Green Synthesis of Zero Valent Iron Nanoparticles from *Spinacia oleracea* (spinach) and Its Application in waste water treatment

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Abstract: "Nanotechnology" could help in solving the problems concern with water purification and quality. Zero valent Iron Nano-particles are widely used in the field of environment remediation because of its capacity to remove pollutants, fast reaction kinetics and to treat ground water by forming a permeable reactive barrier of zero valent iron to intercept and declorinated by hydrocarbons such as trichloroethylene in ground water**.** Spinacia *oleracea* leaves extract was used for synthesis of zero-valent Iron nanoparticles. The current study carried out on FeNP synthesis at room temperature or hydrothermal route by mixing plant extract with metal salt solution in a fixed ratio. Synthesized nano-particles were characterized by UV-visible spectroscopy and phase contrast microscope. As per our knowledge, this is the first study that evaluates the efficiency of zero-valent iron nanoparticles synthesized from *Spinacia oleracea* leaves extract for treatment of municipal waste water in terms of COD and BOD.

Key Words: Zero valent iron nanoparticles, Phase contrast microscope, UV visible spectra, CPD and BOD reduction.

INTRODUCTION

Nanotechnology is one of the emerged branch with a great potential and boost nowadays. Materials with dimensions 1-100 nm offers the wide range of bioremediation application because nanoparticles provide increase surface area to mass ratio. It can be divided into three categories: treatment and remediation, sensing and detection, and pollution prevention. Nano scale zero valent iron has become a valuable material for its environmental remediation abilities [1, 2, 3]. Zero valent iron is a particle with average particle size 10-100 nm and a specific surface area of 20-25 m2/g. Iron in oxidation state 0 is very unstable, thus reactive and represents one of the strongest reducers [2, 4]. High reactivity and relatively large surface area facilitate to combine processes like reduction, absorption and coagulation into one technological step. Reaction products are ferrous and ferric oxides and hydroxides that are commonly found in nature. Those advantages make the technology environment-friendly. Bio based methods might be a greener option for designing the nanomaterial with reduced environmental impact. Green biosynthesis of nanoparticles performs dual functionalities. They act as both reducing and capping agent are of much interest and promising. The current study infers the use of zero valent iron (nZVI) nanoparticles for wastewater treatment and bioremediation. The present study evaluates the efficiency of zero-valent iron nanoparticles synthesized from *Spinacia oleracea* leaves extract for municipal wastewater analysis.

MATERIALS AND METHODS

2.1 Materials

Ferrous chloride was purchased from HI media of analytical grade and used directly without any purification. *Spinacia oleracea* leaves were collected from the local farm of Rajkot, Gujarat, India. All the experiments were performed using Deionized (DI) water. Preparation of *Spinacia oleracea* leaves extract *Spinacia oleracea* leaves collected from the local farm of Rajkot was drawn in the laboratory and washed thoroughly with deionized water to remove the dirt and sundry. The extract was prepared by boiling of 6g of leaves powder at 60 ºC in boiling water bath [3, 4, 5].

2.2 Preparation of Iron Nanoparticles from leaves extract

FeNPs were synthesized by adding the extract to 0.1 M FeCl3 at the volume ratio 2:3 at 10 ºC in continues magnetic stirring for 30 min. The immediate appearance of black colour indicated the reduction of Fe+3 ions. Then the solution was centrifuged at 5000 rpm for 10 min in cooling centrifuge at 5 ºC. The pellet was dissolved in deionized water followed by characterization was done using UV- Visible spectra and phase contrast microscope [6, 7, 8].

2.3 UV Visible spectrum analysis

UV visible spectroscopy analysis infers the reduction of pure Fe^{+3} ions to Fe° by taking the aliquots (0.3 ml) of zero valent iron nanoparticle solution which was diluted in 3 ml distilled water. Systronics 118 was used for UV-Vis spectral analysis at the range of 200-700 nm. Absorption peak was observed between 400-450 nm regions due to the excitation of surface Plasmon vibrations in the FeNPs solution, which is identical to the characteristics UV-visible spectrum of metallic Iron and it was recorded [3,4].

2.4 Phase contrast microscopy

The morphological features and size of the nanoparticles were analyzed with the help of Phase contrast microscope DM750, Leica. The reaction mixture was prepared by adding 1 ml of FeNP in 5 ml of deionized water followed by sonication using the ultrasonic bath for 30 min, and a drop of it was placed on the slide to characterize.

Acceleration voltage in the instrument was kept at 200 kV, and nanoparticles were observed.

2.5 Application of Iron nanoparticles in BOD & COD (Biological & Chemical Oxygen Demand) Reduction of Waste Water

The municipal wastewater collected from the local area of Rajkot, Gujarat, India was treated with zero-valent iron nanoparticles to analyse the efficacy regarding Biological & Chemical Oxygen Demand (BOD and COD). The initial concentration of BOD, COD, pH and temperature was measured. A dose of 1 gm/l of nanoparticles were added to the wastewater. The solution was stirred at 160 rpm at room temperature without any pH adjustment for 24 hours. After treatment, the Nano composites were magnetically separated, and the supernatant was filtered through Whitman Grade GF/C filter paper. The filtrate was analyzed for BOD and COD [12, 13, 14]. All the experiments performed in triplicates and average values were noted.

RESULT AND DISCUSSION

Spinacia oleracea leaves extract is used to produce Iron nanoparticles. Fe^{+3} ions were reduced into Fe^{0} nanoparticles when plant extract mixed with the $FeCl_3$ solution in 2:3 ratio. The reduction of Fe^{+3} into Fe^{0} results in an immediate change in pH of the solution and colour changes to Black from brown. As Ferric Chloride displays bright yellowish colour in the distilled water, on mixing the plant extract with the aqueous FeCl3 solution, it changed the tone of the solution immediately and reduced the pH, which was the indicator for the formation of iron nanoparticles. We found the change in pH from high acidic to low acidic. Several studies have observed the similar type of results in their research [5, 6]. The previous data has shown the same, though they have used eucalyptus leaf extract in his research instead of *Spinacia oleracea* leaves for the treatment of eutrophic wastewater. Eutrophication, the severe issue nowadays, nanoparticles prepared via green synthesis have shown more significant impact when compared chemical method. It has a great role in bioremediation. [1, 12, 16]. Initially, we measured Municipal wastewater parameters as shown in Table 1.

Table 1: Characteristic Parameters of Municipal Waste Water

Parameter	Initial Level	Final Level(With FeNP)
COD	405 mg/L	85 mg/L
BOD	56 mg/L	22 mg/L
pH	5.5	5.5
Temp	29 °C	29 °C

3.1 Characterization of Iron Nano particles

The metal nanoparticles have free electrons, which give the SPR absorption band, due to the combined vibration of electrons of metal nanoparticles in resonance with the light wave. The sharp bands of iron nanoparticles were observed between 400nm to 450nm. Zero-valent Iron nanoparticles show the sharp peak at 404 nm. The UV spectra of iron nanoparticles showed in Figure 1. The absorption peak showed Surface Plasmon Resonance (SPR) band due to the varying size range of metal nanoparticles. SPR Formation is due to the phytochemicals present in the plant extract, and its interaction with metal charge particles results in the change in particle shape and size. Previous studies have also shown the absorption peak ranges from 400 to 560nm in their research [5,6,10,11].

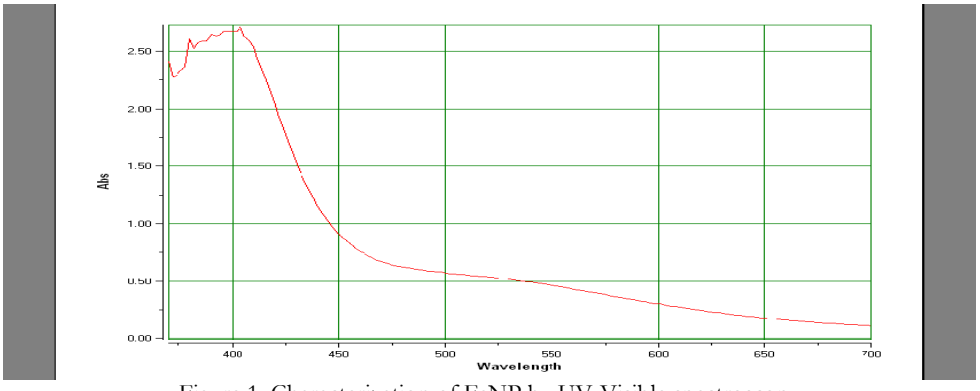

Figure 1. Characterization of FeNP by UV-Visible spectroscopy

Morphological structure of FeNPs was interposed under phase contrast microscopy. The size of nanoparticles noted between 200 to 300 nm as shown in figure 3.

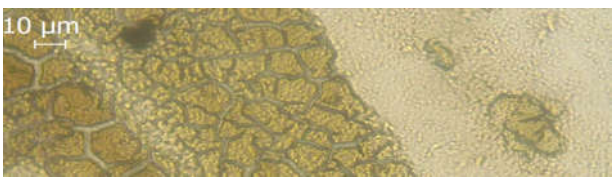

Figure 3. Phase contrast microscope result of FeNP.

3.2 Application of FeNPs in wastewater treatment

The initial concentration of COD and BOD present in municipal wastewater listed in table 1. Proper treatment of such wastewater is necessary before they can be discharged into natural water. When Zero-valent Iron Nano-particles incorporated into the sewage, it tends to remove BOD from 56 mg/L to 22 mg/L and COD from 405 mg/L to 85 mg/L. Hence, after 15 days, Removal efficiency for BOD was found 60.31% and for COD 73.82%. The similar type of removal efficiency observed earlier [1, 9, 12]. Suhendrayatna et al (2012) observed the removal efficiency of BOD and COD were 50.15 and 56.72% in his study of photo-reduction process by Saccharin spontaneous to treat municipal wastewater.

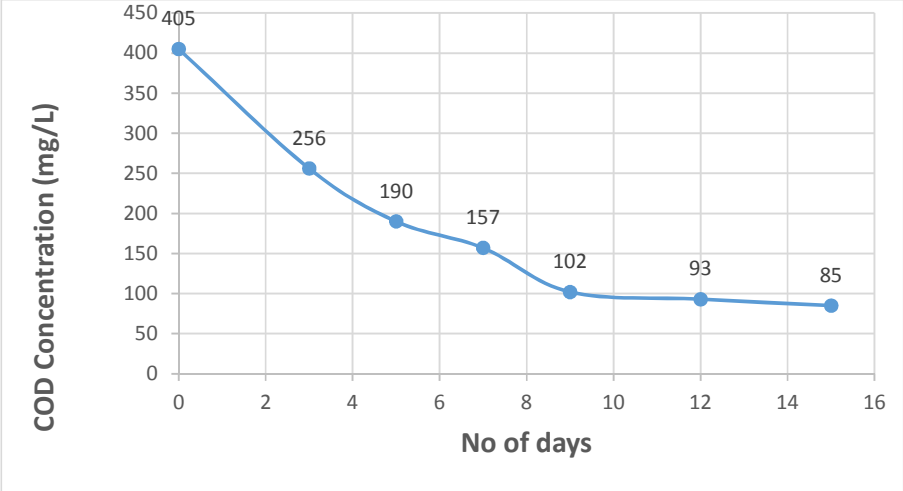

Figure 4. COD reduction from Municipal Waste Water by FeNP from *Spinacia oleracea* leaves extract.

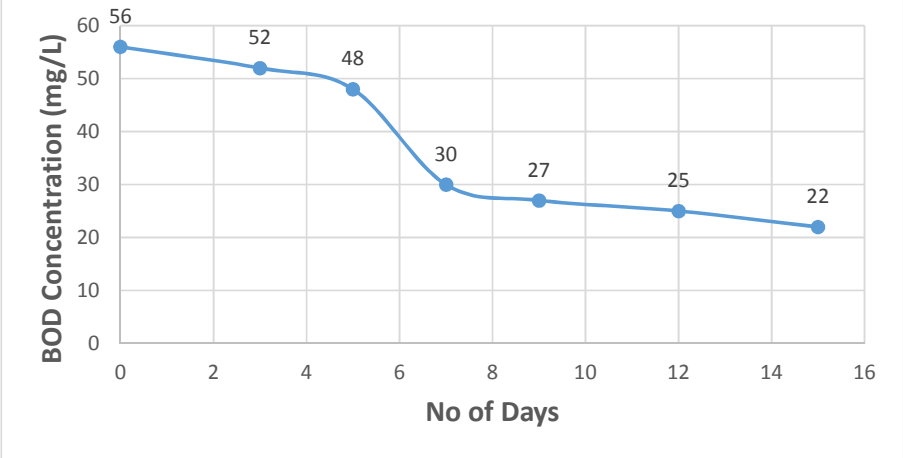

Figure 5. BOD reduction from Municipal Waste Water by FeNP from *Spinacia oleracea* leaves extract.

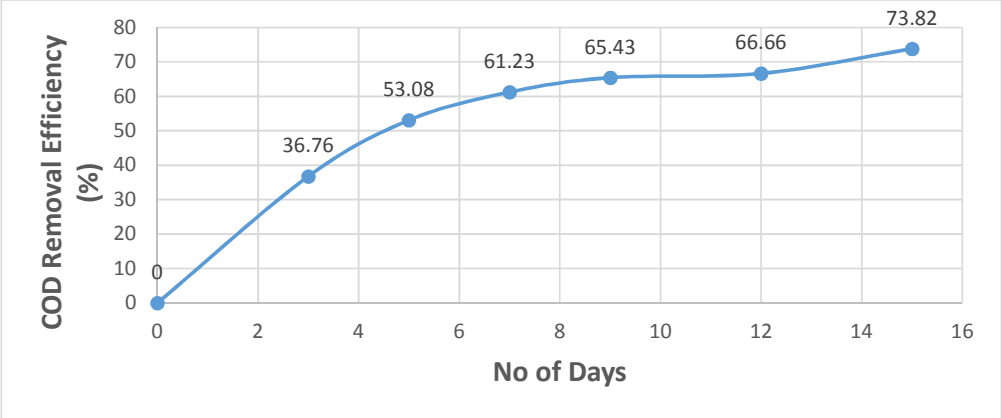

Figure 6. COD Removal Efficiency by FeNP from *Spinacia oleracea* leaves extract.

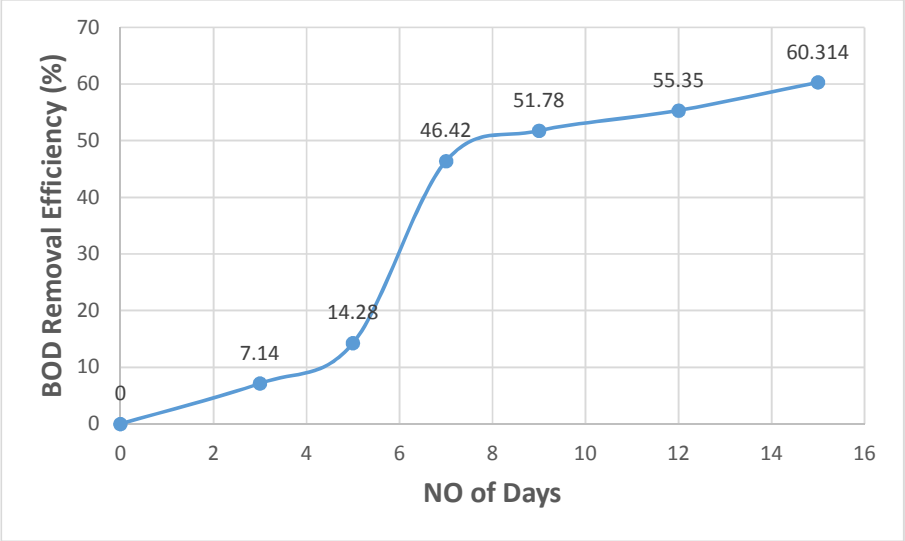

Figure 7. BOD Removal Efficiency by FeNP from *Spinacia oleracea* leaves extract.

LIMITATIONS:

Study lacks the analysis of total nitrogen and total phosphorus removal efficiency of zero valent iron nanoparticles. Further in future we would like to analyze the effect of FeNPs in dye degradation.

CONCLUSION

Within the limitations, the current study has shown the removal of BOD and COD from the municipal wastewater. For a Healthy future of Nano biotechnology, Green synthetic strategy should be adopted for nano-particles synthesis. Zero-valent Iron nanoparticles synthesized from *Spinacia oleracea* can be able to remove COD and BOD 73.82% and 60.314% respectively. This new green chemistry holds several valuable attractions and offers an efficient and economical way to environmental bioremediation protection.

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