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Nano Scale Zero Valent Iron Particles for Dye Removal in Textile Industry and Treatment of Effluent

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Abstract— *Nano-remediation procedures are designed so that only one contaminant or similar class of contaminants is being considered. In the present work, a holistic approach was applied towards processes which simultaneously occur after the treatment of real effluent water and dye removal of from a small biological wastewater treatment plant (SBWTP) with nano scale zero-valent iron (nZVI) particles.*

Since textile dye compounds which is harmful to human beings, a simple and sensitive method to remove this pollutant from wastewater is using Nano ZeroValent Iron (nZVI) catalyst. Four independent variables—including catalyst amount (0.1–0.9 g), pH (3.5–9.5), removal time (30–150 s) and dye concentration (10–50 mg/L)—were transformed to predict the responses of effluent. The result showed that under the optimized experimental conditions the removal of textile dye was over 95%.

Keywords— *nZVI: Nano-remediation: SBWTP.*

I. Introduction

Nowadays, the aquatic environment is globally polluted with various industrial or human activities, and water contaminated with pathogenic organisms is used by millions of people. Scientific evidence indicates that water scarcity will occur globally, even in regions which are now considered to be water rich.

There are 3 basic needs that a man possesses food, clothing, and shelter. The textile and clothing industry is bound to be huge, as it fulfills the second basic requirement of man. It is worth $480 billion at present and is expected to reach $700 billion, shortly.

But the sad fact is that the human greed to look appealing and wear glamorous clothes has ended up harm to the environment. The textile industry is considered as one of the most pollutants releasing industries of the world. Surveys show that nearly 5 percent of all landfill space is consumed by textile waste. Besides, twenty percent of all fresh water pollution is made by textile treatment and dyeing.

The textile industries uses millions of gallons of water every day. The problem does not rest in the high usage, though! The waste is not treated to remove pollutants from it before it is disposed to water bodies.

The liquid effluents released by the textile industry are the most disturbing area of concern. This is because the toxic material released through liquid waste is large in quantity. It consists of chemicals such as formaldehyde, chlorine, and heavy metals. Besides, it is disposed into water bodies that reach far away areas and is consumed by a large number of people for drinking or daily activities. They need to be treated to reduce its toxic content before being released into water bodies.

The use of organic raw material can help in fighting the emission of pollutants by the textile mills. Organic cotton is especially beneficial since the production of cotton asks for the maximum amount of pesticides and fertilizers. Besides, the waste generated from textile plants should be processed in a manner that it is free from toxic chemicals before it is disposed [5].

There is no doubt to the fact that the textile industry releases harmful pollutants to the atmosphere in large quantities. It is agreed all over the world that textile industries are one of the most pollutants emitting industries of the world. Almost thousand different types of chemicals are used in this industry. It consumes as well as contaminates fresh water body. There is a need to take actions in this direction.

In order to ensure the availability of clean and safe water sources for humans and other living beings, it is necessary to make proper use of current technologies to wastewater treatment, as well as developing new technologies. [7] The latter must be robust and available in low cost, with low energy consumption and minimal impact on the environment. Most of the conventional purification technologies have some drawbacks. For example, biofouling causes problems to membrane filtration, while the use of UV radiation for water disinfection was energy consuming. When chemical treatment using Cl_2 and O_3 is applied for disinfection, harmful secondary products, like ClO^{3-} and BrO^{3-}, which are of environmental concern, may be produced.

This work aims to enable textile industry to make it more eco-efficient, through analysis and evaluation of their wastewaters and implementation for treating these waste waters using zero valent iron particles.. It is intended to obtain water with quality parameters that allow its reuse or recycling within the industrial plant.

In the present work, a holistic approach was applied towards processes which simultaneously occur after the treatment of real effluent water and dye removal from a small biological wastewater treatment plant (SBWTP) with

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nanoscale zero-valent iron (nZVI) particles. In order to optimise the conditions for the efficient removal of selected elements effluent water samples were treated with different iron loads from each of the investigated nZVI at various mixing and settling times.

Since textile dye compounds which is harmful to human life, a simple and sensitive method need to remove this pollutant from wastewater is using Nano- Zero Valent Iron (nZVI) catalyst. Four independent variables—including catalyst amount (0.1–0.9 g), pH (3.5–9.5), removal time (30–150 s) and dye concentration (10–50 mg/L)—were transformed to predict the responses. The result showed that under the optimized experimental conditions the removal of textile dye was over 95%.

II. Materials and Methods

A. Materials

Reactive voilet 5 (Molecular formula ($C_{20}H_{16}N_3Na_3O_{15}S_4$), Molecular Weight 735.563 g/mol, was obtained from Parshwanath Dyestuff Industries Ahmedabad, buy through online at Rs. 260/ kg and was used without any further purification (Fig. 1 shows the chemical structure of RV5.). Sodium Borohydride (NaBH4), Iron (III) chloride (FeCl3.6H2O), Acetone, HCl and NaOH were obtained from Malappuram chemical lab. Deionized distilled water (DDW) was used in all experiments. The amount of residual RB21 was analyzed by double beam spectrometer.

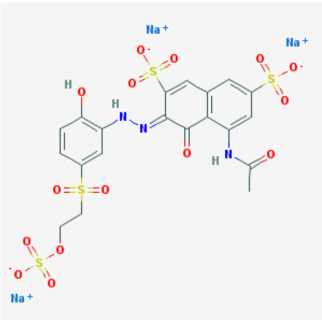

Fig. 1. Chemical structure of RV5.

B. Synthesis of Nano- Zero Valant Iron Particles

For the synthesis of nanoscale Zero Valent Iron (nZVI); 0.5406 g FeCl3.6H2O was dissolved in a 4/1 (v/v) ethanol/water mixture (24 ml ethanol + 6 ml deionized water) and stirred well. On the other hand, 0.1 M sodium borohydride solution was prepared i.e., 0.3783 g NaBH4 was dissolved in 100 ml of deionized water; since for better growth of iron nano particles excess borohydride is needed. The borohydride solution is poured in a burette and added drop by drop (1 drop per 2 seconds) into iron chloride solution with vigorous hand stirring. After the first drop of sodium borohydride solution, black solid particles immediately appeared and then the remaining sodium borohydride is added completely to accelerate the reduction reaction. The mixture was left for another 10 minutes of stirring after adding the whole borohydride solution. The vacuum filtration technique or magnetic separation was used to separate the black iron nano particles from the liquid phase. Two sheets of filter papers were used in filtration. The solid particles were washed three times with 25 ml portions of absolute ethanol to remove all of the water. This washing process is probably the key step of synthesis since it prevents the rapid oxidation of zero valent iron nanoparticles. The synthesized nano particles were finally dried in oven at 323 K overnight. For storage, a thin layer of ethanol was added to preserve the nano iron particles from oxidation.

Despite being differently synthesized, the composition of the nZVI produced is, in general, similar, although there are differences in the crystalline structure and in the size of the Fe0 core and the iron hydroxide shell. These characteristics have an important effect on nZVI reactivity. Smaller nZVI particles have a higher proportion of atoms exposed on their surface, which increases their tendency to adsorb, interact, or react with other substances to achieve surface charge stabilisation. In addition to contaminant removal processes which involve the surface reduction and complexation of intact nZVI, contaminants can also be co precipitated with iron corrosion products.

Fig. 2. Solution of nZVI.

C. Sample Collection of Textile Effluent

The effluent was collected from a small scale dyeing unit at Rayanur of Karur district, Tamilnadu. Karur is famous for its handloom textile products. Concerning its industrial location, it is one of the developing cities in Tamilnadu and textile industries are its dominating industries. The samples were collected in pre-cleaned 5L polythene bottles from the point of discharge of the effluent from the industry and preserved in a refrigerator at 4ºC till the completion of the investigation

III. Experimental Setup

These samples were analyzed without any treatment in order to evaluate functioning of the plant and to determine the variability of the effluent water composition regarding the dye concentration, microbiological and chemical contaminants present in wastewater. To study the influence of nZVI treatments on remediation efficiency, in each experiment, aliquot samples were taken to determine microbiological and chemical composition of untreated effluent water and water after the remediation. Depending of the type of analysis being

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performed, 4–20 L of effluent water was collected at the outflow of the plant into a plastic container and the sample was immediately delivered to the laboratory, where experiments were carried out at room temperature (22 ± 1digree Celcious). In order to study the processes which influence the removal efficiency or disinfection of the effluent water from the plant by means of nZVI, the samples were treated with nano zero valent iron, prepared by laboratory means. The samples were then mixed with different concentrations of nano zero valent iron in a blender at 700 rpm for different time intervals (30–1200 min) and left to settle (180 or1200 min). After treatment, the samples for examination of inorganic contaminants were transferred to a 2000 mL non-sterilised. Plastic bottles and capped, whereas for microbiological investigations sterile plastic bottles and caps were used. To avoid disturbance of the settled particles, the clear solution was carefully taken from the top layer of the remediated water by 100 mL glass beaker or by a sterile syringe, respectively. In these samples, the content of microorganisms were determined. An untreated effluent water sample was also transferred to a sterile plastic bottle to determine the initial content of parametrs. The same treatment procedures were applied in non-sterilized beakers for estimation of the efficiency of the removal of inorganic elements of plants. A set of 30 experiments were designed to optimize the dye removal efficiency of nZVI. Four independent Variables called catalyst dosage, pH, removal time and initial concentration were investigated and each variable in the design was studied by five different coded levels. The amount of residual Reactive Violet - 5 was analyzed by spectrometer.

IV. Result and Discussion

A. Dye Removal Efficiency

A set of 30 experiments were designed for to optimize by Nano ZVI catalyst. Four independent variables called catalyst dosage, pH, removal time and initial concentration were investigated and each variable in the design was studied by five different coded levels.

TABLE I. Different values of variables used for dye removal.

Variable	Symbol coded	Values				
Catalyst amount	X1	0.1	0.3	0.5	0.7	0.9
P^H	X2	3.5	5	6.5	8	9.5
Removal time	X3	30	60	90	120	150
Dye concentration	X4	10	20	30	40	50

The catalyst used for the dye removal of textile effluent were nano scale zero valent iron particles. Its value varied between 0.1g to 0.9g. The P^H and removal time is also varied for different concentrations of dye. Experimental data to remove RV-5 from wastewater are given in table II.

ZVI appeared to be a very active and strong catalyst for removal of textile dye from aqueous solution. In the present study, removal time, initial concentration of RV5, the amount of catalyst, and pH were the most significant effects on the removal of RV-5,On optimizing the experimental conditions for the removal of RV-5 from wastewater. According to the analysis results, 0.5 g ZVI catalyst, natural pH, 90s removal time, and initial concentration of 30 mg/L, were the optimum conditions Consequently useful information about this alternative wastewater technology was obtained by considering the effects of NZVI on optimizing the potential parameters of Reactive Voilet 5 dye removal.

TABLE II. Dye removal efficiency.

Run	Catalyst Amount (mg/l)	P^H	Removal Time(s)	Dye Concentration(mg/l)	Removal efficiency (%)
	X1	X2	X3	X4	
1	.3	5	60	20	70
2	.7	5	60	20	92
3	.3	8	60	20	79
4	.7	8	60	20	89
5	.3	5	120	20	80
6	.7	5	120	20	95
7	.3	8	120	20	85
8	.7	8	120	20	93
9	.3	5	60	40	73
10	.7	5	60	40	85
11	.3	8	60	40	74
12	.7	8	60	40	78
13	.3	5	120	40	87
14	.7	5	120	40	99
15	.3	8	120	40	79
16	.7	6.5	120	40	93
17	.1	6.5	90	30	68
18	.9.5	3.5	90	30	94
19	.5	9.5	90	30	81
20	.5	6.5	90	30	83
21	.5	6.5	30	30	75
22	.5	6.5	150	30	98
23	.5	6.5	90	10	98
24	.5	6.5	90	50	80
25	.5	6.5	90	30	94
26	.5	6.5	90	30	94
27	.5	6.5	90	30	98
28	.5	6.5	90	30	97
29	.5	6.5	90	30	99
30	.5	6.5	90	30	95

B. Characteristics of Textile Industry Waste Water Before Treatment

The textile dyeing effluent sample was found to be dark violet in colour with objectionable bad odour. The electrical conductivity recorded were 360µmho/cm. The temperature of the sample at the time of collection is 40ºC. The values of total suspended solids (TSS), total dissolved solids (TDS) and total solids (TS) were found to be 2000 mg/l, 8000 mg/l and 10000 mg/l respectively. The effluent has a pH of 9.5 and a total alkalinity of 430 mg/l. Total hardness of effluent recorded was 460 mg/l. Dissolved oxygen content (DO) is 3.5 mg/l. Biological oxygen demand (BOD) and chemical oxygen demand of sample were 90 mg/l and 571 mg/l respectively. The amount of chlorides, sulphates, phosphates and nitrates were 1298 mg/l, 948 mg/l, 2.18 mg/l and 80 mg/l respectively. The amount of lead, nickel, zinc, chromium and copper recorded the values of 1.3 mg/l, 0.9 mg/l, 5.46 mg/l, 1.83 mg/l and 3.21 mg/l respectively. The amount of oil and grease estimated was 14.7 mg/l. The results of the physicochemical analysis showed that the textile effluent is characterized by the presence of colour with objectionable odour, high electrical conductivity, high TSS, TDS values, alkaline pH, high BOD and COD, low DO, high amounts of chlorides and sulphates, nitrates and also showed the presence of heavy metals and microorganisms, oil and grease. Colour of the effluent depends on the dyes used.

TABLE III. physical parameters of textile effluent before treatment and permissible BIS limits.

Sl no	Parameters	Sample	BIS permissible limit
1	Colour	Dark violet	-
2	Odour	Bad odour	-
3	Electrical conductivity	360	600
4	Temperature	40	>40
5	TSS	2000	100
6	TDS	8000	2100
7	TS (mg/l)	10000	

TABLE IV. Chemical parameters of textile effluent before treatment and permissible BIS limits.

Sl. no	Parameters	Unit	Effluent	Bis permissible limit
1	pH		9.3	5.5-9
2	Alkalinity		430	200-600
3	Hardness	mg/l.	460	600
4	Dissolved oxygen	mg/l.	3.5	-
5	BOD	mg/l.	90	30
6	COD	mg/l.	571	250
7	Chloride	mg/l.	1298	1000
8	Sulphate	mg/l.	1118	1000
9	Phosphate	mg/l.	218	5
10	Nitrate nitrogen	mg/l.	80	50
11	Lead	mg/l.	1.3	.1
12	Oil and grease	mg/l.	14.7	10
13	Total phosphorous	mg/l.	22	20
14	Total nitrogen	mg/l.	60	30
15	Ammoniacal nitrogen	mg/l.	.06	.03
16	Total organic carbon	mg/l.	21.4	12

The color value of waste water is extremely pH dependent and it invariably increases as the pH of the effluent were raised or lowered. The textile waste water was highly colored showing the presence of high concentrations of unused dyes. The textile effluents show high colour and this may be the combined results of pH, temperature and acidic conditions that do not allow the chromophore group of dye to degrade making the effluent highly colored. The bad odor could be due to unpleasant odor of the volatile compounds. Unpleasant or pungent odour for the textile effluent was reported. The electric conductivity (EC) is usually used for indicating the total concentration of the ionized constituents of water and an indirect measurement of ions or charge carrying species in the effluents. High TSS and TDS detected could be attributed to the presence of high colour and they may be the major sources of the risky heavy metals The high pH of effluent indicates the excessive use of the dyes. pH value of waste water has no health implication but many chemical reactions are controlled by the pH. Biological activities and some chemical treatment processes are usually restricted by the pH. Federal Environmental Protection Agency (FEPA) recommends pH value of range 6 – 9 for effluent to be discharged into the stream, as either high or low pH will be harmful to man, aquatic animals and will disturb biological activity of stream if discharged untreated. Total alkalinity has been reported as a major factor which influences the pH. Alkalinity is the capacity of water to neutralize acid and is characterized by the presence of hydroxyl ions in it. The hardness of water is not a chemical parameter but indicates the water quality mainly in terms of Ca^{2+} and Mg^{2+} and expressed as CaCO3in mg/l . The hardness has no known very adverse effect. Their low concentration in the textile wastewater may be due to the use of soft water in the dyeing and printing process to avoid coagulation of the dyes.

C. Characteristics of Textile Industry Waste Water after Treatment

Sl. no	Parameters	Unit	Effluent	Bis permissible limit
1	pH		8	5.5-9
2	Alkalinity		400	200-600
3	Hardness	mg/l.	430	600
4	Dissolved oxygen	mg/l.	5.5	-
5	BOD	mg/l.	28	30
6	COD	mg/l.	240	250
7	Chloride	mg/l.	840	1000
8	Sulphate	mg/l.	1012	1000
9	Phosphate	mg/l.	2.1	5
10	Nitrate nitrogen	mg/l.	40	50
11	Lead	mg/l.	.12	.1
12	Oil and grease	mg/l.	9.8	10
13	Total phosphorous	mg/l.	22	20
14	Total nitrogen	mg/l.	60	30
15	Ammoniacal nitrogen	mg/l.	.06	.03
16	Total organic carbon	mg/l.	21.4	12

V. CONCLUSIONS

In order to optimise the conditions for the efficient removal of dye effluent water samples were treated with different iron loads from each of the investigated nZVI at various mixing and settling times. Since textile dye compounds which is harmful to human beings, a simple and sensitive method to remove this pollutant from wastewater is using Nano ZeroValent Iron (nZVI) catalyst. Four independent variables—including catalyst amount (0.1–0.9 g), pH (3.5–9.5), removal time (30–150 s) and dye concentration (10–50 mg/L)—were transformed used to predict the responses. The result showed that under optimized experimental conditions the removal of the textile dye was over 95%. According to the analysis results, 0.5 g ZVI catalyst, natural pH, 90s removal time, and initial concentration of 30 mg/L, were formed the correct optimum conditions

The results of the physicochemical analysis showed that the textile effluent is characterized by the presence of colour with objectionable bad odour, high electrical conductivity, high TSS, TDS values, alkaline pH, high BOD and COD, low DO, high amounts of chlorides and sulphates, nitrates and also showed the presence of heavy metals, microorganisms, oil and grease. Color of the effluent depends on the dyes used in it. Different color marks are used for dyeing different lots of cloth. Both synthetic and natural colours easily disperse in the water. The color value of waste water is extremely pH dependent and it invariably increases as the pH of the effluent were raised or lowered. The bad odor could be due to unpleasant odor of volatile compounds in it. Unpleasant or pungent odour for the textile effluent was reported. The electric conductivity (EC) is usually used for indicating the

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total concentration of the ionized constituents of water and an indirect measure of ions or charge carrying species in the textile effluents. High TSS and TDS detected could be attributed to the presence of high colour and they may be the major sources of the heavy metals in it. The high pH of effluent indicates the excessive use of dyes. Federal Environmental Protection Agency (FEPA) recommends pH value of range 6 – 9 for effluent to be discharged into the stream, as either high or low pH will be harmful to man, aquatic animals and will disturb biological activity of the stream if discharged untreated. After treatment with nano zero valent iron the PH has been reduced to about 8. Low concentration of hardness in the textile wastewater may be due to the use of soft water in the dyeing and printing process to avoid coagulation of the dyes. The dissolved oxygen was increased after treatment to ensure healthy habitat to the aquatics. The high BOD of 90 mg/l has been reduced to 28 mg/l after treatment. The COD value is also reduced from 570 mg/l to 240 mg/l after treatment with zero valent iron. It determines the oxygen required for the chemical oxidation of organic matter and assesses the quantity of chemically oxidizing matter in the water. Chloride in the waste water may be due to water softening process or when sodium chloride is used to recharge the softeners. The high concentration of sulfate in the untreated waste water is due to use of sulfuric acid in various steps of the dyeing and printing process. Presence of heavy metals in the waste water may be due to use of some dyes in which these metals are get complexed. It have been reported that the major problem associated with textile processing effluents is presence of heavy metals, which arise from materials used in the dyeing process or in a considerably in high amount, from the metal containing dye. These heavy metal related issues can be considerably reduced by use of this nano zero valent iron. The result showed that under optimized experimental conditions the removal of the textile dye was over 95%.

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