Photo-catalytic decolouration of Rhodamine B dye using ZVI nanopowder synthesized by chemical reduction method.

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Abstract

Background: Photocatalytic degradation of Rhodamine B (RB) Dye was carried out with ZVI nanopowder. The effect of parameters such as the amount of catalyst, concentration of the dye on photo catalytic degradation of RB is studied

Methods:

Zero valent iron (ZVI) powder with crystallite size around 50 to 60 nm was prepared by chemical reduction route. The product was characterized by X-ray diffraction (XRD), Transmission electron microscope (TEM).

Findings: The results reveal that the maximum decolorization (more than 95%) of dye occurred with ZVI catalyst in 6 - 8 hours of UV irradiation.

Application: The results suggest that, the ZVI may potentially offer a simple and low-cost option for abatement of dyes. Possible applications of ZVI in water treatment plants are proposed and the potential benefits are discussed.

***Keywords*:** ZVI Nanoparticles, Rhodamine B, XRD, TEM

1. Introduction

Quantity and quality of drinking water has been a critical issue for the imminent decades. Among the factors that contribute to the looming water crisis are continued population growth and urbanization, deteriorating water infrastructure, growing number of emerging contaminants and uncertain future water availability and quality due to climate change. Dyes can be applied for various industrial uses, including inks, cosmetics, soap, and foods. Rhodamine B (RB) is widely used as a colorant in textiles and food stuffs, and also a well-known water tracer fluorescent [1]. It is harmful to human beings and animals, and causes irritation of the skin, eyes and respiratory tract. The carcinogenicity, reproductive and developmental toxicity, neurotoxicity and chronic toxicity toward humans and animals have been experimentally proven [2,3]. Thus, keeping the hazardous nature and harmful effects in view, it was considered worthwhile to make systematic efforts to degrade RB from aqueous medium.

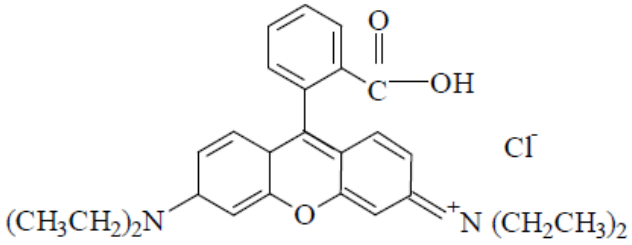
Effluents from industrial facilities are enriched typically of high organic contents and colour strength. Thus, textile wastewater must be treated before discharge as to minimize the threat to the environment. The strong colour in wastewater can decrease the transparency of water and make it unfeasible for re-usage. However, removal of colour from wastewater is a great challenge. At present, the major techniques for treating dye wastewater are adsorption process and biological treatment [4-11]. Some of them require significant capital investment and plant modifications or are expensive to install and/or difficult to operate. It is thus highly desirable to develop a simple, effective, inexpensive method for the removal of dyes. Nanotechnology has become one of the promising technologies for waste management and removal of organic contaminants. Potential benefits of TiO_2 Nanoparticles for colour degradation have already been identified by researchers [12].

Out of numerous metallic Nanoparticles, ZVI (Zero Valent Iron) Nanoparticles has been used to remediate contaminated groundwater and has been shown to remain reactive in anaerobic subsurface for multiple years [13]. While ZVI particles initially used to treat chlorinated solvents and hexa-valent Chromium [14] and have also been used over the last two decades to remove a broad range of chemical contaminants, from heavy metals and radionuclides to agrochemicals and explosives. ZVI has certain advantages compared to other metallic nanoparticles

(TiO_2, ZnO) like it is having low cost, availability of iron in rural villages in the form of low- cost materials and simplicity in handling and scalability. Ertugay et al., 2013 [15] showed Sonocatalytic degradation of Direct Blue 71 azo dye at the presence Zero-Valent Iron (ZVI). Hou et al., 2011 [16] revealed Degradation of rhodamine B by Fenton process with ZVI.

In this study, nano sized ZVI powders were prepared by chemical reduction route and particles were characterized for their size and shape by XRD and TEM, respectively. Moreover, the effect of ZVI nanocatalyst on photocatalysis of RB dyes (C.I. No: 45170, formula weight = 479×02, structure Figure 1) under UV irradiation was investigated. The effect of catalyst dosage, concentration of dye on photocatalytic effect was carried out.

Figure 1. Structure of Rhodamine b



2. Material & Methods

2.1. Synthesis of ZVI Nanoparticles

Nano sized iron nanoparticles were produced by reduction of ferric iron in the presence of sodium borohydride. These particles were prepared freshly each day by adding 0.16 M $NaBH_4$ aqueous solution drop wise to a 0.1 M $FeCl_3$-$6H_2O$ aqueous solution at ambient temperature and under atmospheric conditions [17]. The preparation of solutions involved the following steps: sodium borohydride ($NaBH_4$, 0.6053 g) solids were dissolved in 100 mL of 0.1 M NaOH solution (0.16 M $NaBH_4$ in 0.1 M NaOH solution), and then 2.7030 g of $FeCl_3.6H_2O$ was dissolved into 100-mL pure water (0.1 M $FeCl_3.6H_2O$). $NaBH_4$ solution can be made either in water or NaOH solution, although $NaBH_4$ is unstable in water and can quickly result in a loss of reduction power. Addition of the NaBH4 to the $FeCl_3$ solution in the presence of vigorous magnetic stirring resulted in the rapid formation of fine black precipitates according to the following reaction:

$$2FeCl_3 + 6\,NaBH_4 + 18\,H_2O \longrightarrow 2\,Fe^{O} + 6B\,(OH)_3 + 21H_2 + 6\,NaCl \qquad (1)$$

The particles were washed 3 to 4 times with double distilled water to remove any impurities. Black precipitate was dried in an oven at 100°C for 6-8 hours to obtain black powder in order to remove moisture content. The dried particles were homogenized in abrasives and stored in air tight bottle for further use.

2.2. Characterization of ZVI NPs

TEM Analysis of NPs was characterized for their size and shape using a Transmission electron microscope. Crystallographic structural analysis was carried out by an X-ray diffractometer (Shimadzu XRD-6000, Japan) using Cu–Ka radiation (λ = 1.5405A°) in a 2y range of 5–601 at a scan speed of 0.11 s^{-1}, maintaining applied voltage at 40 kV and current at 40 mA [18].

2.3 Photocatalytic study

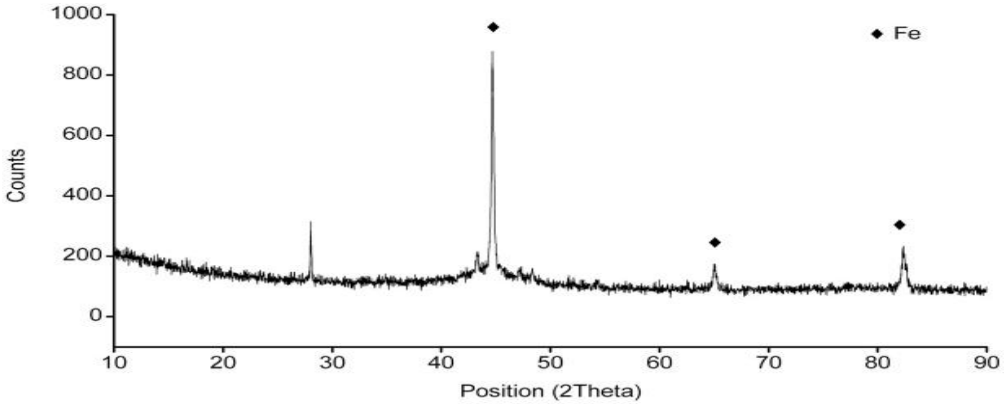
In photocatalytic experiments, different concentration of RB dye (10, 20, 30, 40 ppm) and the catalyst dose (5, 10, 15, 20 mg) were taken separately and exposed to UV light. Four 15 W low-pressure mercury UV tubes (Spectronics) emitting near UV radiation with a peak at 365 nm were used. Dye containing tube without nanoparticles was also placed on UV sources to know direct photolysis of dyes could occur but mineralization of dyes only takes place in the presence of a photo catalyst. Distilled water was used throughout the experiment. Dye samples of about 2–3 ml were taken out at a regular interval from the test solution, centrifuged for 4–5 min at 950–1000 rpm and their absorbance were recorded at 555 nm using a spectrophotometer. The photo degradation efficiency was calculated from the equation given below

Photo degradation efficiency = Initial $_{OD}$ – Final $_{OD}$ / Initial $_{OD}$ X 100

3. Result and Discussion

3.1 Crystal size & shape

Figure 2. XRD spectra of ZVI



X-Ray diffraction of ZVI surface composition is shown in Figure. 2. It indicated that surface species of prepared ZVI was detected at 46.7ɵ. From the half-maximum width of the fitted peaks, average crystallite sizes and size distributions of ZVI was estimated using the Scherrer equation which found to be around 55nm [19, 20]. The peak at 29ɵ shows the presence of excessive $NaBH_4$.

Figure 3. TEM image of ZVI

TEM picture of the sample was taken to determine the morphology and size of the nanoparticles and to compare them with the particle sizes obtained using XRD. The TEM micrograph of the ZVI nanoparticles shows spherical structure of catalyst (Figure. 3). TEM study indicated that all the crystals were completely separated from each other and uniformed with a particle analytical grade with size of 50 -70 nm. Similar phenomenon was observed by other researchers [21, 22]. Size of nanocatalyst obtained by XRD and TEM was highly correlated with one another.

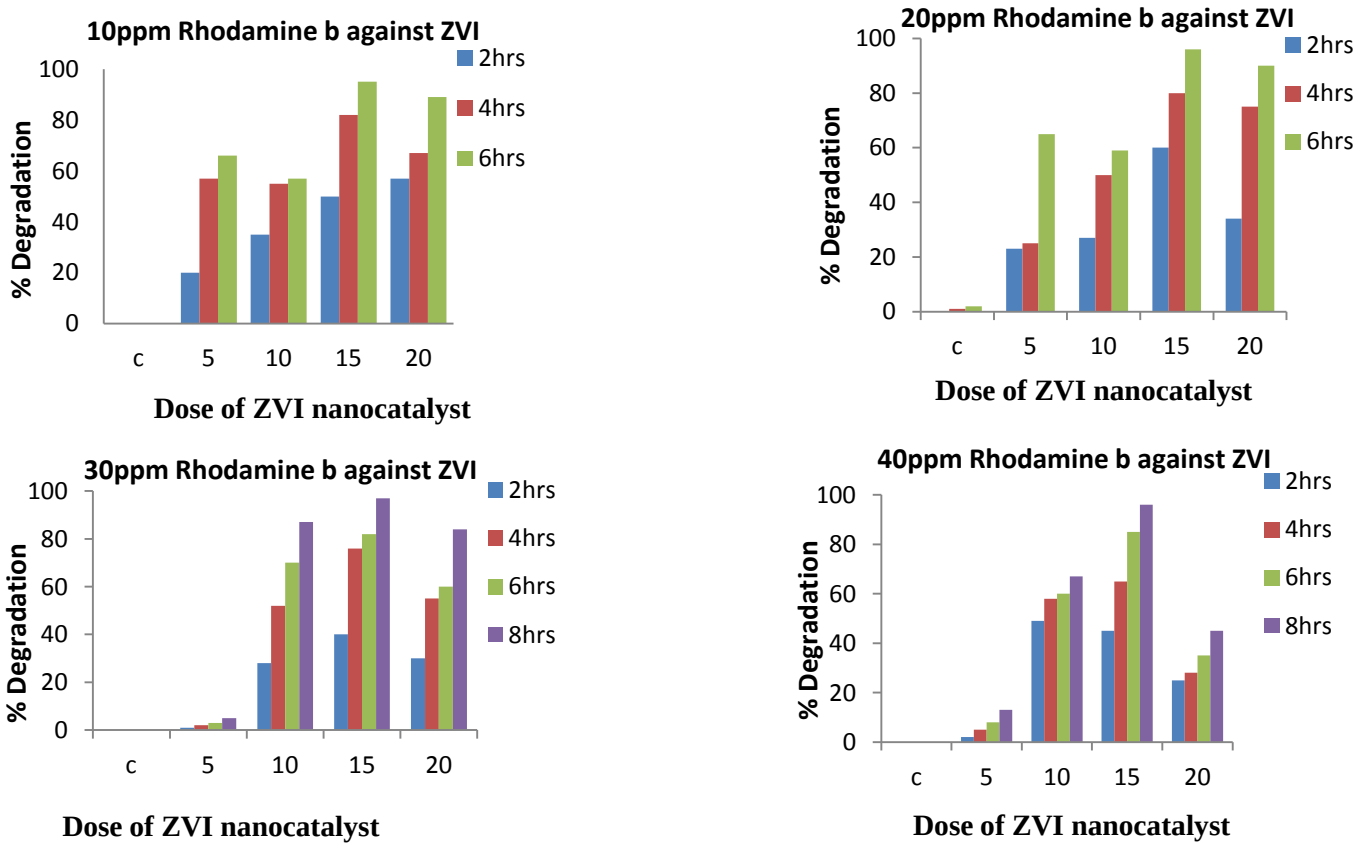
3.2 Photocatalytic study

The dye removal using ZVI nanoparticles without surface modification (Dye: 10-40 mg/L, nanocatalyst dose: 5,10,15,20 mg and pH = 7) is shown in Figure 4. In order to identify possible losses of RB in the system, control experiments without catalyst were performed. The course of RB photo catalytic degradation used catalyst ZVI at various amounts added to different dye concentration The maximum dye removal efficiency of ZVI was obtained by 97%, in 10ppm of RB concentration at 15 mg of catalyst dose, by 96%, in 20ppm of RB concentration at 15 mg of

catalyst dose, by 95%, in 30ppm of RB concentration at 15 mg of catalyst dose and by 96% and in 40ppm of RB concentration at 15 mg of catalyst dose. Hence, 15 mg adsorbent can be taken as an optimum dose. Time taken for complete removal of colour by lower concentrated dye (10, 20 ppm) was 6 hours and 8 hours for higher concentrated dye (30,40 ppm). It is observed that a good correlation between the light absorption properties and the photocatalytic activity of the samples was encountered. The increase in dye adsorption with adsorbent dosage is due to the increasing of adsorbent surface area, availability of more adsorption sites, high reactivity and optimum dose of catalyst [23]. However, at very high dose the dye removal capacity decreased with the increasing amount of adsorbent with low reactivity and overlapping or aggregation of adsorption sites resulting in decrease of total adsorbent surface area available to the dye.

There is no doubt that electron injection from the dye to the positive holes of nanocatalyst yields the dye cationic radical. After this stage, the cationic radical, Dye•+, can undergo hydrolysis and/or de protonation pathway of the dye cationic radicals, which in turn are determined by the different adsorption modes of RB on the particles surface[24]. Total mineralization of the organic dye pollutants usually follows proposed mechanism described below [25, 26].

Figure 4. Degradation of Rhodamine B by ZVI nanocatalyst



Photocatalysis occurs by following proposed mechanism given in step wise manner.

1. Absorption of efficient photons ($h\nu \geq EG$=3.2 eV) by ZVI

$$(ZVI) + h\nu \rightarrow e{-}CB + h{+}VB \quad (1)$$

2. Oxygen ionosorption (first step of oxygen reduction; oxygen's oxidation degree passes from 0 to −1/2)

$$(O_2)ads + e{-}CB \rightarrow O_2\bullet{-} \quad (2)$$

3. Neutralization of OH− groups by photoholes which produces OH◦ radicals

$(H_2O \Leftrightarrow H+ + OH-)ads + h+VB \rightarrow H^+ + OH\bullet$ (3)

4. Neutralization of $O_2^{\circ-}$ by protons

$O_2^{\circ-} + H+ \rightarrow HO_2^{\circ}$ (4)

5. Transient hydrogen peroxide formation and dismutation of oxygen

$2HO_2^{\circ-} \rightarrow H_2O_2 + O_2$ (5)

6. Decomposition of H_2O_2 and second reduction of oxygen

$H_2O_2 + e- \rightarrow OH^{\circ} + OH-$ (6)

7. Oxidation of the organic reactant via successive attacks by OH• radicals

$R + OH^{\circ} \rightarrow R\bullet + H_2O$ (7)

8. Direct oxidation by reaction with holes

$R + h+ \rightarrow R+^{\circ} \rightarrow$ degradation products

4. Conclusion

In this paper, ZVI was synthesized and its dye removal ability was carried out. The synthetic method was found to be significant for the formation of nano –catalysts /material with particle size 55 nm and structure spherical for ZVI. Rhodamine B was used as a model dye-compounds. 95% decoloration of dye was achieved by the catalyst which reveals that ZVI has considerable potential as an adsorbent for the removal of Rhodamine-B.

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