Use of Zero-valent Iron Nanotechnology to Remove Two Azo Dyes and Study Their Decomposition Kinetics

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Abstract

Zero-valent iron nanoparticles were prepared and used in the study of its reaction kinetics with RR120 Reactive Red and Direct Blue DB2 commercial azo dyes. SPM, AFM, and SEM techniques were used to diagnose these nanoparticles. The best dose of nanoparticles used in the decolorization of the dyes was (0.1, 0.5) g / L when the solutions recorded a value of pH equal 3.5 at the time of 60 minutes, they achieved a removal ratio of 100 % and 98 % for dyes RR120, DB2 respectively. The first order interaction rank was the best when studying the interaction of nano iron with dyes, the coefficients were of k1 (0.1465, 0.0899) min^{-1} and t1/2 (4.73, 7.7) min^{-1} for dyes RR 120 and DB 2 independently. The presence of sodium chloride salt enhances and increases the decolorization of dyes, while the presence of sodium sulfate salt has a negative effect on the decomposition process and reduces the removal rate.

Keywords: Commercial Azo Dyes and Iron Nano Particles.

استخدام تقنية الحديد النانوي صفري التكافؤ في ازالة اثنين من صبغات الازو ودراسة حركية تحللهما

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بغداد – العراق

الخلاصــة

حضرت دقائق الحديد النانوية الصفرية التكافؤ واستخدمت في دراسة حركية التفاعل مع أصباغ الآزو التجارية RR120 الأحمر التفاعلي والأزرق المباشر DB2. استخدمت تقنيات SPM، AFM و SEM لتشخيص هذه الجسيمات النانوية. كانت أفضل جرعة من الجسيمات النانوية المستخدمة في إزالة اللون من الأصباغ (0.1 و0.5) غم/لتر عندما سجلت المحاليل قيمة pH تساوي 3.5 في وقت 60 دقيقة، وحققت نسبة إزالة 100% و98% للصبغتين RR120 و DB2 على التوالي. كانت رتبة التفاعل من الدرجة الأولى هي الأفضل عند دراسة تفاعل الحديد النانوي مع الصبغتين، وكانت المعاملات k_1 (0.1465 و0.0899) min^{-1} و$t_{1/2}$ (4.73 و7.7) min^{-1} للصبغتين RR120 و DB2 بشكل مستقل. يعزز ويزيد وجود ملح كلوريد الصوديوم من إزالة الصبغتين، في حين أن وجود ملح كبريتات الصوديوم له تأثير سلبي على عملية التحلل حيث يخفض معدل الازالة.

الكلمات المفتاحية: أصباغ الازو التجارية ودقائق الحديد النانوي.

Introduction

The textile industries are improving a major source of natural contamination since an unnerving sum of color contaminants are delivered through the coloring works Chandra and Raman. 2016. It is enrolled that there are up 100,000 sorts of trade product colors with an unpredictable assessed making of 7×10^5–1×10^6 tons universal yearly (Emilie, *et al*., 2016). There is a great danger to the environment as a result of the liberation of many of the benzene rings contained in the dyes. (Hasan and Ahmed, 2018) fabricate the deterioration of coloring wastewater significantly more complex, in this way driving to critical natural impact on surface water (Irem, *et al*., 2018). There are different organic, physical, and chemical strategies for color expulsion such as chemical oxidation, chemical coagulation, film filtration, photochemical debasement, and oxygen consuming or anaerobic organic corruption. Each of these technique encounters from one or above limits, and no one of them are competent to fully evacuate colors from wastewater (Magdalena, *et al*., 2016). The distribution of Nano zero valent press (NZVI) contributes certain assistances, which is utilized as considered textile in holey receptive troubles, including (a) an increment within the deterioration on return rate, (b) cost reduction and economically preferable , (c) locale up the danger of emission of harmful intermediates, and (d) the release of a non-hazardous conclusion produce (Suvanka, *et al*., 2016). Past investigates has showed up that NZVI can effectively change a few colors, like, Orange II, Crocein Orange G Orange I, Dusk Yellow (Nam and Tratnyek., 2004) and AB24 (Lin, *et al*., 2008). In aqueous solutions, the iron nanoparticles behave as a free electron donating reducing agent, which have reduced organic compounds NZVI is especially little with its remove extending from 50 to 100 nm, which commits it a huge side region. Volume portion and gets to be it favorably responsive by its incredible surface action (Nese and Filiz, 2017). Consequently, it contains a bigger chance of drawing nearer into interaction with color atoms and subsequently deterioration them. Moreover, their surface capacities are over to numerous times way better than bigger measured powders press. This particular sorts NZVI particles much extra receptive in a reduction-oxidation handle. For the reason that its especially small measure and extraordinary surface zone, NZVI is thought to be a encourage effective innovation for color squander treatment (Fang, *et al*., 2015). The study aims to Prepare NZVI in the laboratory, study the decomposition kinetics of RR120 and DB2 dye solution using appropriate doses of nanoparticles, investigate the effect of the amount of NZVI added, the concentration of the dye, pH, and finally the use of inorganic salts to find its effect on the decolorization of the solution of dyes.

Materials and Methods

Dyes and Chemicals

The dyes RR120 and DB2 under study were supplied by the company from Ciba Specialty Chemicals. Some qualities of RR120 and DB2 are illustrated in Table (1). Both dyes options used have been determined via diluting the widespread options which had been equipped through dissolving precisely viewed dyes in distill water. Next chemical substances have been furthermore used in the experiments: The reducing agent ($NaBH_4$) Sodium borohydride and ($FeSO_4.7H_2O$) Ferrous Sulfate hepta hydrate had been sold from Fluka.

Table (1) Properties of RR120 and DB2.

Properties	RR120	DB2
Chemical Formula	$C_{44}H_{24}Cl2N_{14}Na_6O_{20}S_6$	$C_{32}H_{12}N_6Na_3O_{11}S_3$
Molar Mass	1470 g/mol	831 g/mol
Color, λ Max (nm)	Bright Red, 535	Deep Purple, 570

To fix the pH value of the dye solution use NaOH (95%) and H_2SO_4 (95%) were used to alter the pH which was purchased from Application, Chem. NaCl (95%), Na_2CO_3 (95.0%), and Na_2SO_4 (95%) had been obtained Merck Company.

Preparation of NZVI Particles

Nano Zero-valent iron was prepared according to the following reaction (Eq.1)

$$2Fe^{+2} + BH_4^{-1} + 3H_2O \longrightarrow 2Fe0 + H_2BO^{-3} + 4H^{+} + 2H_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

The first to attend these nanoparticles is (Wang and Zhang, 2002). The reducing agent sodium borohydride (1.6 mol / l) is added dropwise with constant stirring to an appropriate volume of aqueous ferrous sulfate (1.0 mol/l). This reduction process takes place in the presence of nitrogen gas at room temperature to prevent the oxidation of the formed iron nanoparticles. The stirring time used to be 20 min, and the stir charge used to be 150 rpm in an ultrasonic bath. The response was allowed to settle for 15 minutes. When the reducing agent is added to the iron salt, the nanoparticles will form in a gray-black color. At the end of the reaction, the filtrate is disposed of using suitable filter papers to prevent the loss of the formed nanoparticles. These particles are washed using ethanol for several times and then left to dry. Iron nanoparticles are re-stored with ethanol and in a cool place for use in subsequent experiments.

Batch Experiments

In this research paper, the volume of 100 milliliters of dye solution treated by zero-valent nano-iron was adopted, and doses of NZVI were used within the range (0.025- 0.5) g/L for RR120 and DB2 dyes, respectively. All the experiments conducted were controlled the pH of the treated solution using 1.0 mole per liter of sodium hydroxide and sulfuric acid, in addition, an ultrasonic trough was used in order to disperse the nanoparticles and prevent their agglomeration during the reaction. The combination was once shaken the use of a thermostatically managed shaker immediately. The shaker velocity was, 120 rpm. The samples have been withdrawn (5 ml) at specific time internals (2, 4, 6, 8, 10, 15, 20, 25, 30, 45, and 60 min). The samples have been filtered via a 0.45μm membrane filter.

Analytic Methods

A Japanese-made (UV-VIS) device was used to measure the residual concentrations of the dyes under study at wavelengths of 570 and 535 nm. A quartz cell with a track length of 1.0 cm was used.

Results and Discussion

Decolorization activity was expressed in all optimization study in terms of decolorization efficiency (%), and it was calculated as follows:

$$\text{Degradation efficiency } \% = \frac{C_0 - C_t}{C_0} \times 100\% \quad \ldots\ldots\ldots\ldots \quad (2)$$

Where C_0 is the preliminary concentration of RR120 or DB2 and Ct is the concentration of RR120 or DB2 of response time t (Min).

Characterization of the Synthesized NZVI particles

Figure (1a) Shows (SEM) scanning electron microscopy snap pictures of

NZVI particles. The dominant feature of the prepared nanoparticles is the spherical shapes that tend to clump. Figure (2) shows that these nanoparticles with dimensions ranging (150-170) nm represent the highest percentage, while nanoparticles with dimensions (250 to 300) nm appeared due to the assembly sought by these particles.

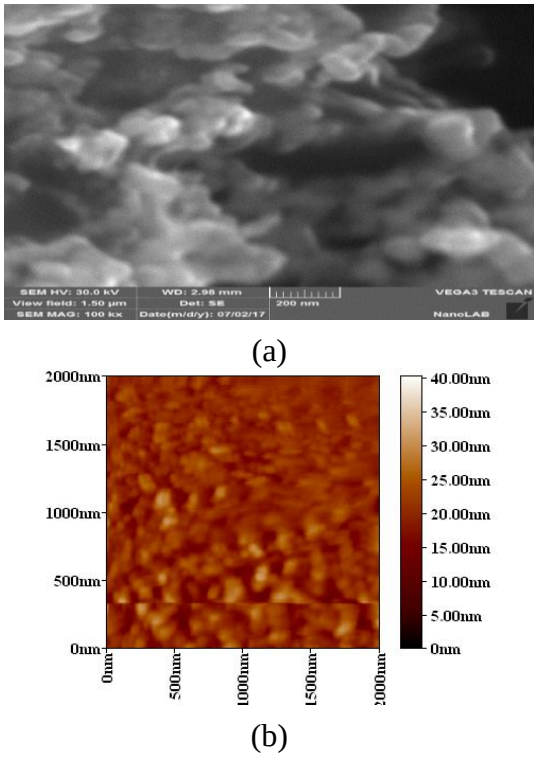


Figure (1) (a) SEM Image NZVI at 30 Kv. (b) Image of NZVI Particles Using AFM Technique.

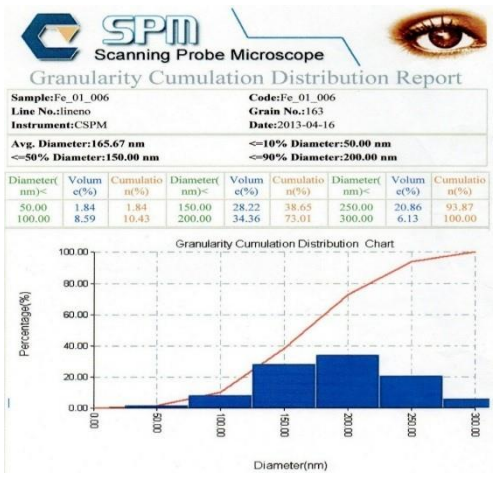
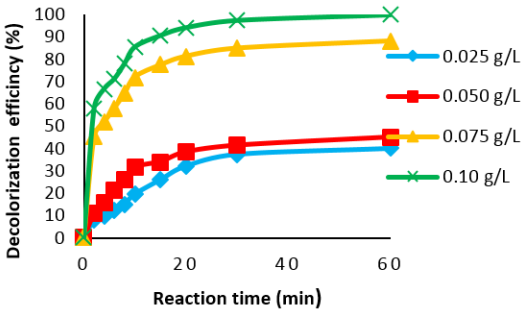


Figure (2) Particle Size Distribution (PSD) of NZVI Particles Using Scanning Probe Microscope (SPM).

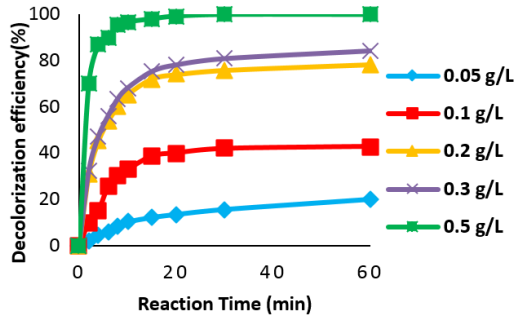
SEM technique Figure (1a) nanoparticles similar to chained clusters with a percentage of more than 70% with dimensions less than 200 nm. The AFM technique gives a clear picture of the atomic surface and the atomic diameter scale of the nanoparticles Figure (1b), while the SPM technique Figure (2) gives the density distribution of these prepared nanoparticles according to their dimensions.

Effect of NZVI Dosage

Figure (3) shows the most important factor in the study of decomposition of dyes, which is the effect of changing the use of nanoscale iron dose. Figure (3a) shows the doses used to hydrolyze the RR120 dye. The percentage of removal (26% and 40%) appeared at (15 and 60) minutes, respectively, by using an amount of NZVI of 0.025 g /L, While the dose of 0.1 g/L achieved a higher percentage of removal and chromatic dissolution of the dye amounted to (91% and 100%) in the same previous time period. Figure (3b) shows the effect of DB2 dye by changing the amount of NZVI used in its decolorization. When the amount of 0.05 g/L of nanoparticles was used, a percentage of (12% and 20%) was achieved at the time (15 and 60) minutes, while the percentage of chromatic dissolution of the dye increased by increasing the dose of the zero-valent iron to 0.5 g/L to (98 % and 100%) at the same previous time period. This change in the percentage of decomposition is attributed to the increase in the surface area of the nanoparticles by increasing the dose used, which leads to providing a larger surface area for the purpose of interaction with the dye solution. Eventually, the massive qualitative surface region will end result a greater reactivity towered the dyes by using NZVI (Hasan, *et al.*, 2021) and (Noubactep, *et al.*, 2012).

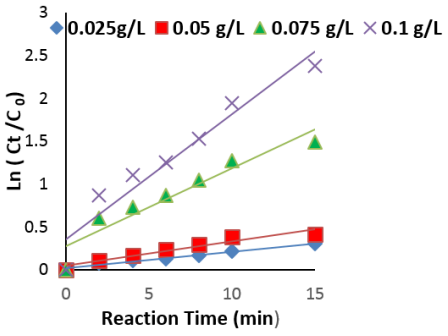


(a)



(b)

Figure (3) Effluence of NZVI Dosage on the Decolorization Efficiency of Dosage (a) RR 120 and (b) DB2 Decolorization Process Experimental Working Conditions for Adsorption: [Dye]=1x10^{-4} M; pH 3.5 and Temperature.



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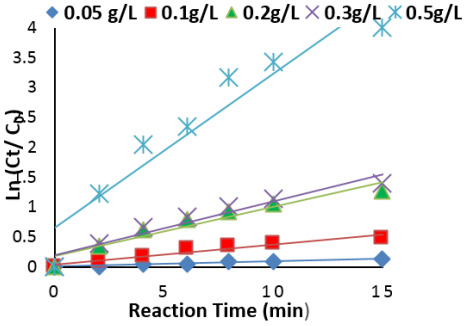


(b)

Figure (4) Plot of First – Order Kinetic Sample of RR120 (a) and DB2 (b) at Differant NZVI Dosag. Experimental Working Condations: [Dye]= 1×10-4 M; pH = 3.5 and Temperatur 30 °C.

The Kinetic of Influence of NZVI Dosage on Dye Decolorization

Figures (4 a and b) are the linear regression plots with decay time for a first-order reaction. When studying the effect of changing the dose of nanoparticles, the interaction kinetics of these nanoparticles with dyes over time was investigated side by side. It was found that first-order interaction is more likely to describe this interaction rather than zero-order and second-order reactions.

These results are consistent with the results of previous research papers. Jing-Feng, *et al.*, 2016 and Reactive Black 5 (Sudipta, *et al.*, 2010). Table (2) shows the obtained coefficients according to the zero, first and second orders.

The Effect of pH on the Adsorption Process

Due to the importance of the pH of the dye solution to be studied and its effect on the extent of its decomposition, the efficiency of decomposition was studied with the change of the pH of the solution with the change of time. Figure (5 a, b) schematics illustrate this effect for dyes RR120 and DB2, respectively. The decolorization effectively with 15 and 60 min response instances reached the most fee of 91% and one hundred percent respectively, at pH 3.5, while at pH 5.0, the decolorization affectivity have been 60% and 71% at (15 and 60) min reaction time, moreover, the values were fifty one percent and 62% at pH 9.0.

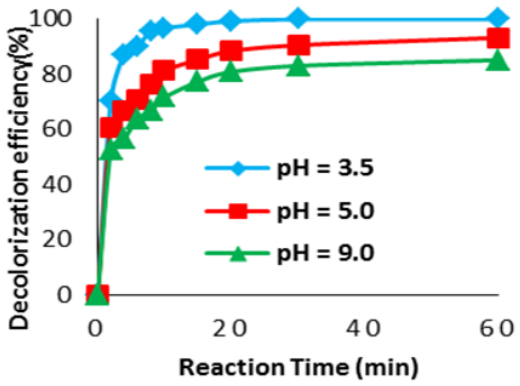
Table (2a) for RR120 Dye and Table (2b). for DB2 Dye, Characteristics of Kinetic Types and Correlation Coefficients for Each NZVI Dosage. Working Conditions: [dye] = 1.0×10^{-4} M, pH 3.5 and Temperature 30°C.

(a)

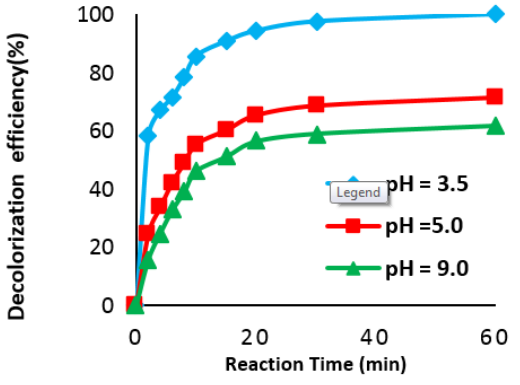
NZVI (G/L)	K_0 (M Min^{-1})	R^2	K_1 (Min^{-1})	$T_{1/2}$ (Min)	R^2	K_2 (M^{-1} Min^{-1})	R^2
0.025	2×10^{-6}	0.9013	0.019	36.47	0.9851	224	0.9461
0.05	2×10^{-6}	0.9026	0.0283	24.49	0.9618	357	0.9249
0.075	4×10^{-6}	0.7242	0.0909	7.62	0.9813	2228	0.9026
0.10	5×10^{-6}	0.6577	0.1465	4.73	0.9566	6358	0.9299

(b)

NZVI (G/L)	K_0 (M Min^{-1})	R^2	K_1 (Min^{-1})	$T_{1/2}$ (Min)	R^2	K_2 (M^{-1} Min^{-1})	R^2
0.05	7×10^{-8}	0.9126	0.009	77.0	0.9742	96	0.9571
0.10	3×10^{-6}	0.9085	0.0333	20.8	0.9626	435	0.9386
0.20	4×10^{-6}	0.8024	0.0819	8.5	0.9539	1712	0.9278
0.30	5×10^{-6}	0.7985	0.0899	7.7	0.9752	2030	0.9542
0.50	5×10^{-6}	0.5183	0.2576	2.7	0.9255	30861	0.9033



(a)



(b)

Figure (5) Effect of pH on Dyes Decoloriztion Efficiency. Experimental Working Conditions for Adsorption: [Dye] = $1x10^{-4}$M, NZVI= 0.1g L^{-1} for RR120 dye (a) and 0.5 gL^{-1} for DB2 Dye (b) and Temperature 30°C.

The solutions of the two dyes reacted negatively by increasing the pH. It is believed that the reason for this is the accumulation of iron hydroxide deposits on the surfaces of the nanoparticles, which will provide a barrier that reduces the reaction and decomposition of the dyes on their surfaces (Zhang, 2003). Therefore, the acidic pH was preferred to increase the efficiency of the hydrolysis of the two dyes. The impact of pH on the decolorization efficiency of dye DB2 proven in Figure (5b). The elimination efficiency 15 and 60 min reached 98% and one hundred percent respectively, at pH 3.5 and 86% and 93% at pH 5.0. At pH 9.0, the removal efficiency reached 77% and 85% with 15 and 60 min response times, respectively. It was both concluded from these finding that acidic pH used to be favored for both dyes RR 120 and DB 2 and to be concluded from these findings too that pH 3.5 used to be chosen as the most preferred over others pH.

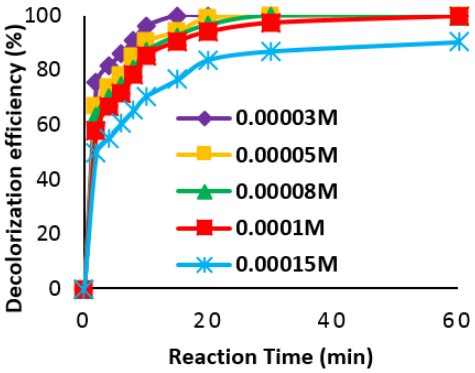
Effect of the Primary Concentrations of Dyes

The initial concentration of dyes is an important characteristic that should be

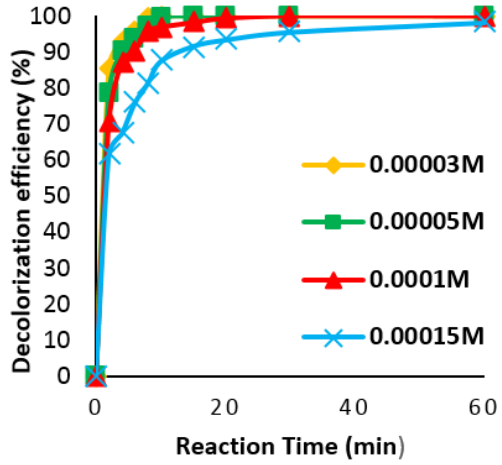
studied for wastewater treatment application. The results are shown in Fig. (6) (a and b). Figure (6a) shows that the increase in dye RR120 concentration has reversed effect on dye color removal efficiency. The decolorization efficiency was in the range of 75-100 % when the dye concentration was (1.5×10^{-4} - 3.0×10^{-5}) mol / L with a reaction time 15 min, the reduction in the rate of reaction may due to the contamination of nano particles on the, surface leading to the competitive adsorption and degradation (Fang, *et al*., 2011). Through previous studies (Carroll, *et al*., 2013). Figure (6b) indicated an important reason that has a significant impact on increasing the efficiency of chromatic decomposition, which is the degree of complexity of the chemical composition of pigments. The simpler of the chemical composition, the higher removal efficiency, as the removal percentage increased from 91% to 100% in the first 15 minutes of the reaction by decreasing the initial concentration of the dye (DB2) from1.5×10^{-4} mol/ L to 3.0×10^{-5} mol/ L.

The Influence of Salt on the Adsorption Process

The effect of some inorganic salts on the efficiency of decomposition of dyes RR120 and DB2 was studied, where the salts used sodium carbonate, sodium chloride and sodium sulfate as shown in Figure (7 a, b). The results indicate the positive effect and the enhancement of the removal efficiency with the presence of sodium chloride salt. This result is in agreement with previous research papers (Lee, *et al*., 2007). This behavior might also be ascribed to truth that chloride salts are acknowledged as erosion promoter (Wang, *et al*., 2008). While the nearness of Na_2CO_3 has small impact on debasement effectiveness of the colors. The nearness of Na_2SO_4 decreases the decolorization proficiency since SO_4^{-2} particles may compete with color atoms and involve the receptive destinations on the NZVI surface (Jing - Fing, *et al*., 2016).

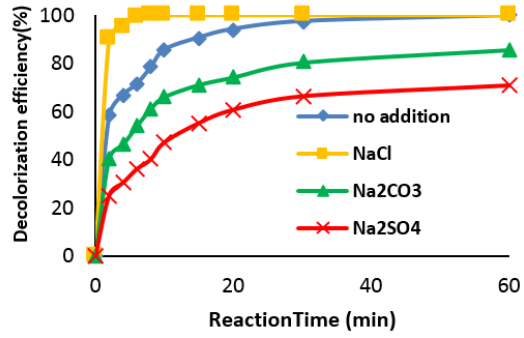


(a)

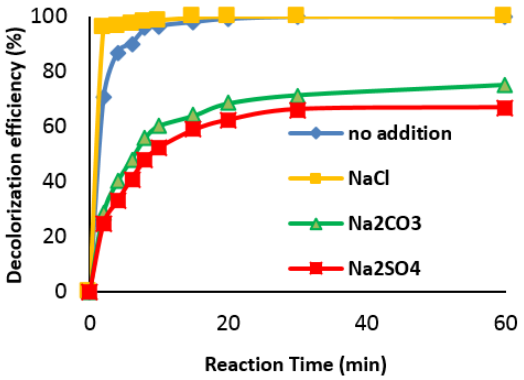


(b)

Figure (6) Effluence of Primary Dyes Concentration on its Decolorization Efficiency Using NZVI. Experimental Working Conditions for Adsorption: pH =3.5, NZVI = 0.1gL^{-1} for RR120 (a), 0.5 g L^{-1} for DB2 (b) and Temperature 30°C.



(a)



(b)

Figure (7) Influence of Addition of 1.0% Inorganic Anionic on RR120 (a) and DB2 (b) Decolorization Affectivity. Primary Conditions: [Dyes] = 1.0×10^{-4}M, pH =3.5, NZVI for (RR120) = 0.1g. L^{-1} and 0.5 g. L-1 for (DB2), Temperature 30°C.

Conclusions

In this study, zero-valent iron nanoparticles were synthesized in the laboratory and these nanoparticles were diagnosed using several techniques like SEM, AFM and SPM. The primary – arrange active show can well clarify the colors corruption prepare utilizing NZVI. The impacts of pH on the color expulsion rate was diverse for the color arrangements utilizing NZVI. The nearness of NaCl upgrades the decolorization productivity of color arrangements whereas the nearness of Na_2SO_4 decreases the decolorization proficiency.

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