Textile dye removal using nZVI particles supported on cation exchange resin

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Abstract : A resin supported zero valent iron nanoparticle was prepared using cation exchange resin Indion-225 (H^+) and studied for its color removal efficiency. Fe^{2+} ions were incorporated in the resin followed by its reduction with sodium borohydride. In the previous paper, we studied the efficiency of powdered ZVI nanoparticles for removal of color from aqueous solutions by using batch method. Effect of various operational parameters like pH, auxiliaries, reaction time,doses of nanoparticle and concentrations of dye solution were also evaluated for removal of reactive dyes. In the present study, removal of reactive 198 dyefrom simulated and actual dyeing effluent has been studied by column method using resins supported nZVI. The effect of dye concentration and flow rate were evaluated on aqueous dye solutions. Adsorption capacity was found toincrease with the increase in dye concentration from 500 mg/l to 3000 mg/l.The color intensity of treated water gradually increased with the increase in volume of dye solution passed through the column. The exhausted column could be regenerated by passing $NaBH_4$ through the column, thus could be reused for color removal. Reduction of color from actual effluent was less than the color removed from simulated effluent. The color removal efficiency of resin supported nZVI was more than the powdered ZVI nanoparticles.
Keywords : Cation Exchange Resins, Effluent, Reactive Dye, ZVI nanoparticles.

1.Introduction

Textile industry is regarded as the biggest polluter in increasing the water pollution but on a contrary, it is also focusing on the growth and exceeding economy of a particular country. Dyeing and printing operations of wet processing method in the dyeing houses produces tones of colored wastewater. This non-biodegradable dye color pose a major challenge in front of environmental scientists and effluent treatment plant operators. Because synthetic origin dyes are known as recalcitrant compounds in their disposal due to the presence of N=N bonds and organic groups substances[1]. Moreover, anionic reactive dyes are the largest category of commercial dyes utilized in cotton or cellulose textile industries[2]. These contains chromophores of azo and anthraquinone group, known for their difficult de-coloration and mutagenic effects. To combat de-colorationo f the effluents, many technologies have been introduced including biodegradation, chemical reduction and membrane separation processes[3].

Currently, zero valent iron (Fe[0]) nanoparticles have received significant attention due to its high reducing properties and large surface area[4]. Scientists are focusing on the long term performance, enhanced efficiency and to mitigate the high agglomeration drawback of iron particles. To solve this issue, researchers have developed the method of nanoparticles loading onto solid support/substrate of larger particles. In this respect, few approaches have been explored with anion exchange resins[5],carboxymethyl cellulose[6](CMC)and with biodegradable polymeric surfactant[7].Studies have been also done with common substrates such as:granular activated carbon,clay, mesoporous or macroporous silica, alginate beads, polymers and membrane pores[8-10].Many studies have observed that immobilized particle maintains good reduction ability and are easy to operate.

Our previous paper was based on synthesis, characterization and removal of color from aqueous solutions by ZVI nano-particles. These nanoparticles showed maximum adsorption capacity for reactive dyes from aqueous solution. In the present paper, we have supported these nano-particles on cation exchange resin, a co- polymer of styrene and divinyl benzene(DVB) having sulphonic acid group($-SO_3H$). Columns of supported nanoparticles were prepared and color removal efficiency of these columns was evaluated. Its application in removal of color from simulated dyeing effluents as well actual dyeing effluents was also explored. The exhausted column has regenerated by its reduction with sodium borohydride to explore the possibility of reusing the column again and again.

2. Experimental

2.1. Materials Used

Ferrous sulphateheptahydrate ($FeSO_4.7H_2O$) and reducing agent Sodium borohydride ($NaBH_4$)used for preparation of ZVI were procured from Merck chemicals, Mumbai. Commercially available strong acid cation exchange resin Indion -225(H+) used as solid support was purchased from Ion Exchange India Ltd. New Delhi.Reactive red dye (Reactive Red 198) was obtained from Clariant, Mumbai (India) and was used as received without any purification. Actual dyeing effluent was collected from equalization tank of ETP installed at a textile dyeing house situated at Mohan Nagar, Ghaziabad, UP.

2.2. Synthesis of resin supported ZVI nanoparticles

For preparation of resin supported ZVI nanoparticles, 10 ml of Indion225-H$^+$resin was filled in a glass column and washed with distilled water. The resin was converted from H$^+$ ion form to Fe^{2+} ion form by passing 300 ml of0.1M solution of $FeSO_4.7H_2O$ through the resin column. It was washed several times by distilled water to remove the excess iron sulfateheptahydrate. After that,75ml of $NaBH_4$(0.4M) was passed through the column for reduction of ferrous ions into zero valent ions(Fe^{2+} to Fe^0). The excess reducing agent was washed thoroughly with distilled water. Finally, the column was washed with 99% alcohol to remove excess chemicals and to prevent the resin supported ZVI particles from oxidation. Freshly prepared resin supported ZVI was used for all the studies. All the studies were carried out at room temperature (25 ± 5^0C).

2.3. Preparation of simulated dyeing effluent

Simulated dyeing effluent was prepared in the laboratory by the exhaust dyeing method[11].Grey cotton fabric sample was used and processed for de-sizing, scouring, bleaching and dyeing. Table 1 represents the dyeing recipe which was used in the preparation of simulated effluent.

Table 1 Dyeing recipe for preparation of simulated dyeing effluent

Components	unit	Required quantity
Reactive Red 198 Dye	gpl	0.2
Sodium Carbonate (Na_2CO_3)	gpl	20
Sodium Hydroxide (NaOH)	gpl	10
Hydrogen peroxide (H_2O_2)	gpl	3
Desizer (alpha amylase)	gpl	10
Surfactant(ExtranMA02,Neutral)	gpl	1
Sodium chloride (NaCl)	gpl	40

Grey cotton fabric was first pretreated by carrying out desizing, scouring and bleaching. For de-sizing,100 g fabric was treated with 10 gpl of de-sizer in a hot water bath for one hour. The fabric was washed with water and then scouring was done by adding 10gpl sodium hydroxide and 1gpl extran and 20gplNa_2CO_3 and boiling for 3-4 hours. Bleaching was done by adding 3gplH_2O_2in the water bath and keeping for half an hour. Temperature of the water bath was maintained as prescribed in the method. The fabric was then washed with cold water and dried. Bleached cotton fabric was dyed with reactive red dye (Reactive Red 198) in the hot water bath at 40° C. The dye bath liquor was prepared by dissolving 1 g reactive dye in 5 liter distilled water. Auxiliaries such as NaCl(20 gpl) and Na_2CO_3(10 gpl) were added slowly for the next one hour by increasing the temperature up to 60°C. In this process salts recipe was taken as 2:1 (NaCl: $NaCO_3$) and dye was taken as (x%) of weight of fabric. As per the industrial standards, material to liquor ratio (MLR) was taken as 1:50 and shade was chosen as 1% (normal range is 0.5-2%). The unspent dye liquor was collected as simulated dyeing effluent and immediately analyzed for its physicochemical properties as per Standard Methods for the Examination of Water and Waste Water[12]. Results are summarized in Table 2.

2.4. Evaluation of dye adsorption by resin supported nZVI from pure dye solution

Dye solutions of various concentrations (500, 1000, 1500, 2000, 2500, 3000mg/L) were prepared in de-ionized water. De-coloration experiments were performed by passing 100 ml of the dye solution through the glass column containing 10 ml of resin supported nZVI. Adsorption capacity was determined by measuring the absorbance of the dye solutions before and after passing through the column by using UV-Vis spectrophotometer of Shimadzu (U.V-160A), Japan. Dye concentration was calculated from the equations obtained from the standard calibration graph. The dye removal capacity of resin supported nZVIwas evaluated by the following equation:

$$R_C = \frac{(C_o - C_R) \times V_D}{V_R}$$

Where, R_C= Dye removal capacity, C_o= Original dye concentration, C_R= Residual dye concentration, V_D= volume of dye passed, V_R= Volume of resin supported ZVI.The same process was carried out with the different concentrations of dye solutions. Fresh resin supported nZVI columns were prepared for each experiment. The results of adsorption capacity and % dye adsorption are plotted in Figure 2 & 3 respectively.

2.5. Evaluation of dye adsorption by powdered nZVI from simulated effluent and actual dyeing effluent

Batch method was used for evaluation of dye adsorption by powdered ZVI from simulated effluent. Sand filtered simulated dyeing effluent (2L) was equalized with powdered ZVI nano-particle (0.2g) for 24 hour. Treated effluent was analyzed for color and other physicochemical properties by APHA method. The results are summarized in Table 3 and 4.

2.6. Evaluation of dye adsorption by resin supported nZVI from simulated and actual effluents

Filtered simulated dye effluent was passed through the column containing 10 ml of resin supported nZVI and intensity of color absorbance of treated effluent was measured at regular intervals (ranging from 100-2600 ml). The absorbance of simulated effluent was measured before and after passing through the column by using a UV-Vis spectrophotometer at their maximum wavelength. The percent reduction in the dye color was calculated and the results are plotted in Figure 4.Physicochemical parameters such as pH, color, COD, BOD,, TSS, oil and grease, chromium, residual chlorine and sulphide of simulated effluent and treated effluent (after passing 2600 ml of the effluent through the column) were also evaluated. Table 3 showed the results of treated and untreated simulated dyeing effluent. Same analytical process was carried out for the actual effluent (untreated) collected from the equalization of an ETP. The untreated effluent was first gravity settled and sand filtered in order to remove the suspended impurities like cotton fiber etc. Removal of dye from the filtered effluent was evaluated by column method as described in case of dye uptake from pure dye solution. Untreated actual, filtered and resin supported nZVI treated effluents were also analyzed for their physicochemical properties by the APHA method. Results were summarized in Table 4.

2.7. Regeneration and recycling of exhausted resin supported nZVI column

The exhausted resin supported nZVI column was regenerated by passing 75 ml of the reducing agent $NaBH_4$ per 10 ml of the material. The regenerated column was reused for dye removal from simulated dyeing effluents by the method as described earlier. The efficiency of resin supported nZVI nano-particle for its reuse in dye removal was checked by performing three cycles. The results were plotted in Figure 5.

3. Results and discussion

3.1. Immobilization of ZVI nano-particles

Indion -225(H^+) used as solid support for immobilization of ZVI nano-particle is a cross linked copolymer of polystyrene and divinyl benzene (DVB) containing sulphonic acid functional groups (Figure 1).
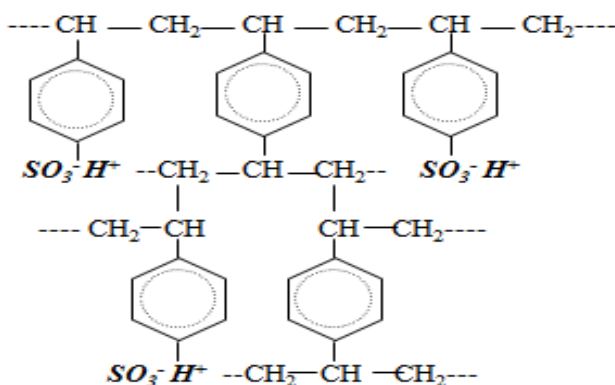

Figure 1: Structure of Indion -225(H^+), strong acid cation exchange resin

**Table 2: The characteristics of the cation exchange resin are as follows[13]**

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Appearance	Golden yellow to brown beads
Matrix	Styrene divinylbenzene copolymer
Functional Group	Sulfonic acid
Ionic form as supplied	Hydrogen, H^+
Total exchange capacity	1.8 meq/ml, minimum
Moisture holding capacity	49 -55 %
Particle size range	0.3 to 1.2 mm
Maximum operating temperature	120 ^{0}C
Operating pH range	0 to 14
Resistance to reducing agents	Good

The effective size of the resin (0.45 to 0.55 mm) suggests that it was suitable for column operations. The resin was stable up to 120^0C and could be used for treatment of hot effluents. It could also withstand variable pH of the effluent i.e. both acidic as well as alkaline effluents. Since the resin has good resistance to reducing agents, sodium borohydride(reducing agent) could be used for reduction of Fe^{2+} attached the resin to convert it to Fe^0 without affecting quality of the resin.

Mechanism of reaction:

When $FeSO_4.7H_2O$ solution was passed through Indion 225-H^+ resin column, it got converted from H^+ ion form to Fe^{2+} ion form as shown in equation 1.

$$2RH^+ + Fe^{2+} \rightarrow R_2Fe^{2+} + RH^- \qquad \textbf{(eq.1)}$$
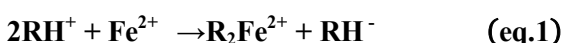
The Fe^{2+} form of the cation exchange resin acts as a redox ion exchanger[14].When reducing agent $NaBH_4$ (0.4M) was passed through the column ferrous ions (Fe^{2+}) attached to the resin was reduced to zero valent ions (Fe^{2+} to Fe^0).

$$R_2Fe^{2+} + 2\ e^- \ \rightarrow\ R_2Fe^0 \ \ (eq.2)$$
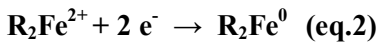
The ratio of $FeSO_4.7H_2O$, and $NaBH_4$, passed through the column was kept at 4:1 as evaluated in our previous study. Washing of immobilized ZVI and preservation with alcohol was done to prevent its oxidation. Loading of ZVI on the resin prevents iron from corrosion which might increase its adsorption efficiency and avoid its agglomeration behavior. It is necessary to prepare freshresin supported ZVI because old material was likely to get oxidized into ferrous ions due to air exposure.

3.2. Mechanism of color compound breakdown by resin supportednZVI

Resin supported nZVI showed high adsorption capacity for dyes due to its reducing behavior. nZVI has electrostatic and magnetic properties due to which dyes get attached to the nanoparticles. The nano-zerovalent iron attached to the resin reduced the reactive dye molecule's chromophore having sulphonate functional group. The nano-zero valent iron undergoes oxidation and performed destruction of the color as shown in equation 3.

$$R_2Fe^0 + Dye\ molecule \ \ \rightarrow\ Reduced\ dye + R_2Fe^{2+} \ \ (eq.3)$$

3.3. Effect of Concentration of dye on adsorption capacity

The adsorption capacity increased with the increase in dye concentration from 500-3000 mg/l in the feed solution as shown in the figure 2.However, percent adsorption of dye from the solution remained almost constant (ranging in between 95-97%) as shown in the figure 3.It might be due to the presence of cation resins with large surface area supported the available sites for nZVI to increase its adsorption capacity[15].
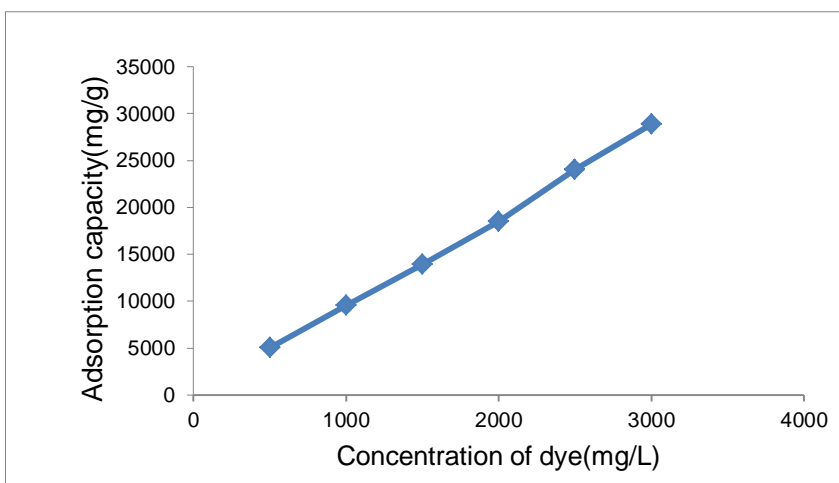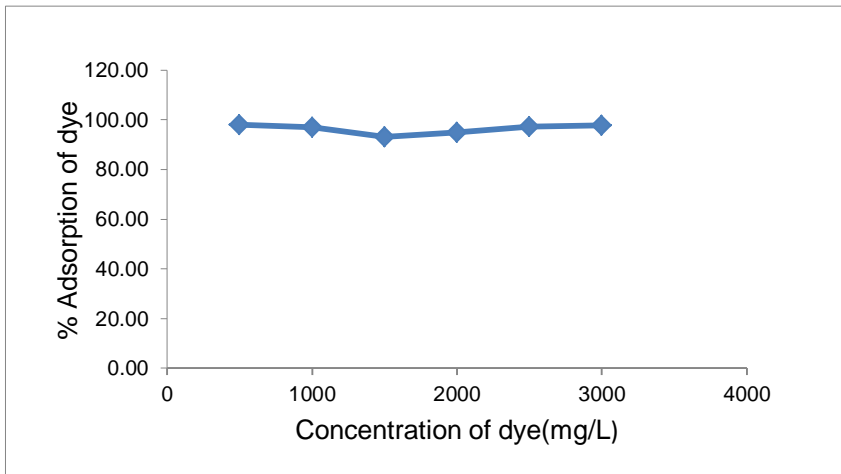

Figure2 Adsorption capacity of immobilized ZVI at different dye concentrations

Figure 3 Percent adsorption of dye from solutions having different dye concentrations

3.4. Effect of Flow rate of dye on adsorption capacity

The uptake of Reactive Red 198 dye by resin –supported nZVI studied at 1, 2.5, 5, 7.5, 10 ml/min flow rates with three concentrations 500, 1500, 3000 mg/l showed decreasing trend on increasing the flow rate as shown in Figure 4. Maximum color reduction of 98.2% to 94.7 % was observed at 1ml/min in all concentrations and followed a decreased pattern of 70.1 % to 54.4 % at 10 ml/min.It might be due to the reduced contact of time between dye molecules and adsorbent. So, 1 ml/min flow rate can be set for the further reduction of color through column study.
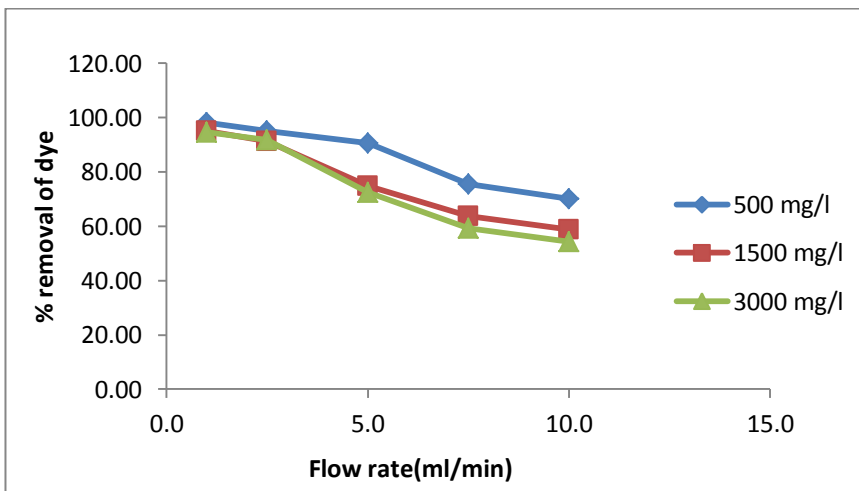
Fig 4 Effect of flow rate on percent removal of dye from dye solutions of different concentrations

3.5. Effect on percent reduction in color with increasing volume of simulated dyeing and actual dyeing effluent

From the figure 5, it was observed that percent removal of color from filtered simulated dyeing effluent gradually decreased(from 98.9 % to 89.7 %) as the effluent volume was increased from 100 ml to 2600 ml. Usually 90% removal of color is required in the industry to meet the norms of pollution control board hence the 2600 ml was considered as the maximum volume of simulated effluent that can be treated by 10 ml of the immobilized ZVI.As similar, actual untreated filtered dyeing wastewater was used as a feed solution with the volume of 100-2600 ml and found that resin- supported nZVI could reduced the color from 72.7% to 67.3% as the volume of effluent increased. The reduction in color might be due to the exhaustion capacity of adsorbent and the column bed height.
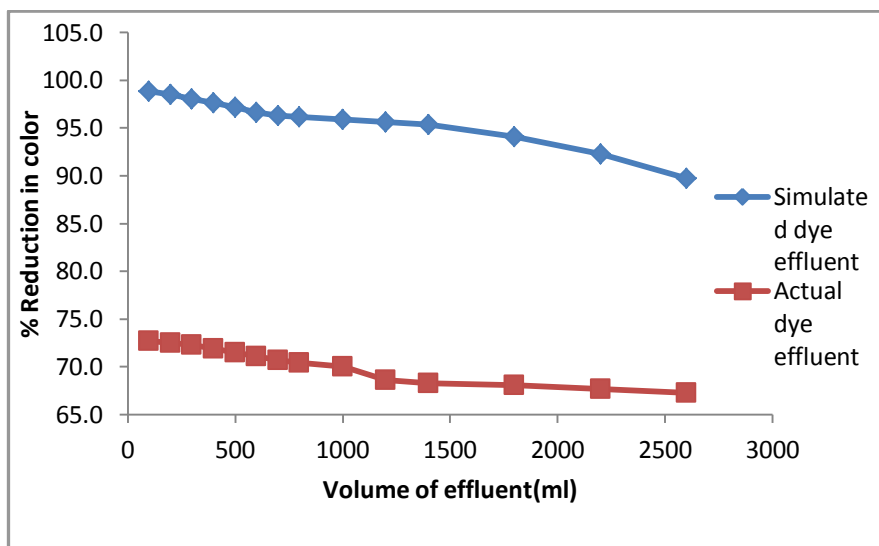
Figure 5 Percent removal of color from simulated and actual dyeing effluents

3.6. Physicochemical characteristics of simulated and actual dyeing effluent

The physicochemical properties of simulated effluent treated with immobilized ZVI were compared with the effluent treated with powdered ZVI nano-particles synthesized during our previous study. Table 3 showed that both powdered nZVI and resin supported nZVI removed the color from simulated very effectively. The resin –supported nZVI was more effective in color removal (89.70%) than the powdered nZVI (84.96 %), Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD) and Chromium. It may be due to presence of cation exchange resin.Sulfide and Residual chlorine were not present in the treated and untreated simulated effluent.

Table 3 Characteristics of simulated dyeing effluent after treatment with powdered and immobilized ZVI

Parameters	Original Simulated Dyeing Effluent	Effluent treated with powdered nZVI	(%) Reduction	Effluent treated with resin-supported nZVI	(%) Reduction
Color(AU)	1.330	0.2	**84.96**	0.137	**89.70**
pH	10.94	10.72	**2.01**	10.54	**3.66**
TSS (mg/l)	1790	NA*	**NA**	NA**	**NA**
COD ,mg/l	1359.1	1165.0	**14.28**	856	**37.02**
BOD, mg/l	680.5	562.8	**17.30**	162.3	**76.15**

#Oil and grease (mg/l), Chromium (mg/l), Sulfide (mg/l), Residual Cl_2 (mg/l) were found to be absent in the effluent
*The treated effluent was tested after filtration
** The treated effluent was filtered before passing through the column

Table 4 showed that color removal efficiency from filtered industrial effluent by the resin- supported nZVI was less (67.3 %) than from simulated dyeing effluent (89.7 %). This might be due to presence of so many constituents including unknown dyes, chemicals and auxiliaries in the actual effluent. Reduction in (COD), (BOD) was found to be less than from the simulated effluent. Chromium, Sulfide and Residual chlorine were not present in the actual effluent. There was a considerable reduction in Oil and grease (50%)by the resin supported nZVI than powdered nZVI. This indicated that resin- supported nZVI could also used for color removal from filtered actual effluents though the results may not be so effective as in case of simulated dyeing effluent.

Table 4 Characteristics of actual dyeing effluent after treatment with immobilized ZVI

| Parameters	Actual Effluent	Filtered Effluent	Effluent treated with powdered nZVI	(%) Reduction	Filtered effluent treated with immobilized nZVI	(%) Reduction
Color, AU	NA*	1.329	0.509	**61.7**	0.435	**67.3**
pH	9.1	8.73	8.55	**2.06**	8.5	**2.6**
TSS (mg/l)	692	NA*	NA	**NA****	NA	**NA**
COD,mg/L	2112	1251.4	983.6	**21.4**	922.3	**26.3**
BOD,mg/L	612.4	248.5	132.2	**46.8**	120.8	**51.4**
Oil and grease,mg/l	10	4	2.5	**37.5**	2	**50.0**

#Chromium(mg/l), Sulfide, (mg/l), Residual Cl_2, (mg/l) are found to be absent in the effluent.
*The treated effluent was tested after filtration
** The treated effluent was filtered before passing through the column

3.7. Regeneration of exhausted resin-supported nZVI and its recycling

There was a gradual increase in the removal of dye from simulated effluent after regeneration of the exhausted ZVI as shown in the figure 6. When 200 ml effluent was passed through the column almost 99 % reduction in color was observed during all the three cycles. As the volume of effluent passed through the column, percent reduction in color decreased, more during the first cycle (from 99 to 90.7%), lesser during second cycle (from 99 to 94 %) and least during the third cycle (from 99 to 96.3 %). This suggested that the efficiency of resin-supported nZVI increased after the subsequent regeneration cycles. This might be due to more efficient reduction of Fe^{2+}/Fe^{3+} to Fe^0 attached to the resin while regenerating the column with sodium borohydride, $NaBH_4$which was probably insufficient in the first cycle and increased during the second cycle and further increased during the third cycle. Thus, the resin-supported nZVI could be reused for color removal from colored effluents with an increasing efficiency of the material during the subsequent cycles.
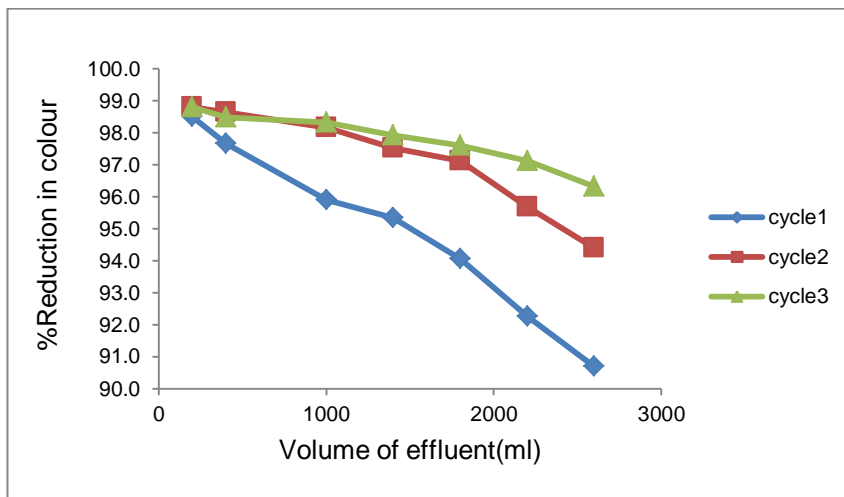
Figure 6 Comparison graph of regeneration cycles with $NaBH_4$

Conclusion

Theresin-supported ZVI nanoparticles were very effective in the removal of color from aqueous solutions (95-97%), and simulated dyeing effluents (89.7%). It can also be used for removal of color up to 67.3% from actual effluents. Very small quantity of resin-supported nZVI (10 ml) was required to treat about 2600 ml of the effluent. It could be used for removal of color from both acidic as well as alkaline effluentsbecause the cation exchange resin used in the study for support of nZVIhas good resistance to pH.Along with color it could also removes considerable amount of COD, BOD and Oil and grease from the

effluent. The exhausted resin supported nZVI could easily be regenerated simply by passing sodium borohydride. Thus, it was observed that the resin supported nZVI nanoparticles were more suitable for column operation than the powdered ZVI nanoparticles. Hence, the method of loading nanoparticles on the cation exchange resin substrate may prove to be a promising technology that increases the color removal efficiency as well as its industrial applicability.

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