

## Synthesis and Characterization of Zero Valent Iron Nanoparticles for Textile Wastewater Treatment

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**ABSTRACT:** Textile manufacturing industry produces a huge amount of pollutants from its textile dyeing units. To combat the problem of water pollution, various processes are being already adopted by textile industries to treat wastewater before its discharge into the nearby environment. However, the inadequate traditional treatments are leading towards the development of different technologies with major concern on material's high efficacy. One of the newest advancement in this area is nanotechnology. The zero valent iron nanoparticles (nZVI) are gaining extreme importance, due to its potential capabilities of reducing chemical substances, dye colour and other constituents from the waste effluent. In the present article, synthesis of nZVI particles was carried out by borohydride chemical reduction method using ferrous heptahydrate sulphate salt. Its characterization such as surface morphology and structure was analyzed by using X-Ray diffraction (XRD), Scanning Electron Microscope (SEM) and Brunauer- Emmett-Teller method (BET). Further, the stability of nanoparticles was also investigated via chemical and thermal processes at different pH ranges and temperatures. The results revealed that the synthesized nanoparticles were as per the available literature in terms of size, surface morphology, structure & stability. Hence, ready for the batch experimental studies on laboratory scale.

**Keywords:** Nanotechnology, Waste Water Treatment, Textile Industries, Borohydride Chemical Reduction Method.

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### INTRODUCTION

Enormous population increase, reckless industrialization and urbanization have caused the insufficient availability of water reserves to meet the rising demands of

countries. In consonant, textile industries are considered as the largest consumer of water and generator of effluent. The untreated disposal flows into the ecosystem and pollutes the both surface water and groundwater. As a result, the useable water

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quality in the environment is rapidly deteriorating. Thus, to find an innovative and efficient method for purification and treatment of water and wastewater is a vital concern in front of government of developing nations (Karthik *et al.*, 2014; Shubair *et al.*, 2018). Conventionally, physicochemical and biological processes have been employed for the treatment of dye-containing wastewater. Moreover, the limitations of traditional methods in terms of concentrated sludge production, fouling problems, high cost of adsorbent material, formation of toxic amines as by-products (Solanki *et al.*, 2013; Ghaly *et al.*, 2014; Bora *et al.*, 2014; Beyene, 2014; Crini *et al.*, 2019) restricts their use in the mills.

In this regard, nanotechnology is spreading its spark in the field of research to explore, control, incorporate, manipulate, and manufacture things at the nanometer scale (1-100nm) for the development of applied and technical sciences (Subramanian 2012). Recently, a great deal of attention has been paid on the use of nanoscale materials over the granular scale particles. From the last few decades, nanoparticles have been extensively investigated for groundwater and soil remediation, water treatment, gas cleanup due to their typical novel size-dependent properties, high reactivity and large specific surface area (Li *et al.*, 2006; Chatterjee *et al.*, 2010; Zhao *et al.*, 2016; Tyagi *et al.*, 2018; Pei *et al.*, 2020).

Moreover, iron nanoparticles are the promising metal ions to represent their potential application in groundwater treatment and site experiments for environmental remediation. Due to its relatively low toxicity and biodegradability, it opens the gates of research in water purification and removal of dye colour. To date, micro size zero valent iron (ZVI) applications as permeable reactive barrier (PRBs) for the degradation of chlorinated solvents is remarkable (Fu *et al.*, 2014). Nonetheless, several studies

have successfully investigated their destruction, stability and transformation behavior with pollutants (Mukherjee *et al.*, 2016), organic dyes (Dutta *et al.*, 2016) and heavy metals (Boparai 2011; Huang *et al.*, 2013; Zou *et al.*, 2016; Almomani *et al.*, 2020). Nano ZVI offers its use as nano adsorbent ions for the pollutant removal or separation from wastewater due to their electron donating behavior and oxidation-reduction mechanism with contaminants. The high surface area to volume/mass ratios of nanomaterials will greatly improve the adsorption properties of sorbent materials (Bethi *et al.*, 2016).

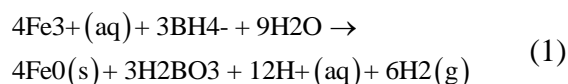
The objective of this paper is to synthesize the nZVI from (Fe) sulphate salts by using reducing agent sodium borohydride in 99% ethanol medium and characterize the synthesized material in terms of adsorbent characteristics. The most widely used method for environmental purposes is the borohydride reduction of Fe(II) or Fe(III) ions in aqueous media (Yuvakkumar, 2011; Ravikumar *et al.*, 2016). In the current study, synthesis was performed under an open air atmosphere to know the oxidation behavior of particles. The easily available and economical precursor of iron sulphate heptahydrate salt has been used over iron chloride salt which undergoes fast oxidation.

## MATERIAL AND METHODS

Ferrous sulphate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) and sodium borohydride ( $\text{NaBH}_4$ ) were procured from Merck chemicals to prepare nanoparticles. Drimarene reactive Red 198 dye was received from M/s Clariant (India) Ltd. All other reagents used were of analytical grade.  $\text{Fe}^0$  nanoparticles used for the study were synthesized in the laboratory.

Synthesis of ZVI nanoparticles was done by chemical reduction method. Sodium borohydride was used for reduction of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  aqueous mixture. Molar solution of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (0.05M) was

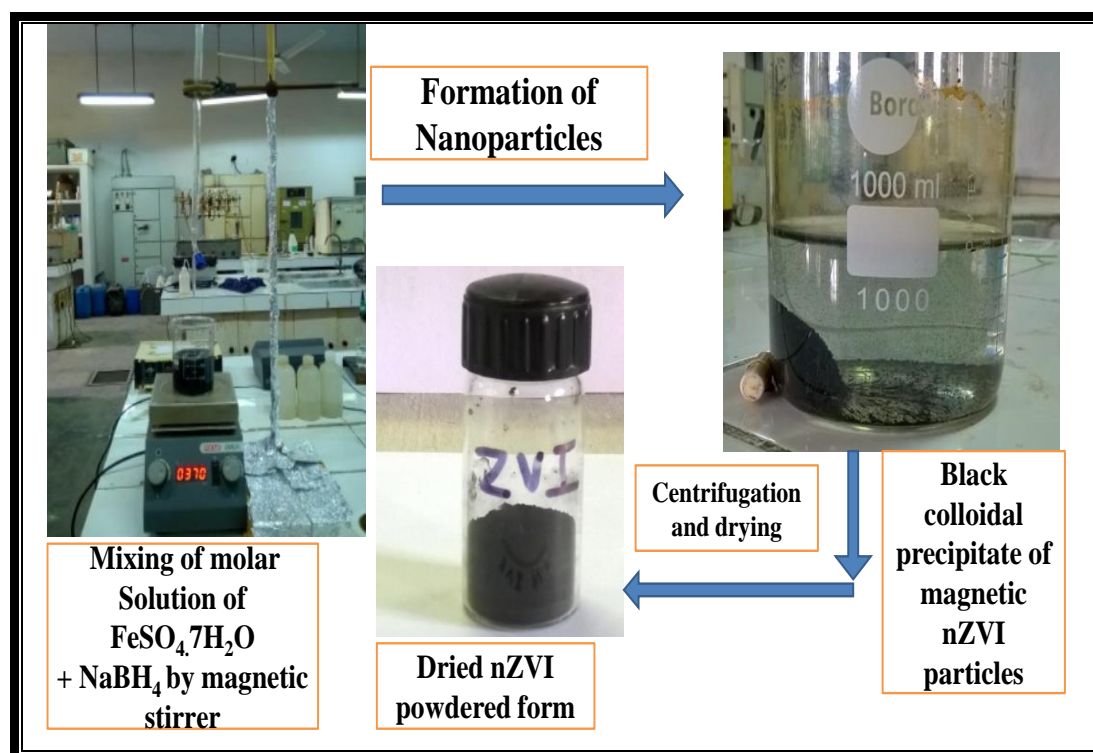
reduced by using NaBH<sub>4</sub> (0.2M). NaBH<sub>4</sub> (0.2M) was added slowly into FeSO<sub>4</sub>·7H<sub>2</sub>O (0.05M) under continuous stirring by magnetic stirrer at room temperature (25 ± 2<sup>0</sup>C). The mixing volume was taken in 4:1 ratio for faster reduction of particles. Temperature and pH have remained constant as atmospheric conditions to observe any oxidation effect on iron. The process involves the reaction for the synthesis of suitable nanoparticles with the different mixing volume ratio (2:1, 3:1, 4:1, 5:1, 10:1, 20:1) of ferrous sulfate heptahydrate iron crystals (Fe<sub>2</sub>SO<sub>4</sub>·7H<sub>2</sub>O, 0.05M, 100ml) and sodium borohydride (NaBH<sub>4</sub>, 0.2M, 25ml) as shown in equation (1):



During the reduction reaction color changes immediately from clear brownish to black with the formation of colloidal precipitate as shown in fig.1. Furthermore, solution containing magnetic iron nanoparticle was stirred continuously for

another 5 minutes and the particles were separated by centrifugation at 3800rpm for 3 minutes. Experimental parameters such as pH, reactant concentrations, stirring speed, titration rate, contact time and external temperature can, to some extent, influence the composition and surface properties of produced iron particles to some extent. Hence they need to be maintained constant in the experiments to produce consistent samples. After separation, the precipitate was washed 3-4 times with distilled water to remove excess sodium borohydride and then by ethanol for at least 4 times. The washed precipitate was transferred in an ethanol medium and then oven dried overnight at 60<sup>0</sup>C. It was believed that a thin layer of ethanol prevent it from oxidation.

The synthesized nanoparticle was characterized with the help of various instrumental techniques such as XRD (X-Ray Diffraction), SEM (Scanning Electron Microscopy) and BET (Brunauer–Emmett–Teller) isotherm studies.



**Fig.1. Synthesis of zero valent iron nanoparticles in laboratory.**

X-Ray Diffraction method was used to examine the material structure of iron nanoparticles. Analyses depicts the patterns were recorded over a 2-theta ( $2\theta$ ) configuration by using Rikagu Benchtop Mini Flex diffractometer, Japan operated at a voltage of 40Kv with X-ray source Cu- $\kappa$  radiation ( $1.546\text{\AA}$ ) and graphite monochromator to produce X-rays. Iron nanoparticles were spread on a glass slide and scanned from  $3^0$ - $50^0$ . Scanning covered all major species of iron and iron oxides. The scanning rate was set at  $2.0^0/\text{min}$ . The crystalline phase was identified by comparing with XRD diffraction patterns in the literature.

Scanning Electron Microscopy observations were performed to characterize the mean particle size and morphology of nano-particles using a FEI-QUANTA 200F machine, USA. It is a field emission scanning electron microscopy operated at the accelerating voltage of 200V-30kV under high vacuum mode. Imaging under SE mode was typically conducted at 3 kV accelerating voltage. The dried sample was mounted onto a carbon tape coated with gold sputter thin film and observed. The magnification was adjusted above 1,00,000 x i.e. 1,20,000 x-1,60,000 x.

The specific surface area of nanoparticles was analyzed by Brunauer-Emmett-Teller (BET) adsorption isotherm method (Brunauer 1938). It is based on determining the extent of nitrogen adsorption on a given surface followed by desorption of nitrogen as temperature ramps up to room conditions. Dried samples were first degassed at  $170^0\text{C}$  for 40 minutes. The particles were dried at different temperatures i.e. room temperature,  $90^0\text{C}$  and  $200^0\text{C}$  and then exposed to nitrogen gas (analysis adsorptive). The amount of nitrogen adsorbed and desorbed by the particles was measured to determine the surface area by using surface area analyzer (Micromeritics ASAP 2010, USA) at 77.3 K.

The nanoparticle was equilibrated with solutions of different pH values at  $25^0\text{C}$  for 2 hours to evaluate its chemical stability. Distilled water (100ml) was taken in several conical flasks and their pH was adjusted in the range 1 to 13 with HCl and NaOH. Powdered nanoparticles (0.1g) was added in each conical flask containing pH adjusted distilled water. The mixtures was shaken on an electrical shaker for 2 hours at  $25 \pm 2^0\text{C}$ . The samples were then filtered using previously dried filter papers. The filter papers were dried in a hot air oven at  $103^0\text{C}$  for 1-2 hours and weighed after cooling in a desiccator. During filtration, sample residues were rinsed with distilled water 2-3 times to remove the excess of acids or alkalis and then placed in an oven at  $103^0\text{C}$  for 2 hours. The residue along with filter paper was weighed after cooling in a desiccator. For determination of thermal stability weighed amount (0.1 g) of adsorbent in a beaker was kept at different temperatures (30, 45, 60,  $75^0\text{C}$ ) and reweighed after cooling in a desiccator. Equation (2) and (3) represents the calculation for the percent loss of adsorbent.

$$\text{Percent weight loss of adsorbent} = \frac{w_a - w_{ra}}{w_a} \times 100 \quad (2)$$

$$W_{ra} = (w_r + w_{fp}) - w_{fp} \quad (3)$$

where,

- $w_a$  = weight of adsorbent taken
- $w_{ra}$  = weight of residual adsorbent
- $w_r$  = weight of residue
- $w_{fp}$  = weight of filter paper/beaker

The absorbance of the dye solution of known concentration was analyzed using spectrophotometer at  $\lambda_{\text{max}}$  and the calibration curve was drawn and slope and intercept were determined. With the help of these, a concentration of dye was quantified. The quantity of the dye uptake of the fibers (mg/gm) was determined using the following equation (4):

$$Q = C_i - C_f \quad V / W \quad (4)$$

where Q = quantity of dye uptake

C<sub>i</sub> and C<sub>f</sub> = initial and final concentration of the dye in the solution (mg/gm)

V = volume of the dye bath (l)

W = weight of the fibre (g)

## RESULTS AND DISCUSSION

In the present investigation, zero valent iron nanoparticles were synthesized having a valency of zero yielding non-crystalline nanoscale Fe(s) in aqueous solutions of Fe<sup>2+</sup> (aq) and Fe<sup>3+</sup> (aq). The present study also interprets that nZVI particles, prepared from the chemical reduction method of Fe<sub>2</sub>SO<sub>4</sub>.7H<sub>2</sub>O and NaBH<sub>4</sub>, shows maximum adsorption capacity for dye adsorption with the ratio of 4:1 (v/v) i.e. 5339 mg/g (fig. 2). It might be because of stoichiometric chemistry of extent of the

reaction mechanism followed by the interaction of moles of BH<sub>4</sub><sup>-</sup> and Fe<sup>2+</sup> and Fe<sup>3+</sup> (Pullin *et al.*, 2017). The predicted volume ratio of aqueous solutions mixing also shows that aqueous media reactions were very rapid at room temperature (25±2°C) and no oxidation occurred in the mixture, so in this study, no ambient atmosphere of inert gas or N<sub>2</sub> gas was used.

The present study observed that the chemical reduction method is an easy laboratory method and could be performed under room temperature. Due to the large surface area of nanoparticles and more number of reactive sites than micro-sized particles, Nanoscale zero-valent iron was preferred for adsorption and reduction.

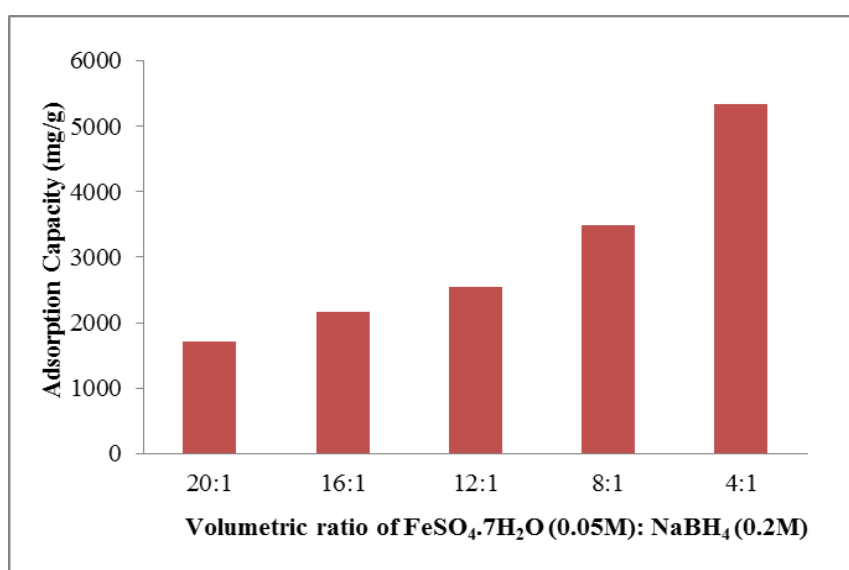


Fig. 2. Dye uptake of reactive Red-198 dye with different volumetric ratio of molar solution of ferrous sulfate (FeSO<sub>4</sub>.7H<sub>2</sub>O, 0.05M) and sodium borohydride (NaBH<sub>4</sub>, 0.2M), concentration of dye, 100 ml of 3000mg/l, adsorbent dose, 0.01 g nZVI.

The XRD pattern of synthesized nZVI under ambient conditions was shown in fig. 3. The peak reveals the existence of an amorphous phase of iron. The characteristic broad peak at 2θ of 45.6° indicates that the zero valent iron (Fe<sup>0</sup>) is predominantly present in the sample, whereas the small peaks at 2θ of 4.7° indicates the presence of FeO. The mean crystallite size is found to be of 1.98nm

and size of one crystal particle is approximately 29.6nm. The smaller amount of iron oxides could also be seen. It is found that disordered Fe<sup>0</sup> particles are present in the fresh sample of synthesized particles and shows partial oxidation of iron (Chi *et al.*, 2018). The crystallite size of the iron powder was determined by using the Scherer's equation as follows [5]:

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (5)$$

where,

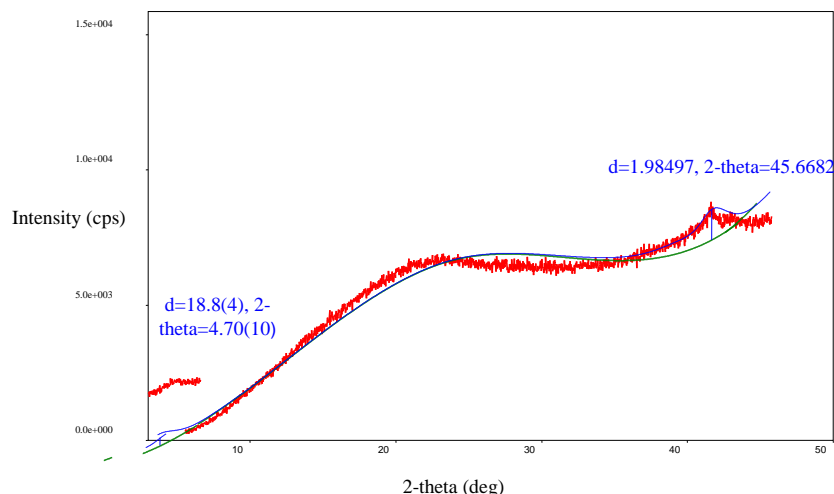
$\lambda$  = wavelength of incident ray (1.5418 Å)

K = shape factor (0.9), t = crystallite size,

$\theta$  is the Bragg angle

$\beta$  = is the line broadening at half the maximum intensity (FWHM), it is also denoted as  $2\theta$

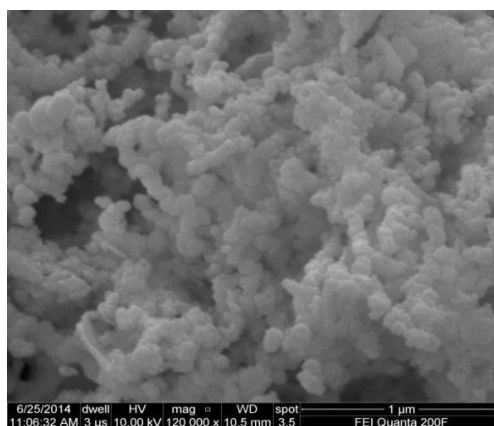
D = Mean size of the ordered (crystalline) domains



**Fig. 3. XRD pattern of nanoscale zero valent iron.**

The mean crystalline size, d comes around 1.98497nm and size of one crystal particle is near about 29.6nm from the XRD pattern. However, it is reported that 16% of iron oxides are present along with the Fe<sup>0</sup>, while they found no peaks in the XRD pattern (Cao *et al.*, 2005). The surface morphology of nZVI is shown in fig. 4 and fig. 5. Images depicted that iron nanoparticles are present in clusters as nanospheres and reported as to form chain or linear structures. The laboratory

synthesized nanoparticles are largely spherical and show a single particle size, around (50-80nm). Some particles are having a size of less than 30nm, some are having a size of  $\leq 100$ nm, whereas  $\geq 90\%$  particles are having a size less than 100nm. In the images, few flaky forms indicated the presence of iron oxide. The present findings shows that the particles having smaller average size in nanometers could be considered as nanoparticles and might be used as an adsorbent.



**Fig. 4. SEM image of freshly prepared nanoparticles showing chain forming nanospheres or nanoclusters.**

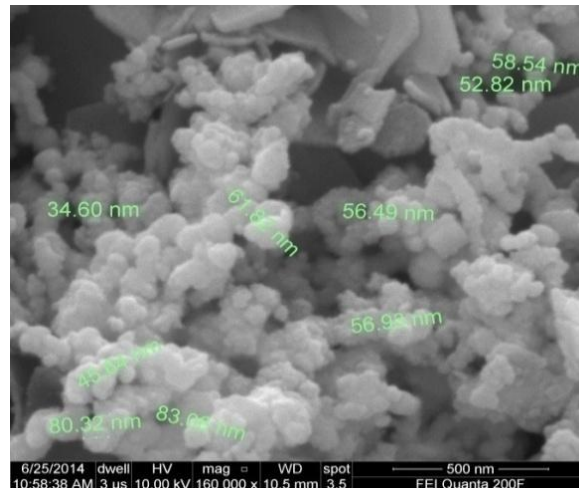


Fig. 5. SEM image showing different sizes of single nZVI particle (34.6-83.0nm). Flakes at the upper side of the image indicate the presence of iron oxide.

Fig. 6 presents the nitrogen physisorption data of nano iron. The specific surface area of the material determines many of its physical and chemical properties, including adsorbent capacity and reactivity with pollutants. The present study observed the value i.e. 24.8 m<sup>2</sup>/g as the specific surface area of then ZVI nano-particle determined by the classic N<sub>2</sub>-BET method. It was found that single point surface area at relative pressure near to a 0.3 value of (P/P<sub>0</sub>) is 24.6 m<sup>2</sup>/g. Langmuir surface area is calculated as 37.8 m<sup>2</sup>/g. The adsorption average pore diameter and total pore volume are found to be 105.8 Å/10.58 nm and 0.066 cm<sup>3</sup>/g respectively. Large surface area of nZVI is due to the presence

of more reactive sites which shows its reaction reactivity towards compounds. The increase in specific surface area means an increase in the total amount of iron on the surfaces. The results of present study are observing large surface area value of 24.8 m<sup>2</sup>/g. In previous study BET surface area value was 29 m<sup>2</sup> g for nZVI (Sun *et al.*, 2006). Furthermore, present findings also shows a greater surface area as compared to commercial iron powder having a size of 1.5 m<sup>2</sup>/kg as reported (Tan *et al.*, 2013) and commercially used activated carbon with the surface area of 500-2000 m<sup>2</sup>/g as investigated. Therefore, nZVI could be used as nano-sorbents for wastewater treatments.

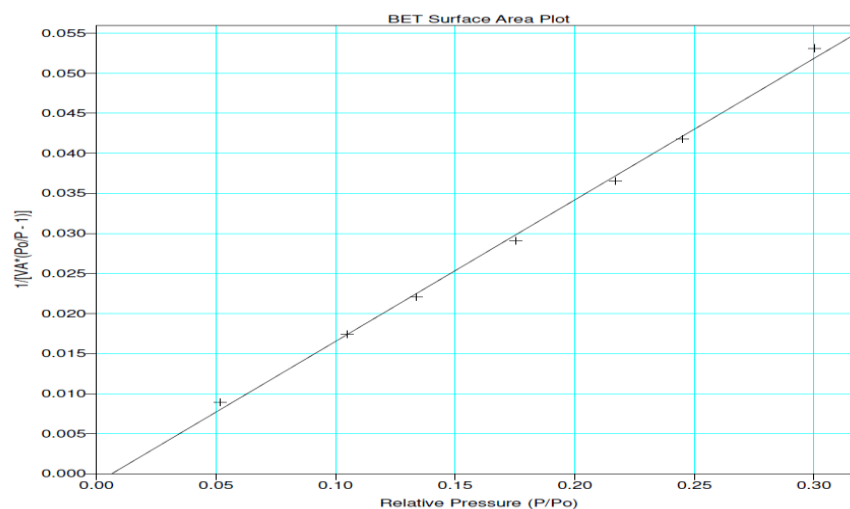


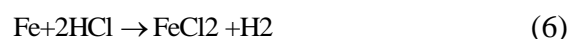
Fig. 6. Linear plot of N<sub>2</sub>-BET adsorption isotherm or BET surface area plot.



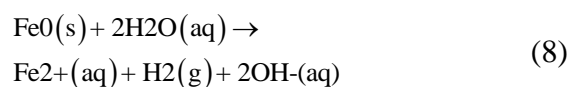
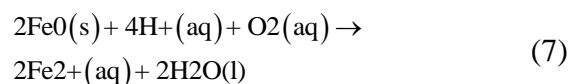
The nature of the nZVI-water interface plays a key role in the reactivity and stability of the nanoparticles because the interface is the place where different processes: corrosion, precipitation, and contaminant adsorption and degradation occurred. Reactive barrier application is an important consideration for the stability of zero valent iron because iron reacts not only with the contaminants present in the waste but also with dissolved oxygen and water (Tan *et al.*, 2013). Zero-valent iron shows a great susceptibility to corrosion in aqueous media while being oxidized to Fe<sub>2</sub>O (fast process) and Fe<sub>3</sub>O (slower process).

Fig. 7 shows that nZVI was found stable at neutral or alkaline medium with very less weight loss of 0.4% at pH= 5 and 1.6 % at pH=10. It could also shows stability at acidic conditions, with weight loss of 3.6% at pH 3 and 1.6 % at pH 4 but not towards decreasing pH because particles undergo decomposition with 83% of weight loss. It could be explained with the solution chemistry fact that when metal dissolves with acids, they produce salt and hydrogen gas. This type of reaction is known as single displacement reaction where an element displaces another compound. The salts formed in this reaction gets solubilizes itself as salts are soluble in

water. This could be explained by reaction of iron with hydrochloric acid which is forming ferrous chloride as salt with the evolution of hydrogen gas as shown in the equation (6):



Furthermore, the solution undergoes oxidation could convert ferrous ions (Fe<sup>2+</sup>) to ferric ions (Fe<sup>3+</sup>) as shown in equation (7) and (8):



So, on increasing the molar concentration of HCl and decreasing the pH, decomposition rate would increase due to higher reaction rate of (H<sup>+</sup>) ions whereas at increasing pH, hydroxide (OH<sup>-</sup>) ions would promote less decomposition because of its slow reaction rate as compared to acids. Studies have been reported on the oxidation and decomposition behavior of similar nanoparticles by adding KCl as electrolyte and found their higher stability at pH 8.5 for more than one month (Bokare 2008).

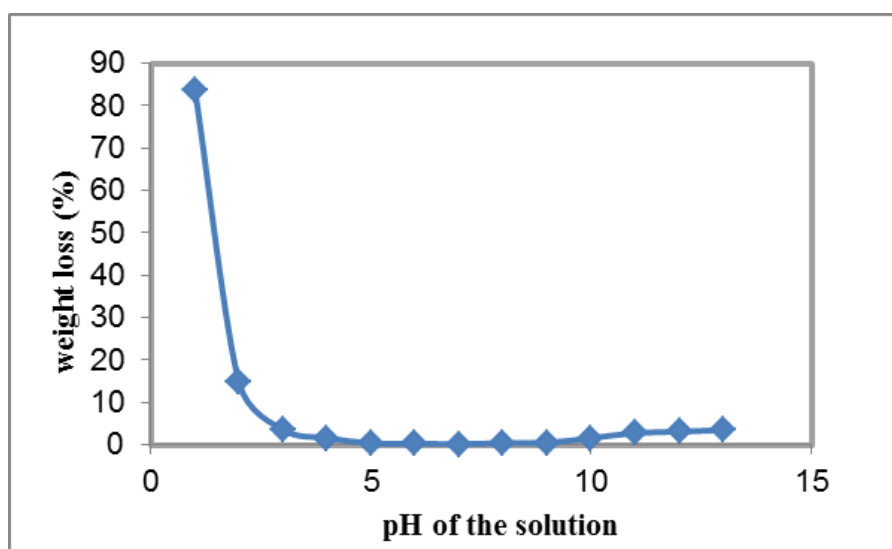


Fig. 7. Percentage of weight loss of the adsorbent (0.1g) at different pH of the 100 ml of solution.



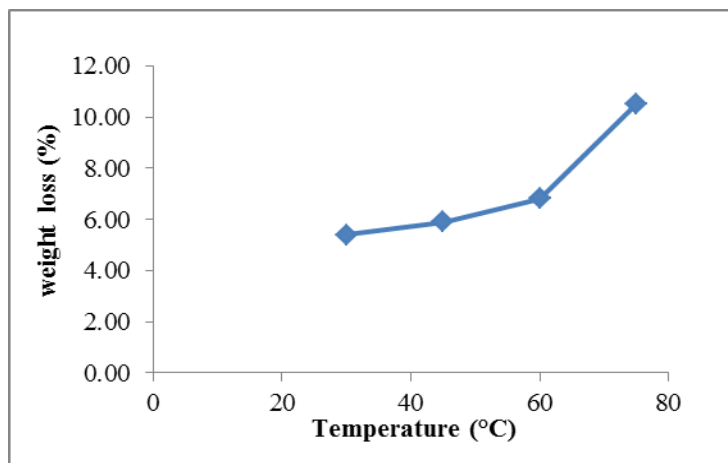


Fig. 8. Percentage of weight loss of the adsorbent (0.1g) at different temperature.

The present study found that on annealing of nZVI by increasing the temperature after 60°C, decomposition of the material occurred with the weight loss of 10.5% as shown in fig. 8. It may be due to the increased reactivity of metals. By increasing the temperature, the rate of reaction increased with the increased average kinetic energy of the molecules due to more collisions of particles. More collisions could overcome the activation energy for the reaction to be carried over by the particles increased the motion of free electrons. Ultimately it would result in a faster rate of reaction. These study results coincide with the study on the thermal analysis of iron particles as he reported decomposition at 383° C with 83% weight loss (Bokare et al., 2008; Tong *et al.*, 2011). The present study findings also showed that nano zero valent iron particles can be used at slightly acidic, neutral to slightly alkaline pH conditions at room temperature (25±2° C) to 80° C depending on their synthesis conditions.

## CONCLUSION

The nano zero valent iron (30-100nm) synthesized by borohydride reduction method under atmospheric conditions was mainly in zero valent oxidation state. It was observed from the study that the key point of synthesis was the volume of NaBH<sub>4</sub> which should be in excess for the proper

growth of iron nanoparticles, maximum adsorption was observed at the ratio (4:1) by mixing 100 ml of FeSO<sub>4</sub>.7H<sub>2</sub>O (0.05M) with 25 ml of reducing agent NaBH<sub>4</sub> (0.2M) in distilled water. Ethanol medium can be used to prevent further oxidation in the prepared material. The nanoparticles are in nanoscale range (from 30-100nm size) when it was characterized by Scanning Electron Microscope (SEM), presence of disordered Fe<sup>0</sup> was found by X-Ray diffraction (XRD) and larger surface area of 24.6 m<sup>2</sup>/g was determined by Brunauer-Emmett-Teller method (BET) adsorption method. These nanoparticles are stable in the temperature range of 30-60°C. This showed that nanoparticles could be used for the removal of textile dyes from the textile effluent as they have alkaline pH and attain room temperature after few hours.

## FUTURE RESEARCH

The following recommendations are being suggested for the future course of action:

1. The nanoparticles are stable over a wide pH range of the solution, so they can be used at slightly acidic pH conditions (pH 3-6).
2. Further, zero valent iron nanoparticles exhibit maximum adsorption capacity with reactive red dye, hence they can be used for other class of dyestuff in batch studies.

3. Due to their large surface area and reducing properties, they might be used for industrial application in the column studies.

### GRANT SUPPORT DETAILS

The present research did not receive any financial support.

### CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

### LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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