Advances in Analytical Chemistry 2019, 9(1): 1-7
DOI: 10.5923/j.aac.20190901.01

Treatment of Contaminated Water with Industrial Dyes by Using Nano Zero Valent Iron (NZVI) and Supported on Pillared Clay

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Abstract In this study Nanoscale Zero-Valent Iron Fe^0(NZVI) and Nano Zero Valent-Iron supported on pillared clay(NZVI/PILC) have been prepared and characterizations by physical method such as Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM). The degradation of acidic aqueous solutions of the Acid red 315 (AR 315) azo dye has been studied by NZVI, pillared clay (PILC) and NZVI-B. The effect of different process parameters, such as solution pH, amount of dosage (NZVI, PILC and NZVI/PILC), time reaction effect and other experimental variable, such as (Azo dye concentration and inorganic salts effect) has been investigated to determined optimization method for removal. The concentration of azo dye measured before and after treatment by using UV-Vis Spectrophotometry method. The experimental results showed that AR 315 azo dye solution (100 mg/L, 1.6×10^{-4}M) was completely removed by NZVI at optimum conditions (amount of NZVI = 1.0 g, 120 min and pH = 3). While the removal efficiency with NZVI/PILC and PILC were 80% and 0% respectively.

Keywords Pillared clay, Supported Nanoscale zero valent iron, Azo dyes

1. Introduction

A great number of synthetic organic chemicals have been released to the environment via industrial activities. Dye classifications is based on the major functionality of the dye, the main classes being azo, anthraquinone, polymethine, phthalocyanine, sulphur, aryl-methane, stilbene and coumarine dyes [Sezer and Ibar, 2005]. Azo dyes, containing one or more azo bond (-N=N-), it's used by a wide number of industries. Textile industry predominantly use them, account for 60-70% of all textile dyestuffs used [Carliell et al., 1995]. This class of compounds can also be present at pharmaceutical, paper and printing, leather and cosmetic industries. Diverse application areas give them majority in view of environmental health. Because of these compounds have recalcitrant nature and structural integrity under relative mild environmental conditions such as sunlight, pH, bacteria, and microbial degradation [Brown and VITO, 1993]. Azo dyes are difficult to degrade and result in the threat of environmental pollution because it is stable, strong color, and high organic content. They contaminations arise from its association with the efficient and inexpensive treatment, the decolorization or degradation of azo dyes [Tan et al., 1999]. The treatment methods for Azo dyes can be divided into three categories [Mezohegyi et al., 2007; Chen and Zhu, 2007; Feng et al., 2003; Li et al., 2005; Li et al., 2002; Khan and Husain, 2007] physical methods, such as flocculation, adsorption, nanofiltration and ion exchange, chemical methods, such as oxidative process with Fenton's reagent, H_2O_2-ozone, H_2O_2-UV radiation, NaClO and O_3, and biological degradation, including aerobic and anaerobic degradation. These are not entirely satisfactory in terms of cost, efficiency and environmental impact [Robinson et al., 2001]. Physical methods are unable to absolutely decompose Azo dyes, and chemical methods with high cost are rarely used in the actual treatment process. Biodegradation processes, the most widely used methods suffered from low degradation efficiency or even no degradation for some dyes [Scott and Ollis 1995]. A new method for the transformation of Azo dyes into easier bio-decomposition compounds with Nanoscale Zero-Valent Iron NZVI has been developed in this study. NZVI is an effective reducing agent for azo dyes [Nam and Tratnyek, 2000; Cao et al., 1999; Perey et al., 2002] and it is less cost than chemical methods, effective and environmentally friendly [Perey et al., 2002; Masciangioli and Zhang, 2003; Chang et al., 2006; Hou et al., 2007; Shu et al., 2007; Fan et al., 2009], NZVI reduction is widely used in treating and remedying and dechlorinate waste waters contaminated with chlorinated compounds

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[Cheng et al., 2006], nitro aromatic compounds [Agrawal and Tratnyek, 1996], nitrates [Huang et al, 1998] and heavy metals [Fiedor et al, 1998], and even for the deoxidization of more complex anthropogenic chemicals including pesticides [Fiedor et al, 1998] and dyes [Eykholt and Davenport, 1998; Bigg and Judd, 2001; Perey et al., 2002; Weber, 1996; Pereira and Freire, 2006]. The azo bond is cleaved when azo dyes are degraded by NZVI treatment process and an aromatic amines and amino-naphthol compounds are formed along with hydrazo (-NHNH-) as an intermediate [Agrawal and Tratnyek, 1996]. Clay are naturally occurring materials, and have been widelyused as adsorbents for pollution control due to their high surface area and uptake ability [Churchman et al., 2006]. Pillared clay e is a kind of layeredclay composed mainly of montmorillonite. Its interlayer cationsare exchangeable with inorganic/organic cations, which serve aspillars between adjacent layers of montmorillonite. Pillared clay (PILCs), usually offer higher sorption capacity toward contaminants in water due to their enhanced surface areas and more functional groups [Zhu and Zhu, 2007; Liet al., 2009] and PILCs may act as the catalyst for reduction of contaminants because of its surface acidity [Belkhadem et al., 2008; Sun et al., 2006].

The aim of this research is to study the application of laboratory manufactured NZVI, PILC and NZVI/PILC for the degradation of AR 315 dye from polluted wastewater and to confirm the relevance of this process to treat azo dyes. Study the degradation of dyes using different dosage of NZVI, PILC and NZVI/PILC. We investigated the influence of the NZVI, PILC and NZVI/PILC dosage, primary dye concentration, and solution pH on the degradation of dyes. Finally, determined the influences of NaCl, Na_2CO_3, Na_2SO_4 and KBr on the decolorization of dyes by NZVI.

2. Experimental Procedure

A-Instrumentation:

Nanoscale Zero Valent Iron Fe^0(NZVI) prepared was used (Ultrasonic Path, Cole-Parmer), (mechanic stirring, Heidolph (RZR1), Germany), Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) type TESCAN VEGA, Baljecain. The concentration of AR 315 dye in aqueous solution was analyzed by UV-Vis Spectrophotometer (Optima, SP-3000 Plus, Tokyo, Japan) at a maximum absorption wavelength of 495 nm and pH (pH meter WTW, inoLab® pH 720/7200, Germany) was used to check the pH of the solution.

B-Materials and methods:

The original clay used was the pillared clay e purchased from InnerMongolia, China. It is composed primarily of Na^+–montmorillonite, with cation exchange capacity of 115 cmol/kg. Ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) and sodium borohydride ($NaBH_4$) from Merck Company (Germany), aluminum chloride hexahydrate ($AlCl_3 \cdot 6H_2O$) and ethanol from BDH and Acid Red 315 (AR 315) from Ministry of Industry and Minerals, it was obtained from Haining Deer Chemical Co., Ltd. (China Supplier), conc. sulphuric acid, sodium hydroxide and other chemicals (Merck, Germany). NaCl, Na_2CO_3, Na_2SO_4 and KBr were obtained from Fluka. Purity of all the chemicals is around 99%. Water used throughout was double distilled. Figure (1) appears the chemical structure of Acid Red 315 dye.

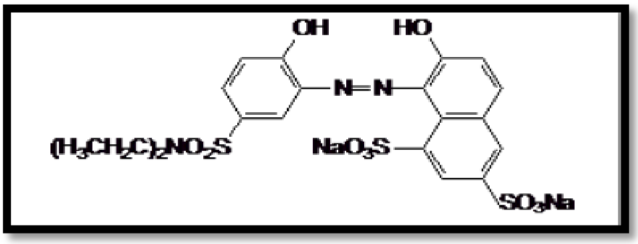


Figure (1). Chemical Structure of Acid Red 315, $C_{20}H_{19}N_3Na_2O_{10}S_3$

Preparation of Nano Zero-Valent Iron Fe^0(NZVI):

NZVI was prepared from $FeSO_4 \cdot 7H_2O$ (7 gm) dissolved in 100 ml distill water to obtain (0.3 mol/L) concentration and put it in round bottom contain three neck. Sodium hydroxide NaOH (0.1 mol/L) prepared by dissolve (0.4 gm) in 100 ml distill water and sodium borohydride $NaBH_4$ (0.4 mol/L) (4 gm) was dissolved in 100 ml NaOH (0.1 mol/L) and put it in separation fennel. Sodium borohydride $NaBH_4$ solution was added dropwise into the (0.3 mol/L)solution of $FeSO_4 \cdot 7H_2O$ through first neck and put mechanic stirring in second neck in middle round bottom, and pass N_2 gas from third neck to the solution to avoid oxidation of Fe^0, after complete the reaction as illustrated in **Figure (2)**. The metal particles formed were settled and filtered. Then the solid was washed with ethanol for several times, and finally keep it in ethanol solution. There action as according to the following equation:

$$FeSO_4 + 2NaBH_4 + 6H_2O \rightarrow Fe^0\downarrow + 7H_2\uparrow + 2B(OH)_3 + Na_2SO_4$$

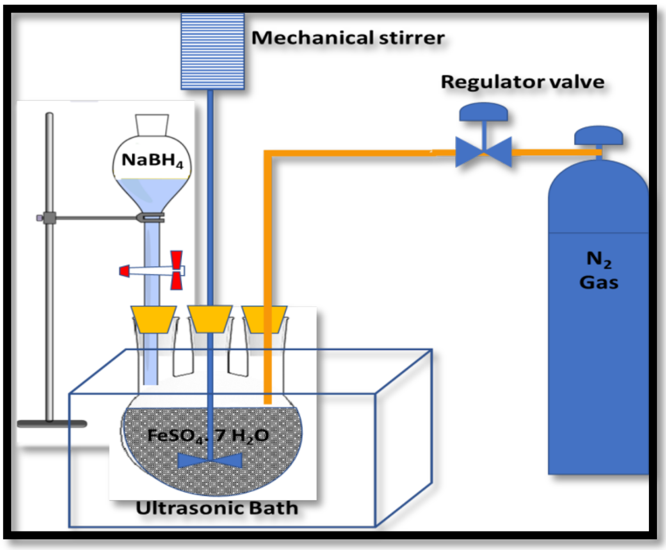


Figure (2). Experimental Setup for NZVI Particle Synthesis

Preparation of PILC and NZVI/PILC Samples:

The pillared clay (PILC) were prepared from the original clay by intercalation with poly (hydroxo Al (III)) cations [Li et al., 2010]. Firstly, (0.2 mol/L) solution of aluminum hydroxide was prepared by dropwise addition of NaOH solution into a solution of $AlCl_3 \cdot 6H_2O$ until the molar ratio $[OH^-] / [Al^{3+}] = 2.2$ was obtained. The resulting pillaring solution was slowly added in a suspension of (10 g) pillared clay e in 500 ml of deionized water until the $[Al^{3+}]$ / pillared clay e ratio reached 10 mmol/g. The resulting mixture was heated at 70°C for 48 h and the modified clay was centrifuged, washed and dried to a constant weight. The sample was mechanically ground to pass through a sieve of 100 meshes and heated at 115°C for 120 min before use. After activation of pillared clay e (PILC), the NZVI/PILC was prepared by a similar procedure as described in preparation of NZVI except that the PILC was uniformly mixed with solution of $FeSO_4 \cdot 7H_2O$ (0.108 mol/L) before the addition of $NaBH_4$ (0.054 mol/L) solution. Sodium borohydride $NaBH_4$ (0.054 mol/L) solution was dropwise added into the (0.108 mol/L) solution of $FeSO_4 \cdot 7H_2O$ from the first manhole and put mechanic stirring from the second manhole in middle round bottom, and passN_2 gas from the third manhole to the solution to avoid oxidation of Fe^0 (Nano Zero Valent Iron supported on pillared clay) (NZVI/PILC), after complete the reaction as illustrated in **Figure (2)**. The metal particles formed were settled and filtered. Then the solid was washed with ethanol for several times, and finally keep it in ethanol solution. A good dispersion of NZVI particles (ca. 35–75 nm) in the clay phase was observed.

Procedure of removal the Azo dyes by (PILC, NZVI and NZVI/PILC):

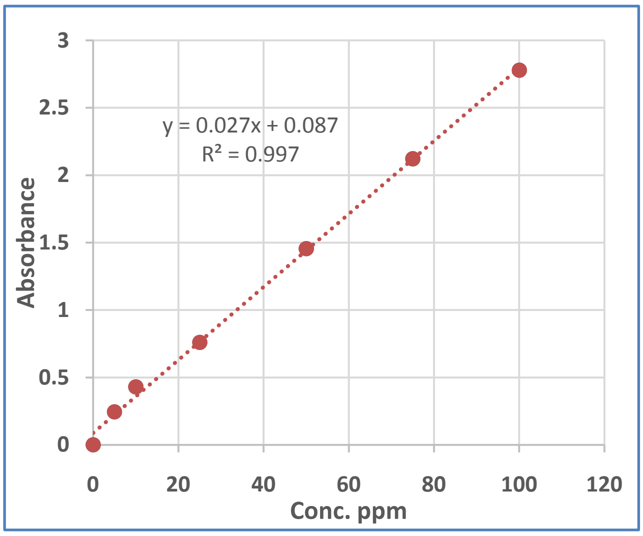


Figure (3). Calibration curve for Acid Red 315 concentration at $\lambda_{max} = 495$ nm

Azo Dyes (Acid Red 315) was prepared of 500 mg/L (stock solution) by dissolving 0.5 gm in 1000 ml of distilled water and then preparation series of azo dyes (Acid Red 315) concentrations at (5, 10, 25, 50, 75 and 100) mg/L for calibration curve using by UV-Vis spectrophotometry as shown in **Figure (3)**. All experiments were performed in an open batch glass system with a stirring bar; taking 100 ml of Acid Red 315 azo dye (AR 315) sample in 250 ml conical flasks from different AR 315 concentration (1, 5, 10, 25, 50, 75 and 100) mg/L. The pH of the reaction solutions was adjusted with NaOH (0.1 M) or (0.1 M) H_2SO_4 solution to find the optimized method to removal the azo dye then mixed with amount of (PILC, NZVI and NZVI/PILC) by stirring continuously and kept at a required temperature for different reaction time particularly at (30, 60 and 120) min. After each time point, the samples were allowed to stand for 30 min. The pH of the mixture was raised to above 12.0 using (10%) sodium hydroxide for precipitation and then filtered for analysis of absorption in UV-Vis Spectrophotometry before and after treatment.

3. Results and Discussion

In aqueous solutions, NZVI iron powder is oxidized (and then settles as precipitate), leading to the production of free electrons, which have the reducing role and hence can reduce organic compounds (Azo dyes) according to the following reactions [Dickinson and Scott, 2010].

$$Fe^0 \longrightarrow Fe^{2+} + 2e^- \quad (1)$$

$$Fe^{2+} + 1/4\, O_2 + 2.5H_2O \longrightarrow Fe\,(OH)_{3(S)} + 2H^+ \quad (2)$$

From the results showed efficiency the removing with Nano zero Valent (NZVI) more than removing with Nano zero Valent Iron supported on pillared clay particles and pillared clay PILC respectively. Azo dyes could be completely removed by NZVI within 120 min or more. This efficiency was much higher than that (100%) by NZVI alone, but also (80%) of reduction by NZVI/ PILC and (0%) by PILC alone was lower than that by NZVI alone and NZVI/ PILC also pillared clay (PILCs), usually offer higher sorption capacity toward contaminants in water due to their enhanced surface areas and more functional groups [Li et al., 2012; Zhang et al., 2011]. In this study the removal efficiency of Azo dye by this composite (pillared clay particles) very less when compared with NZVI/ PILC particles, or compared with NZVI particles.

Percentage of azo dye removed (%) = $(C_0-C_t) / C_0 \times 100\%$.

Characterizations of the synthesized NZVI particles:

NZVI was prepared as shown in **Figure (2)**. The Scanning Electron Microscopy (SEM) image also re veal's that iron nano particles tend to from a chain-like aggregate due to the magnetic attractive force between particles. These chain-like nano iron aggregates were also observed by others [Phenrat et al., 2007 and Zhang, 2003].

Figure (4) Presents Scanning Electron Microscopy (SEM) images of NZVI particles. The laboratory made iron particles were mostly spherical attribute of particles formed in solution. A characteristic average single particle size is near (150–170) nm as shown in **Figure (5)**. A little particles had size as greater as (250–350) nm, whereas greatest (>70%) particles were fewer than 200nm.

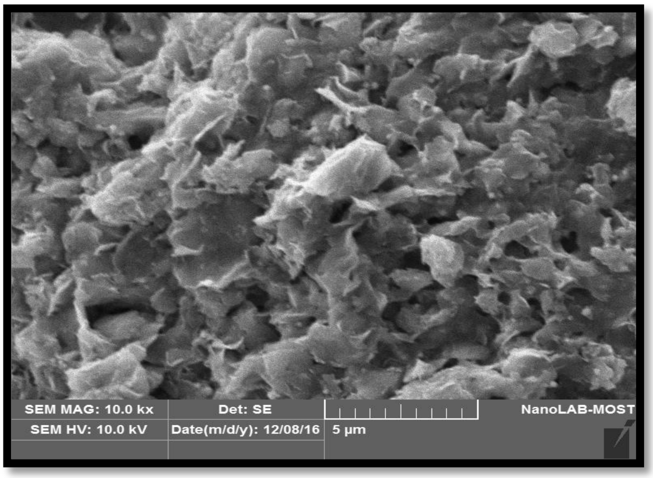
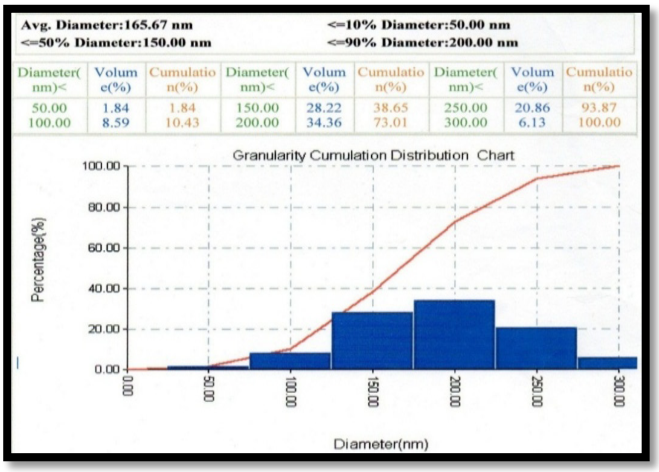


Figure (4). SEM image NZVI particlesat 10 Kv



Avg. Diameter:165.67 nm <=10% Diameter:50.00 nm
<=50% Diameter:150.00 nm <=90% Diameter:200.00 nm

Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)
50.00	1.84	1.84	150.00	28.22	38.65	250.00	20.86	93.87
100.00	8.59	10.43	200.00	34.36	73.01	300.00	6.13	100.00

Figure (5). Particle Size Distribution (PSD) of NZVI Particles Using Scanning Probe Microscope (SPM)

In **Figure (6)**, presents Atomic Force Microscopy (AFM) images of NZVI particles. AFM images showed measuring surface on a fine scale, down to the level of diameters of atoms. The previous explanation is supported by the distribution of the density of NZVI when measuring the size of the particles using Scanning Probe Microscope **Figure(5):**

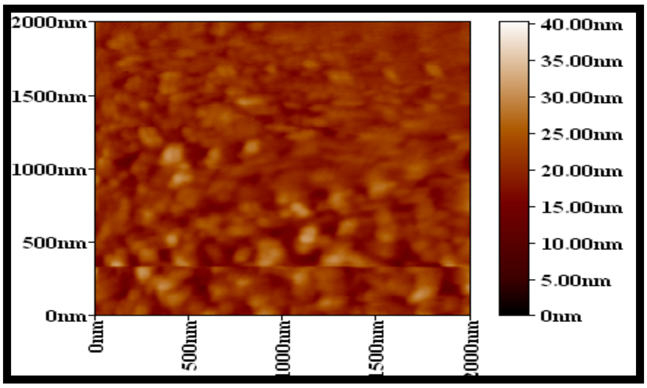


Figure (6). Image of NZVI particles using AFM technique

Characterizations of the synthesized NZVI/PILC particles:

Nano zero Valent Iron supported on pillared clay particles (NZVI/PILC) was prepared as shown in **Figure (2)** and characterization by physical methods such as Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). The Scanning Electron Microscopy (SEM) image for (NZVI/PILC) as shown in **Figure (7)** that tend to from a chain like aggregate due to the magnetic attractive force between particles.

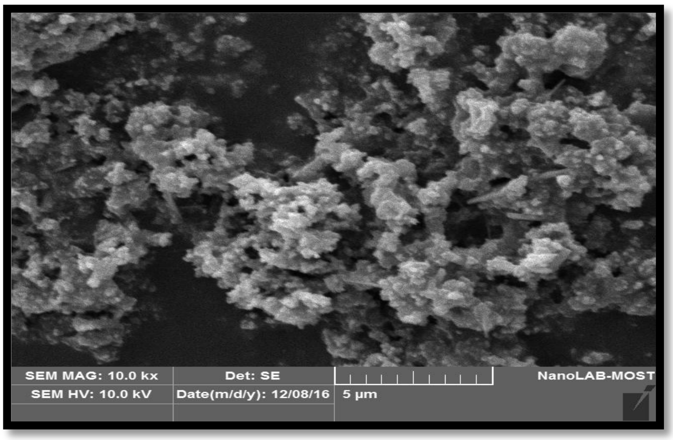


Figure (7). SEM image NZVI/PILC particles at 10 Kv

Effect of reaction time:

The removal efficiency of azo dyes increased with increasing reaction time, with fixed amounts of NZVI and NZVI/PILC particles (1gm), azo dyes 100 mg/L, (1.6×10^{-4}M) at pH=3. The removal efficiency increased in state use NZVI and NZVI/PILC from (93% to 100%) and (69.9% to 80%) at 1 and 2 hours, respectively. These azo dyes (Acid Red 315) can be explained by the fact that the degradation process of the contaminant by Fe-based nano particles is an interface reaction. Therefore, for the first 120 min of reaction, the degradation speed of azo dyes in the solution was rapid and, as the reaction proceeded, the gradual oxidation on the surface of NZVI formed a passivity layer, which covered some reaction sites.

Effect of NZVI and NZVI/PILC Dosages:

The effect of the NZVI and NZVI/PILC dosages on the degradation rate of azo dyes is shown in **Figure (8) and Figure (9)**. When the same dosage of iron of (0.1, 0.25, 0.5, 0.75 and 1) gm was used, the efficiency on azo dye removal by various irons (NZVI and NZVI/PILC) was investigated. It was found that when the NZVI and NZVI/PILC dosages increase, the removal rapidly of azo dyes increased and the degradation efficiencies increased from about (29.7 to 100%) over the first 30 min when dosages of NZVI and (20.6 to 80.3%) when dosages of NZVI/PILC [Zhang et al., 2011]. This is because 1 gm NZVI particles are able to provide enough iron surface-active sites for collision with azo dyes molecules to accelerate the removal efficiencies [Noubactep et al., 2012; Zhang et al., 2009]. When the specific surface area of the nano particles was bigger, there were more corresponding reactive sites, and the absorption and removal abilities were stronger. Accordingly, the increasing amount of nano metals added meant the addition of more reactive sites, thereby improving the efficiency of removal [Wang and Zhang, 1997]. Thus, the acid red removal efficiencies were gradually swelling from (29.7, 61.3, 81.3 to 100%) by raising NZVI dosage from (0.1, 0.25, 0.75 to 1) gm and (20.6, 33, 50, 69 to 80.3%) by raising NZVI/PILC from (0.1, 0.25, 0.75 to 1) the results show that 1gm is an optimal amount of NZVI and NZVI/PILC beyond which no improvement of removal was obtained for 100 ml and 100 ppm from azo dyes.

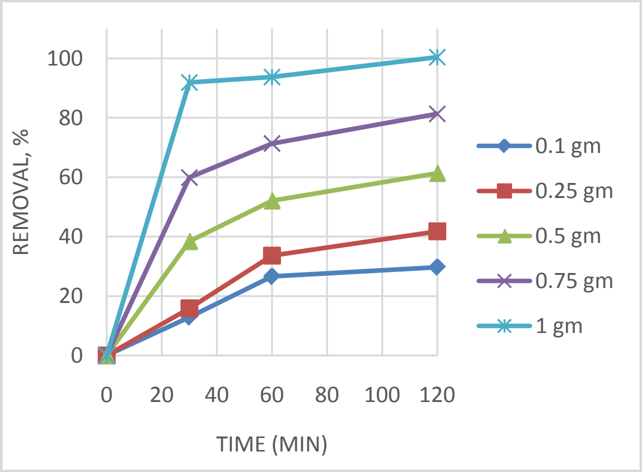


Figure (8). Effect of NZVI dosage on the decolorization efficiency of Azo dye decolorization process, Experimental conditions: [AR 315] = $1.6x10^{-4}$M; and pH=3

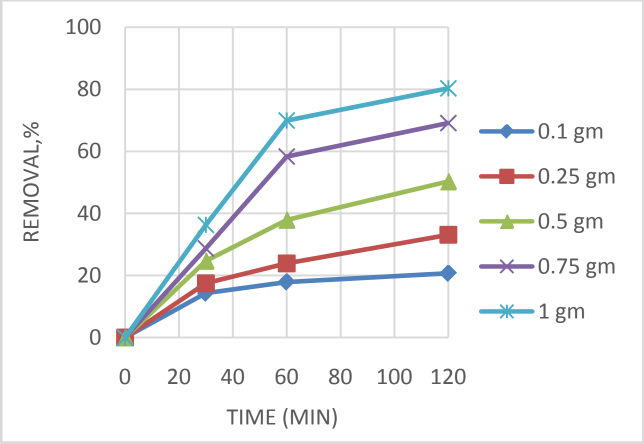


Figure (9). Effect of NZVI/PILC dosage on the decolorization efficiency of Azo dye decolorization process, Experimental conditions: [AR 315] = $1.6x10^{-4}$M; and pH=3

Effect of pH:

The pH was also one of the important factors in the Azo dyes removal by NZVI and NZVI/PILC. The pH of aqueous solution could effect on the dye degradation reactions by NZVI and NZVI/PILC due to the hindrance of ferrous hydroxide produced from ferrous ions and hydroxyl ions in the oxidation of NZVI surface in a high pH solution. The aqueous pH had major effect on the removal efficiency of Azo dyes, when the initial pH values were 2, 3, 7 and 10, the removal efficiencies of Azo dyes by NZVI were approximately (89, 100, 93 and 97)% and by NZVI/PILC were approximately (94, 81, 65, 5 and 2)% after a reaction of 2 h. The removal efficiency of Azo dyes increased with a decrease in the pH up to 3 in state of removal by NZVI/PILC but removal by NZVI increased with the pH up to 3 as shown in **Figure (10)** and **Figure (11)**. The NZVI process was more effective in degradation Azo dyes under acidic conditions. In the more acidic the solution, the more rapid degradation of Azo dyes occurred with more H^+ in the solution, the reaction occurred more easily and the reaction constant was high. However, when the initial pH was 2, the Azo dyes degradation rate decreased. The possible reasons may be attributed to: At lower pH values less than 3, the iron corrosion could be accelerated, producing enough hydrogen (or hydrogen atoms), which were in favor of hydrogenation reaction [Zhang et al., 2006] Furthermore, the lower aqueous pH may help to reactivate the oxidized iron layer, and then enhance the degradation reaction on the surface of NZVI particles.

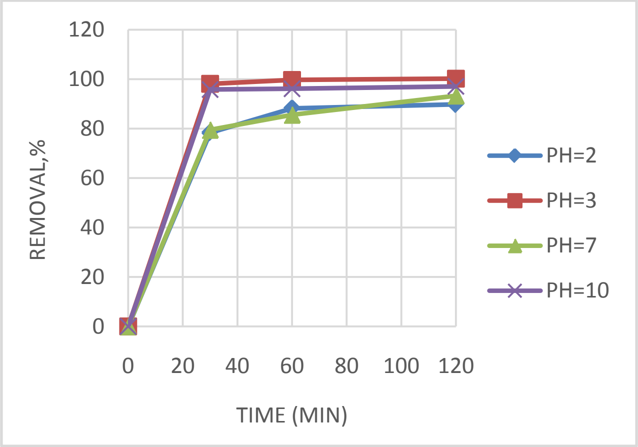


Figure (10). Effect of pH on Azo dyes Degradation; [AR 315] = (1.6×10^{-4} M, 100 mg/L), Amount of (NZVI/PILC) = 1gm, Time = 2 h

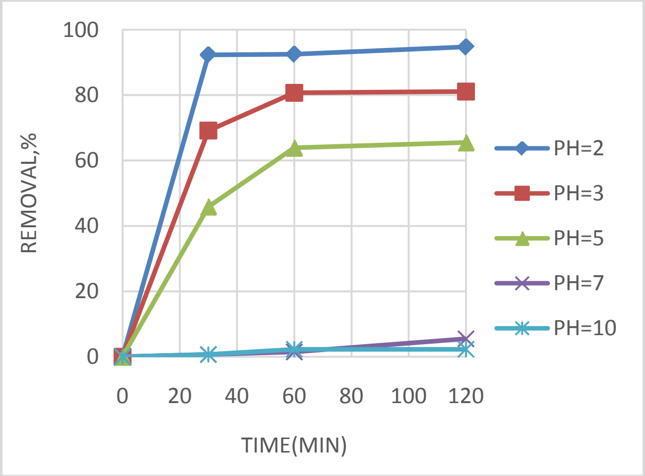


Figure (11). Effect of pH on Azo dye Degradation; [AR 315]=1.6×10^{-4}; amount of (NZVI/PILC) = 1gm; Time = 2h

The influence of inorganic ions on dyes degradation by NZVI:

The influence of the salt on the removal color of Azo dyes (Acid red 315) was examined by using the different salts as NaCl, Na_2SO_4, Na_2CO_3 and KBr as shown in **Figure (12)**. The results show that the found of Na_2CO_3 enhances the decolorization efficiency. While the presence of Na_2NO_3 has little effect on degradation efficiency of the dyes. Either the presence of Na_2SO_4 reduces the decolorization efficiency because SO_4^{2-} ions challenge with dye molecules and take up the reactive places on NZVI surface [Jing et al., 2006].

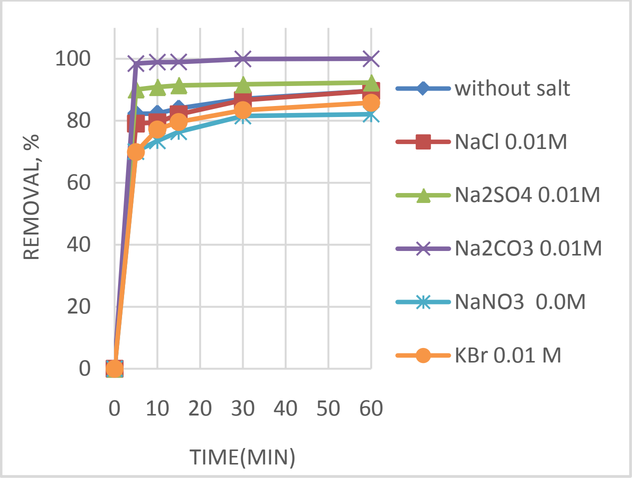


Figure (12). Effect of addition of $1{\times}10^{-2}$ M from inorganic anionic on Azo Dye Degradation; [AR 315] $=1.6{\times}10^{-4}$; amount of (NZVI/PILC) = 1gm; Time =2h

The optimal reacting conditions were determined and it was found to be [[Azo dyes] $=1.6{\times}10^{-4}$, pH=3, amount of (NZVI/PILC) = 1gm, Time =2h]. There is found 100% degradation efficiency of Azo dyes (Acid Red 315) in aqueous solution was achieved after 120 min of reaction when use (NZVI) and 80% degradation efficiency of Azo dyes (Acid Red 315) when use (NZVI/PILC). The UV–visible absorption spectra of Acid Red 315 azo dye before and after treatment at optimum conditions.

4. Conclusions & Recommendations

NZVI and NZVI/PILC was synthesized in laboratory then confirmed by techniques SEM, SPM, and AFM. The decolorization efficiency of dyes increase with an increase in NZVI dosage. The effects of pH, Time and Effect of NZVI and NZVI/PILC Dosages on the color removal rate was different for the dye solutions by using NZVI and NZVI/PILC. This efficiency was much higher than that (100%) by NZVI alone, but also (80%) of reduction by NZVI supported on pillared clay particles and (0%) by PILC alone was lower than that by NZVI alone and NZVI/ PILC. The presence of Na_2CO_3, Na_2CO_3 and NaCl enhances the decolorization efficiency was much higher of dye solutions while the presence of $NaNO_3$ and, KBr lower the decolorization efficiency.

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