



Degradation of various azo dyes by the help of nZVI immobilized in agarose membrane

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Refractory azo-dye compounds used in the textile industry are commonly detected in wastewater. In this study, the decolorization of methyl orange (MO) and several food dyes have been studied by diethylene triamine penta acetic acid (DTPA) stabilized nanoscale zero valent iron (nZVI) particles immobilized in agarose membrane (Im-nZVI-AM). The decolorization rate has been studied with respect to the dosage of nZVI particles and temperature. The degradation of dyes have been studied by measuring the change in ac conductivity of the initial and final dye solution. The decolorization rate increases with the increasing of nZVI particles dosage and temperature of the dye solution. 50% hydrogen peroxide (H₂O₂) concentration has been used to increase the efficiency of degradation. In this study Im-nZVI-AM has been used multiple times to treat the wastewater.

Keywords: Azo-dye, Im-nZVI-AM, degradation, agarose, wastewater.

Introduction

Nanoscale materials are widely used in environmental remediation and this due their larger specific surface area^{1,2}. In the wastewater treatment, nZVI particles are used successfully, though there are still some drawbacks associated with the process and needs to be improved. For example, due to the magnetic property of nanoiron particles, the rapid agglomeration of particles occurs. In addition, nZVI are more prone to react with dissolved oxygen and oxygen-rich compounds. To overcome these problems, nZVI particles were immobilized in or on suitable solid supports. Ramirez *et al.*³ showed that nZVI can be immobilized in Amberlite resin and Nafion membrane. Similar type of work was also done by Chen *et al.*⁴. Ren *et al.*⁵ successfully fabricated a PVDF-GO membrane via electro spinning technology and employed the functionalized nanofiber membrane to immobilize nZVI particles^{4,5}. Thin films are getting popularity now a day in order to immobilize various nanoparticles and nanocomposites. In present work we have tried to immobilize nZVI stabilized by DTPA ligand over agarose membrane and to use it in wastewater treatment at room temperature.

Materials and methods

Chemicals required:

(i) Iron(II) sulphate heptahydrate, (ii) sodium boro-hydrate (NaBH₄), (iii) chelating agent diethylene triamine penta acetic acid (DTPA), (iv) agarose medium EEO Type II, (v) methyl orange (MO), (vi) Tartrazine and (vii) Allura Red.

Methodology

Preparation of stable zero valent iron nano particles using DTPA:

0.1 M FeSO₄.7H₂O i.e. 4.17 g in 150 ml of deionized water and 0.01 M DTPA i.e. 0.4 g in 100 ml of deionized water were mixed in a round bottom flask by a propeller mixing. After that, 0.5 M NaBH₄ i.e. 1.892 g in 100 ml of deionized water was added drop wise to the above mixture⁶. The resultant solution slowly turns black. The black colored solution finally filtered, dried and pulverized. 0.8254 g of DTPA stabilized nZVI particles was obtained.

Preparation of agarose membrane:

0.15 g of agarose powder in 15 ml of deionized water was add and stirred at 80°C (agarose powder is soluble in

water at 80°C) until a clear solution was obtained⁷. The final transparent and viscous solution was dispersed in a small beaker and remains undisturbed for 2–3 min for cooling, which then solidified to become a membrane.

Immobilization of nZVI on the agarose membrane:

0.1 M solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (i.e. 0.278 g in 10 ml deionized water) and 0.01 M solution of DTPA (i.e. 0.04 g in 10 ml deionized water) were prepared. 2 ml of 0.1 M $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.2 ml of 0.01 M DTPA were mixed using a pipette in a small beaker. 0.4 ml of 0.5 M NaBH_4 (i.e. 0.189 g in 10 ml of deionized water) was added into the above solution. The resultant solution turns black with the precipitation of DTPA stabilized nZVI particles. The black colored solution was poured on the agarose membrane. After 2–3 min, it was found that the DTPA stabilized nZVI particles got trapped and distributed uniformly inside the agarose membrane (Fig. 1).

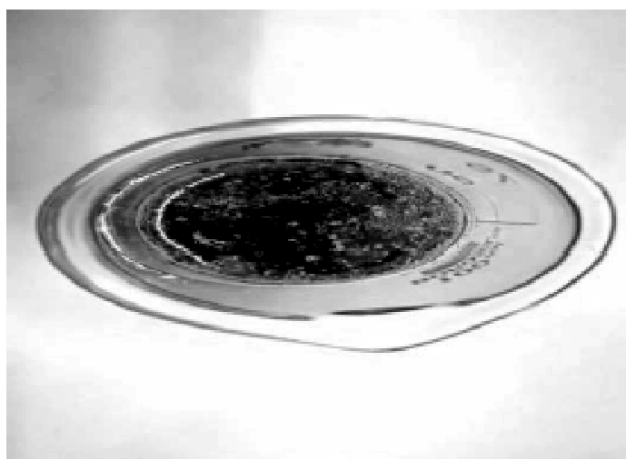


Fig. 1. nZVI particles immobilized on agarose membrane.

Results and discussion

Characterization of nZVI immobilized on agarose membrane:

X-Ray diffraction (XRD) pattern of the DTPA stabilized nZVI particles has been shown in Fig. 2. It shows that a broad peak appeared at 2θ of 44.860 is the characteristic of DTPA stabilized nZVI. The broadening of the peak implies that the synthesized DTPA stabilized nZVI particles possess a chemically disordered crystal structure. All the samples are scanned

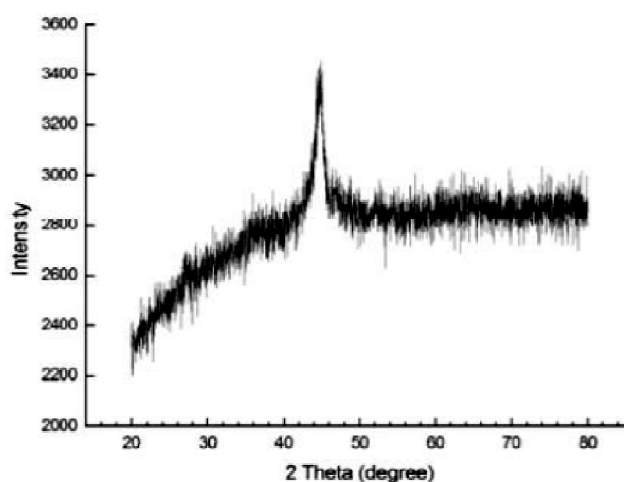


Fig. 2. XRD pattern of DTPA stabilized nZVI particles.

from 20° to 80°. X-Ray diffraction analysis used high power $\text{Cu K}\alpha$ source 40 KV/40 mA.

Field effect scanning electron microscopy (FESEM) image of DTPA stabilized nZVI particles is presented in Fig. 3. It represents that smaller particle size indicates higher surface area to volume ratio and also higher reactivity. It is clear that particles are spherical in size. Analyzing FESEM image the particle size distribution graph of the DTPA stabilized nZVI particles is shown in Fig. 4 and it is clear that the particle size is mainly in the range 4–20 nm.

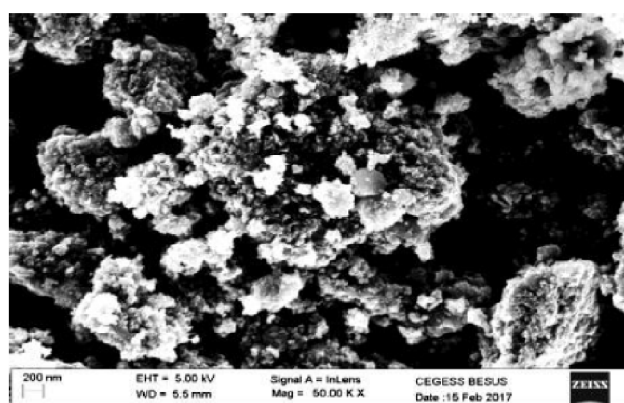


Fig. 3. FESEM image of DTPA stabilized nZVI.

Degradation of azo dyes:

Different concentration of MO, Allura Red and Tartrazine were prepared and degraded by using DTPA stabilized Im-

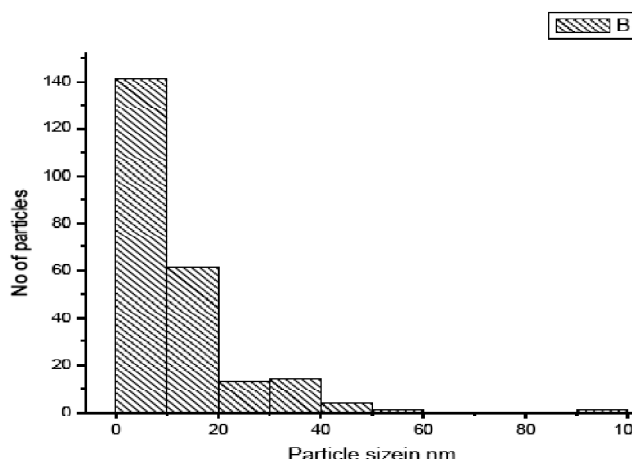


Fig. 4. Particle size distribution of Im-nZVI-AM.

nZVI-AM particles. Fig. 5 shows the color of 100 ppm MO solution before and after degradation using DTPA stabilized Im-nZVI-AM particles. It was found that complete decolorization of MO solution occurs after adding of 0.5 ml of 50% hydrogen peroxide. In case of Allura Red and Tartrazine to get complete decolorization, 0.5 ml of 50% H₂O₂ had to be added.

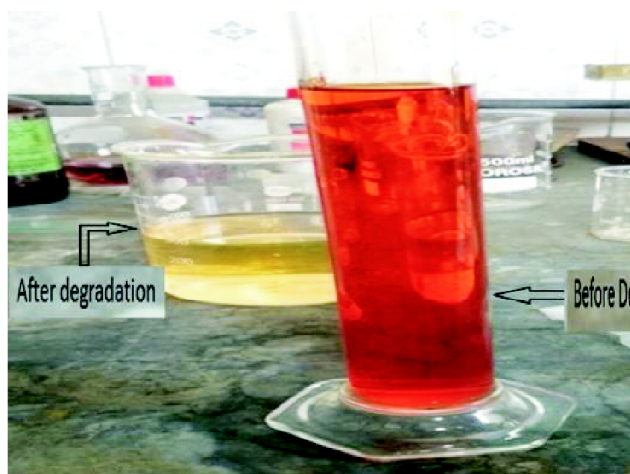


Fig. 5. 100 ppm MO solution before and after degradation.

The degradation of MO and all other food dyes has been studied in a new approach. By using a series LCR circuit ac conductivity of different dye solutions had been measured before and after degradation using DTPA stabilized Im-nZVI-AM. A remarkable change in ac conductivity had been ob-

served. From existing literature it can be claimed during the degradation of azo dyes (like MO, Allura Red, Tartrazine), an organic acid (sulfanilic acid) has been produced, which increases the ac conductivity⁸.

Fig. 6 shows the ac conductivity of MO with different concentration before degradation and it is clear that the ac conductivity increases with the increasing of concentration.

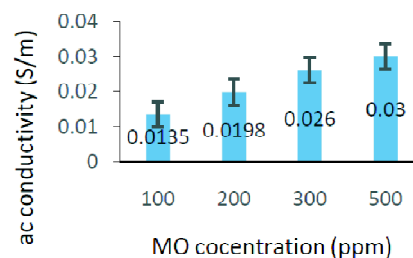


Fig. 6. ac conductivity of MO solution for different initial concentration of MO before degradation (temperature = 25°C, nZVI dosage = 0.4 g/L).

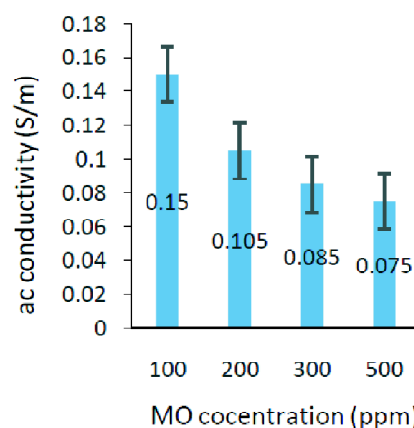


Fig. 7. ac conductivity of MO solution for different initial concentration of MO after degradation (temperature = 25°C, nZVI dosage = 0.4 g/L).

Whereas Fig. 7 shows the reverse nature i.e. the ac conductivity decreases after degradation with the increasing of initial dye concentration. In this study, the ac conductivity measurement during the degradation of MO and other dyes was recorded under a fixed nano dosage (0.4 g/L). As a result production of organic acid decreases with the increase in initial concentration of MO and ac conductivity decreases (Fig. 7).

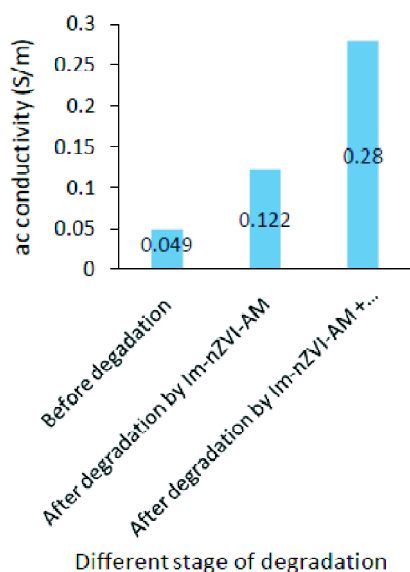


Fig. 8. ac conductivity of Allura Red for different condition (temperature = 25°C, nZVI dosage = 0.4 g/L).

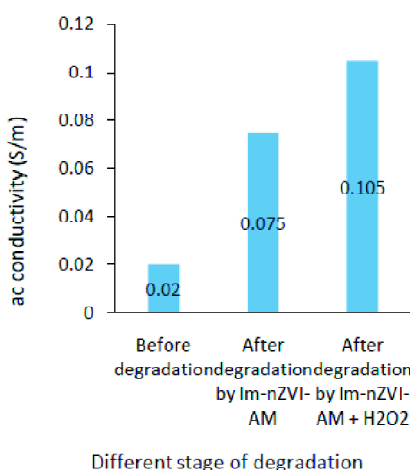


Fig. 9. ac conductivity of Allura Red for different condition (temperature = 25°C, nZVI dosage = 0.4 g/L).

The change in ac conductivity before and after degradation of Allura Red and Tartrazine have been shown in Figs. 8 and 9 respectively. The concentration of Allura Red and Tartrazine was 100 ppm. In this study, 0.4 g/L nano dosage had been fixed for the degradation reaction on as prepared Im-nZVI-AM. From the Figs. 8 and 9, it is clear that ac conductivity increases after degradation. To get complete decolorization 0.5 ml of 50% H₂O₂ were needed to add with the solution, degraded by Im-nZVI-AM and it was observed that

the ac conductivity was increased after degradation using Im-nZVI-AM and H₂O₂ (Figs. 8 and 9).

Effect of dosage of nZVI:

It was found that with the increasing of DTPA stabilized nZVI dosage in agarose membrane for the degradation of MO and other dyes, the degradation efficiency increases. This is because the higher the dosage means more active surface sites and greater surface area for the degradation reaction⁹.

Variation in rate of degradation with temperature:

The MO solution at different temperature (30°C, 40°C and 50°C) having different level of decolorisation, we observed that the rate of degradation increases with rising temperature. If we further increase the temperature above 50°C the surface of the agarose membrane gets spoiled.

The pH of the MO solution decreases after degradation at different temperature of the given solution. The pH value for the MO solution decreases from 8.8 to 7.8, 7.2 and 5.6 when the solution was degrade using DTPA stabilized nZVI at temperature 25°C, 40°C and 50°C respectively. For complete degradation we used 0.5 ml of 50% hydrogen peroxide, which further decrease the pH value to 2.7 within 20 min. The increased in degradation rate with the increase in the temperature of the solution can be explained with the help of Arrhenius relation,

$$K = A e^{(-E_a/RT)}$$

where, K is the rate constant, A is a frequency factor, E_a is the activation energy, R is the gas constant and T is the temperature.

The estimated activation energy for the degradation of methyl orange by nZVI is approximately 23 kJ mol⁻¹. This value of activation energy implies that the degradation of methyl orange by nZVI particles requires a relatively low energy. It also implies that the small temperature change may effect on the decolorization reactions of nZVI (for methyl orange) in treatment process.

Change in pH before and after the degradation of dye solution:

The initial pH of the methyl orange solution is decreased after degradation by Im-nZVI-AM. The initial pHs of the MO solutions were 8.8, 4.1 and 3.3 respectively. After the reaction, pH of degradation reaction was converted to 7.8, 3.2

and 2.1 respectively. This was attributed due to formation of organic acids like sulphanic acid¹¹. Similarly pH of Allura Red and Tartazine was measured. The resultant solution of this two dye after degradation also found to be less than the initial value.

For Allura Red pH value decrease from 8.8 to 5.6 and for Tartrazine it is 8.7 to 5.8. It has been observed that after addition of five drops of 50% hydrogen peroxide to the degraded solution it would become a clear solution in 40 min and the pH value of the final clear solution became 2.1. So, with the increase in the initial pH of azo dye solutions, there was a decrease in the rate of degradation i.e. the higher concentration of hydrogen ions would enhance the reduction based degradation reaction of azo dye compounds¹⁰. Furthermore, the lower aqueous pH may help to reactivate the oxidized iron layer, and thus can enhance the degradation of the surface of nZVI particles.

In acidic solution, H₂O₂ acting as a strong oxidizing agent producing highly reactive hydroxyl radicals (OH^{*}). So, it can degrade the azo-dyes to a large extent.

Capability to degrade a combination of different dye solution:

As prepared nZVI immobilized in agarose membrane is capable to degrade solution containing more than one dye. The degradation was confirmed by significant reduction in the colour of the dye solution.

Regeneration and reproducibility:

Efficient regeneration of an agarose membrane immobilized nZVI within a reasonable time is a requirement of its usefulness in multiple usages. The prepared membrane can be used for multiple times for almost three days after washing it by distilled water. Diffusion of colour solution into the membrane was observed to some extent, but it did not affect the ability to degrade those impurities.

Conclusions

The new findings of this paper clearly demonstrate that immobilization of nZVI on the agarose membrane could result in a stable degrading materials for azo dyes. Improvements in the degradation rates of azo dyes were obtained by adding 50% hydrogen peroxide solution. Satisfying results were recorded.

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