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Iron Nanoparticles Catalyzed Degradation of Organic Dyes in Water for Environmental Remediation

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Abstract—*The potent magnetic and catalytic properties of iron can offer a great deal to the degradation of aqueous organic solutes, thus can be efficiently employed for the removal of toxic pollutants from water bodies. Dyes are known organic water pollutants especially in textile wastewater industries and iron nanomaterials can be used for its degradation. Plant mediated synthesized iron nanoparticles containing iron oxides and zerovalent iron (ZVI) have been used as Fenton like catalyst for the degradation of organic solutes. Iron nanoparticles have been synthesized in a greener manner using green extract of Cinnamomum Zeylanicum (cinnamon) and characterized by UV-visible spectroscopic technique and FTIR spectroscopy. Synthesized iron nanoparticles (FeNPs) from plant extracts have enhanced stability due to the presence of biomolecules, which act both as chelating and reducing agent. Iron nanoparticles from green extract of cinnamon have been used for decolorization of aqueous solutions containing dyes such as methylene blue. The adsorption capacity of FeNP has been explored, as they mimic Fenton's reagent, in the presence of 10% H_2O_2 so that the quenching of dyes from contaminated water can be determined.*

1. "INTRODUCTION"

Organic pollutants are major contaminants present in wastewater from textile industries. Textile industries are important for every growing economy of any country but its contribution to the water pollution of the area is equally dangerous. Significant amount of organic molecules particularly dyes are present in the wastewater effluents from textile industries and they are difficult to degrade. To overcome the problem, several biological, chemical or physical methods were introduced in the past. The physical methods which include liquid-liquid extraction, adsorption or ion exchange are not efficient enough because they do not destroy the pollutants but only transfer them from one phase to another phase, while the biological treatments occur at slow rates and sometimes all contaminants may not be biodegradable and can be even toxic to the microorganism acting on the degradation process. Therefore, more sustainable methods for the destruction of various recalcitrant organic pollutants in water have been adopted using zerovalent iron nanoparticles obtained from green extracts [1, 2].

Dyes are nonbiodegradable organic chemicals and their presence in wastewater have posed bigger threat to the environment and their decolorization owing to their high color and organic concentrations is onerous. Most of the commercial dyes used in textile industries are azodyes having characteristic –N=N- structure attached to the carbon atoms present in organic systems whose stability is dangerous for the environment. Azo dyes are a major class of synthetic colored compounds present in dyes stuff used today. The cleavage of azo bond (-N=N-) in the chromophore of an azo dye leads to the decolorization of the dye solution. Iron particles with nano scale size have been recently reported to demonstrate excellent adsorption of azo dyes. Mimicing the Fenton's process, which employs Fe^{2+}/H_2O_2 and further exploring the enhanced surface activity of nanosized particles, zerovalent iron (ZVI) nanoparticles have been used for the adsorption of methylene blue from water. Since, there are certain disadvantages associated with usage of Fe^{2+} salts with H_2O_2, it was decided to use as a solid form which could efficiently remove the color of the wastewater containing methylene blue as the dye. Most of the studies in the past were focused on degradation of azo dyes solutions using commercial grade microsized zero valent iron (ZVI) and their potential and versatility in environment scavenging had been well established. As a chemical reactant, nanoscale zerovalent iron (ZVI) are capable of exhibiting high reactivity because of their extremely small particle size, large surface area, and mobility. Utilizing these aspects, the main target was to synthesize nanoscale ZVI and characterize them using UV-vis spectroscopy and FTIR analysis and then its application for removing methylene blue from water samples [3-6].

Owing to the high intrinsic reactivity of FeNPs on their surface sites, a simple green method was employed for the synthesis of ZVI nanoparticles. The plant mediated synthesis of ZVI nanoparticles was not only cost effective but also proved to be of great significance because of its non toxic and biodegradable nature. Apart from this, the green extracts also act as dispersing and capping agents leading to the synthesis

of more stable ZVI nanoparticles as they prevent agglomeration and oxidation of ZVI nanoparticles. The nature of the green extract influences the size and reactivity of ZVI nanoparticles.

Plant chosen for the green synthesis of ZVI nanoparticles is cinnamon (*Cinnamomum Zeylanicum*). Cinnamon is an eternal tree of tropical medicine and contains vital oils and other derivatives, such as cinnamaldehyde, cinnamic acid and cinnamate. It is a good antioxidant, anti-inflammatory, antibiotic, antimicrobial and has anti-cancer as well as lipid lowering properties.

2. "EXPERIMENTAL"

2.1 Preparation of plant extract

About 20 g of cinnamon powder was boiled with 200 mL milliQ water in Erlenmeyer flask at 80 °C for 20-30 min. The extract was cooled at the room temperature and filtered using whatman filter paper.

2.2 Synthesis of iron nanoparticles

5 mL of extract was mixed to 5 mL of 0.001 M aqueous solution of $FeCl_3$ with constant stirring at room temperature. The color change was observed from yellow to brown after the reduction was complete.

In another set, the extract and $FeCl_3$ solution was mixed at 50-60 °C with immediate change of color. The reaction mixture was centrifuged at 10,000 rpm for 15 min. The supernatant was kept separately and the residue was washed with milliQ water and dried [7, 8].

2.3 Optimal process study

Methylene blue ($C_{16}H_{18}ClN_3S$) is an azo dye commonly used in the textile industries was selected as a model organic pollutant. ZVI nanoparticles were prepared from cinnamon extract as described earlier and 5 mg of it was added to 8 mL of MB (0.1 g/L, pH 6). The mixture was incubated at 298 K for different time intervals (5-300 min) and then centrifuged at 12000 rpm for 2 min. The concentration of MB at different time point was measured and the adsorption capacity of iron nanoparticles were observed. Centrifugation was used so that multiple samples were handled simultaneously in the batch experiments. During the reaction time range of 5-300 min, the degradation of MB was calculated by formula (Ao-A)/Ao, where Ao and A were the absorbance of the primal and remaining MB respectively measured by UV-Vis spectrophotometer.

3. "RESULTS AND DISCUSSION"

3.1 pH analysis

The pH was determined by using digital pH meter Systronics. The pH of the reduced solution with nanoparticles synthesized was found to be acidic. Apart from the color change, the pH change before reduction and after reduction was found to change from 6.18 to 2.24.

3.2 FTIR analysis

The FTIR spectrum of iron nanoparticles showed major adsorption bands. The peak in the region 3200-3600 cm^{-1} represented the characteristic bands of O-H while the strong band at 530 cm^{-1} corresponds to iron nanoparticles [9].

3.3 UV-vis spectral analysis

UV- Vis spectral analysis was done by using UV-Vis spectrophotometer Systronics 118 at the range of 200-700 nm and the absorption peak at 267 nm due to the excitation of surface plasmon vibrations in the iron nanoparticles were observed (see Fig. 1) [10].

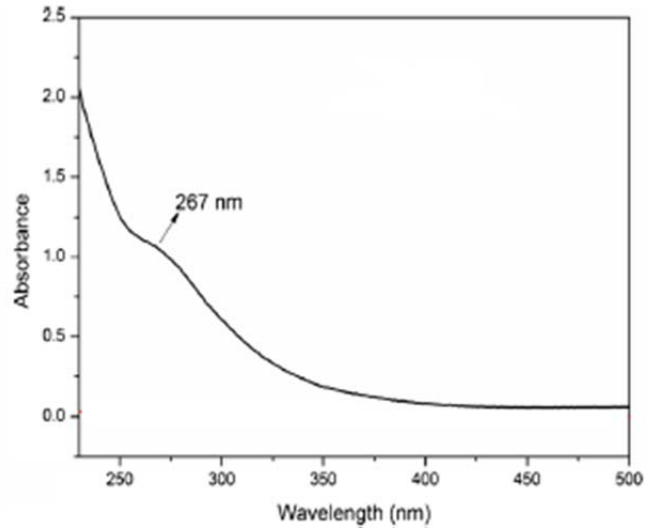

Fig. 1: UV–visible absorption spectra of synthesized ZVI nanoparticles.

3.4 Removal of methylene blue (MB), the organic pollutant dye from water

The maximum UV-Vis adsorption of MB was observed at 664 nm, which almost remained the same during the degradation progress. This indicated the residual concentration level of MB after degradation. This enabled to follow the absorbance at 664 nm after various time intervals, which showed that the decrease in absorption peak with increased time. Finally, it almost disappeared after 240 min, further signifying that the chromophore responsible for characteristic color of the MB were broken down and MB had been degraded on the surface of ZVI nanoparticles (see Fig. 2).

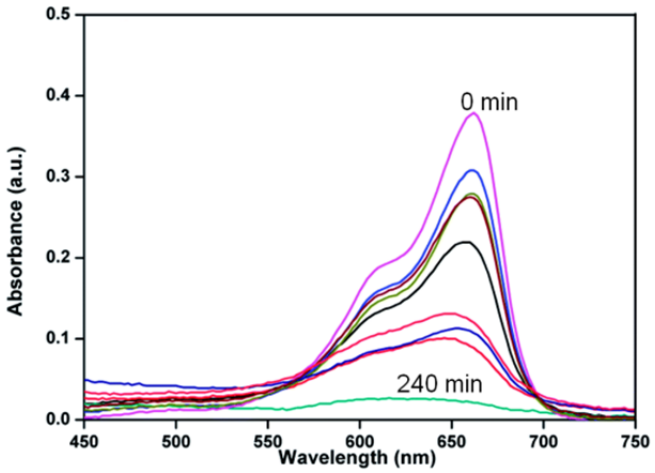

Fig. 2: Degradation of MB.

The pH had significance influence on the adsorption performance of nZVI particles. At higher pH values (range 2-8), the adsorption rates for the adsorption of MB were higher. It took lesser time for the adsorption peak to get diminished in the UV- Vis spectroscopy. The adsorption capacity was maximum at pH 8 and minimum at pH 2 [11, 12].

4. "CONCLUSION"

In summary, zerovalent iron nanoparticles (ZVI) were prepared using green extract of commonly used spice cinnamon and characterized by UV-Visible and FTIR studies. Owing to the high reactivity of nanosized metal particles and their high adsorption capabilities, removal of methylene blue dye was investigated. It was found that ZVI nanoparticles efficiently adsorbed the dye on its surface showing large adsorption capacity. The iron nanoparticles, with enhanced adsorption capabilities are expected to act as cost effective agent for removing organic pollutants from wastewater. This is also expected to further promote environmental nanotechnology and emphasize green methodologies.

5. "ACKNOWLEDGEMENT"

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