PHOSPHATE REMOVAL USING GREEN SYNTHESIZED IRON NANOPARTICLES BY *Syzygium aromaticum*

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Abstract

Water quality is mainly linked to wastewater contaminants and the number of contaminants in the water provides a good indication of the water quality. Among these contaminants, accumulation of the phosphorous in the water bodies promotes the eutrophication process. Phosphorous is a non-renewable mineral, therefore it's crucial to recover phosphorous from the wastewater. This study investigated the green synthesis of nano zero-valent iron particles (GZVI) by Syzygium aromaticum (clove) extract as a sorptive material to remove phosphate from wastewater. The Fourier Transform Infrared spectroscopy (FT-IR) and scanning electron microscope (SEM) characterized the green synthesized novel nanomaterial. The FT-IR analysis data confirms the formation of the zero-valent iron particles by the clove extract and the fabrication of the particles with various compounds such as polyphenols in the extract. According to the SEM images, the GZVI exhibits an irregular spherical shape with a size ranging from ~67 nm to micro level due to the cluster formation. The batch experiment was conducted using ~20 ± 1 mg of GZVI with a phosphate solution with an initial concentration of 20 ppm. According to the batch experiment, phosphate concentration was reduced to 11.9 ppm within the first 10 min and reached 9.7 ppm upon the 60 min incubation. The phosphate removal efficiency by GZVI at 10 min reached 40.59 % and reached 51.32 % at the equilibrium stage. Further, the application of the GZVI to remove phosphate exhibits a promising solution for eutrophication treatment.

Keywords: Green synthesis, *Syzygium aromaticum*, Phosphate removal, Eutrophication

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INTRODUCTION

Phosphorus is an essential macronutrient for the growth of plants and organisms. The phosphorus level in water is a good indication of the water quality. The major phosphorus-discharging sources contributing to excessive phosphorus in the water bodies are industrial, agricultural, and municipal wastewater runoff. Phosphate has become a pollutant due to the excessive use of fertilizers, and phosphorus is also a major constituent in detergents. Phosphorous in the wastewater has several forms, such as inorganic phosphates ($H_2PO_4^-$, HPO_4^{2-}, and $PO_4^{3-)}$, organic phosphates, *etc.* The build-up of phosphorus in the aqueous system promotes eutrophication in the water bodies. Eutrophication is identified as a severe environmental issue affecting the water quality of enclosed water bodies. In the eutrophication process, the uncontrollable growth of the algae consumes the oxygen in the water bodies and affects aquatic plants and animals adversely. (Z. Zhu et al., 2013)

However, phosphorus is a limited and non-renewable resource crucial for producing fertilizers. (J. X. Cao et al., 2016) Therefore, investigations have been focused on developing novel materials to remove and recover phosphate from wastewater before release into the water bodies in the environment. Different techniques have been developed for the past few decades, utilizing ion exchange, reverse osmosis, adsorption, and chemical precipitation. (Anirudhan et al., 2006) However, adsorption is the most widely used method to remove and recover phosphate compared to other methods due to the simple process, cost efficiency, and effectiveness in removing and recovering phosphate (D. Cao et al., 2016).

Recently, iron-based materials have been employed for phosphate removal from water bodies. Among those materials, nano zero-valent iron particles (nZVIs) have emerged as an effective sorptive material for phosphate removal due to the higher intrinsic reactivity of its surface sites (Dutta et al., 2016; Iravani, 2011). Different strategies have been developed for the past few decades to synthesize nZVIs. However, drawbacks such as high energy consumption, expence, the requirement of sophisticated laboratories, *etc*., associated with these conventional approaches limited the use of those strategies. Hence, green synthesis has been recognized as an alternative strategy to develop novel nZVI due to its cost-effectiveness, eco-friendliness, bio-degradability, and non-toxicity. The nZVIs synthesized using green extracts have been employed as a remediation for eutrophication over the years (Lin et al., 2017). Green synthesis received much attention due to using natural sources (Das & Eun, 2018; Huang et al., 2014) and many research groups report the utilization of green extracts to develop novel nanomaterials (F. Zhu et al., 2018). Scientists discovered that the components such as polyphenols/caffeine available in the green extract have emerged as an alternative reducing agent for the synthesis of nZVI. In addition, polyphenols/caffeine can also act as a capping agent to minimize aggregation behavior. This feature of the green extract reduces the aggregation and the oxidation of the nZVI particles (Chen et al., 2011). Different green extracts promote various reactivities of the green synthesized iron nanoparticles (FeNPs) (Makarov et al., 2014; Raveendran et al., 2003). The current study aims to synthesize FeNPs from *Syzygium aromaticum* (clove) bud extract and characterize the synthesized FeNPs (GZVI) using SEM and FT-IR analysis. Further, the ability of the FeNPs in phosphate removal was evaluated.

METHODOLOGY

Materials

Ferrous sulfate heptahydrate (99%, $FeSO_4•7H_2O$), Potassium phosphate monobasic (99%, KH_2PO_4) were purchased from sigma aldrich, ammonium vanadate (v) (99%, NH_4VO_3) was purchased from Dae-Jung and ammonium heptamolybdate tetrahydrate (98%, $(NH_4)_6Mo_7O_{24}.4H_2O$) was purchased from chem labs. Clove buds were collected from local farms in Sri Lanka. Distilled water (DI) was used in all experiments.

Green synthesis of GZVI

Clove buds were cleaned using distilled water and dried in an oven. A weight of 1 g of clove buds was added to 300 mL of distilled water, and the mixture was stirred and heated to 80 °C until the volume was reduced to 100 mL. The GZVI particles were prepared by mixing clove extract with 0.1 mold^{-3} $FeSO_4•7H_2O$ solution at a volume ratio of 2:1 and stirred at 60 °C for 30 min. The reaction mixture colour changed immediately from yellow to black, indicating the formation of GZVI. Afterward, GZVI particles were washed with ethanol and distilled water. Finally, particles were vacuum dried at 50 °C for 12 hrs.

Batch experiment - phosphate (PO_4^{3-}) removal efficiency

Batch experiments were conducted to evaluate the removal of PO_4^{3-} using the green synthesized nZVI (GZVI). The experiment was performed using a fixed dose of GZVI (~20 ± 1 mg) and was added into a series of 50 mL vials containing 25 mL phosphate solution with an initial concentration of 20 ppm. The pH of the phosphate solution was kept at their initial pH values, and solutions were agitated at 150 r/min at a temperature of 298 K. Relevant vials were withdrawn at fixed intervals (0, 10, 20, 30, and 60 min) until equilibrium was reached (60 min). Afterward, the supernatant was filtered through Grade 1 Whatman filter papers to remove the particles. The residual phosphate concentration in the solution was measured using a UV-Vis spectrophotometer. Determination of the PO_4^{3-}concentration in solution was carried out based on the vanadate/molybdate method or yellow method. In an acidic medium, the ortho-phosphate ions (PO_4^{3-}) react with ammonium molybdate and ammonium vanadate to form a yellow ammonium phosphoric vanadomolybdate complex which is measured at 450 nm.

RESULTS AND DISCUSSION

FT-IR analysis

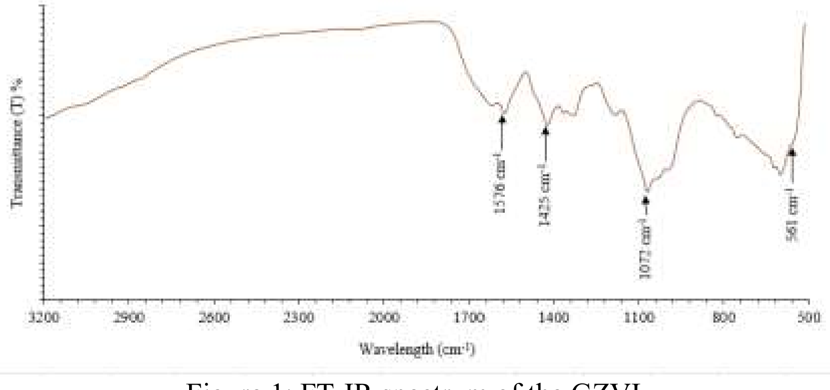

Figure 1: FT-IR spectrum of the GZVI

The Fourier-Transform Infrared spectroscopy of the GZVI was measured in the wavelength range of 4000 cm^{-1} – 400 cm^{-1}. According to Figure 1, the peak at 1576 cm^{-1} corresponds to the C=C aromatic stretching vibration of the GZVI as shown in Figure 1. The sharp peak at 1425 cm^{-1} represents the $-CH_2$ groups and the sharp peak at 1072 cm^{-1} corresponds to the C-N stretching vibrations of aliphatic amines. The peak at 561 cm^{-1} corresponds to the Fe-O stretching vibrations. This confirms the formation and fabrication of FeNPs using clove extract as a reducing and capping agent.(Parthipan et al., 2021; T. et al., 2020; Zhang et al., 2011)

SEM analysis

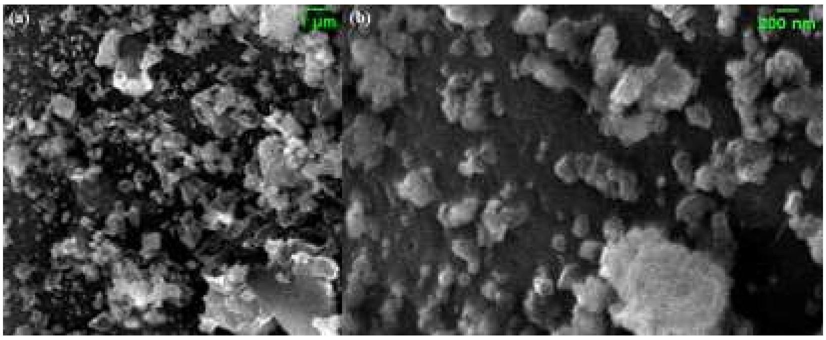

Figure 2: SEM images of GZVI (a) 5 KX, and (b) 25 KX magnification

The morphology and size of iron particles were illustrated by SEM analysis as shown in Figure 2, this indicated the effective synthesis of nanoparticles using the green extract. Which is re-confirmed the FT-IR analysis data. SEM images of GZVI (Figure 2(a) and 2(b)) show that GZVI particles are irregularly spherical-shaped nanoparticles with an average diameter of around 67 nm. (Smuleac et al., 2011) However, wide size distribution from nano region to micro-region occurs due to the lower capping/stabilizing ability of the polyphenolic compounds in the clove extract.

Batch experiment - phosphate (PO_4^{3-}) removal efficiency

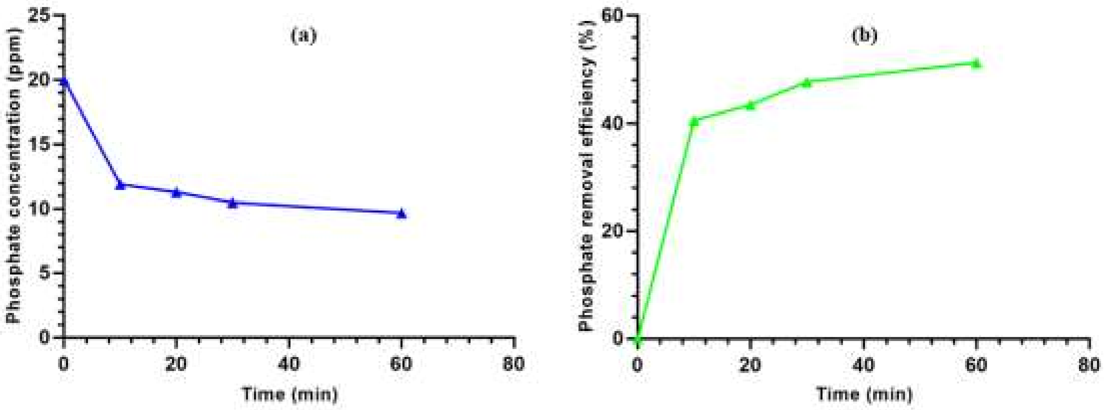

Figure 3: (a) Phosphate concentration and (b) Phosphate removal efficiency of the GZVI

According to Figure 3, the phosphate removal process by GZVI particles could be divided into two stages; a) rapid removal stage and b) gradually slower stage until the equilibrium is achieved with the time. As shown in Figure 3(a), the concentration of the PO_4^{3-} decreases with time and reaches an equilibrium at 60 min. The phosphate solution's initial concentration (20 ppm) reached 11.9 ppm upon the 10 min incubation and reached 9.7 ppm at the equilibrium stage. Similarly, as shown in Figure 3(b), phosphate removal efficiency by GZVI at 10 min reached 40.59 %, and at the equilibrium stage, phosphate removal efficiency by GZVI particles reached 51.32%.

CONCLUSIONS/RECOMMENDATIONS

Here we report the successful synthesis and fabrication of the zero-valent iron nanoparticles using *Syzygium aromaticum* extract. The FT-IR data confirm the attachment of the different functional groups onto the GZVI, and SEM images of the GZVI particles are in irregular spherical shape and size range from nano region to micro-region. Green synthesis is a simple, eco-friendly, cost-effective, and time-efficient approach for the synthesis of nanoparticles compared to conventional synthesis methods. The green synthesized GZVI using clove bud extract effectively removes phosphate from the aqueous systems. Further, studying and characterization are required to analyse the GZVI synthesized using clove bud extract.

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