully by *Syzygium aromaticum* extract. The FT-IR analysis of the GINPs confirms the fabrication of the GINPs surface by different functional groups in the clove extract. According to the SEM images, the GINPs are irregular in shape and show a size variation from nano to micro-region due to the aggregation. The GINPs show a good potential compared to CINPs in degrading methyl orange dye, which can be used to improve water quality. The findings indicate the possible modification of the GINPs by optimizing the reaction conditions. Further, studying and characterization are required to analyse the reactivity of the GINPs synthesized using clove bud extract. Further, the removal and degradation of various pollutants in wastewater are currently investigated.

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