The nanoparticles zero-valent synthesis by black tea extract to remove rb 238 using synthetic and natural wastewater by packed bed reactor

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Abstract. This study aims to synthesize nanoparticles of iron zero valences from black tea (BT-NZVI) and bentonite supported with black tea zero-valent iron (B-BT-NZVI) using black tea extract in an environmentally friendly and sustainable way to remove the reactive blue pigment 238 (RB). The characterization tests for BT-NZVI and B-BT-NZVI were performed by atomic force microscopy (AFM) and scanning electron microscopy (SEM). The zeta potential in the stability of iron nanoparticles was also measured. For measuring the porous material's surface area, the Brunauer Emmett-Teller (BET) method was used the average diameter of iron nanoparticles was less than 50 nm. BT-NZVI and B-BT-NZVI were used as absorbents in the batch system study. Two adsorption balance models, Langmuir and Freundlich, are used to describe the adsorption process. The Freundlich model matches well with Reactive Blue 238 dye data and has proven successful in the adsorption process. Kinetic data acquired using the pseudo-first and pseudo-second model examined under optimal reaction conditions and a variety of NZVI concentrations. both batch and up-flow packed flow bed reactor with peroxide H2O2 can degrade dyes and utilized in industrial wastewater treatment.

Keyword: black tea leaf extract, peroxides, Reactive Blue 238, Batch reactor, Packed bed reactor

1. Introduction
The increase in pollutants and their types in the water according to the different human activities resulting from the expansion of the global economy leads to the deterioration of the environment. The dyes industry is considered extremely hazardous for the environment and living organisms. The total annual production of dyes in worldwide is about 0.7 million tons. The textile industry discards large quantities of pollutants, mostly complex chemicals, in addition to dyes as waste in wastewater, and from the various stages of manufacturing textiles where (200 litres of water are thrown to produce 1 kg of fabric) (Ali, 2019). Azo dyes are considered important commercial dyes, widely used, as they represent 50% of them. Once the water stream is polluted with waste from these industries, it is difficult to treat. Several techniques are used to treat industrial wastewater to dispose of industrial dyes, often using: biological treatment (Paz, 2017), physical and chemical processes, coagulation and flocculation (Zahrim, 2013), and sedimentation (Wang, 2019) Membrane filtration (Alventosa, 2019), electrochemical treatment (Körbahti, 2011) and adsorption methods
Most of these technologies are characterised by high cost; the liquid textile wastes required several treatment stages: First, remove suspended solids by screening, coagulation and sedimentation (Zahrim, 2011). Secondly, the removal of organic matter, the demand for biochemical oxygen (BOD), and the demand for chemical oxygen (COD), these need to trickling filters, activated sludge, and aerated lagoons. These treatment methods are considered inadequate due to the difficulty of degradation by these methods and textile dyes' complex chemical composition (Dutta, 2016). Therefore, an effective, inexpensive, and environmentally friendly option should be used that is emerging to treat such waste.

In recent years, iron-based nanoparticles’ demand has increased due to their unique physical and chemical properties, especially environmental remediation (Ebrahiminezhad, 2018). The development of industrial methods for making FeNPs has appeared in many studies, including photochemical reduction, chemical methods, photochemistry and heat treatment. Toxic chemicals are used, and toxic byproducts releases have the potential to become hazardous to the environment (Badmapriya, 2016). In recent years, the synthesis of green from plant extracts has become a sustainable synthesis of nanoparticles, reducing the use of toxic chemicals and reducing the generation of waste. Some studies about plant extracts using the Fenton process (AFP) method to remove dyes by iron nanoparticles were shown in Table 1.

Table (1): Some studies about plant extracts using the Fenton process to remove dyes by iron nanoparticles (AFP) methods.

| Dye          | Synthesised Material                          | Optimum factors | Major finding                                                                 | Reference                  |
|--------------|-----------------------------------------------|------------------|--------------------------------------------------------------------------------|---------------------------|
| Crystal violet (CV) and Eriochrome Black T (EBT) | Chinensis Roxb Leaves extract                  | [NZVI]= 0.5 g, [dye]=10 mg/L, [H₂O₂]= 2 ml(30%) pH= 6.5, under atmospheric pressure and room temperature (25±2°C), dye solution was 50 mL | A complete 100% degradation efficiency of CV and EBT was achieved within the contact time of 10 min | Ali et al. (2019) |
| Methyl orange | Aqueous leaf extract of Daphne mezereu          | [NZVI]=10mg, [dye]= 20 mg/L, T = 400°C,[H₂O₂]= 1 ml (10%) 8 ml methyl orange(25 mg/l) | The decolouration efficiency was about 81% after 6 h.                          | Beheshtkhoo et al. (2018) |
| Methyl orange | Aqueous extract of Mediterranean cypress (Cupressus sempervirens) | [NZVI]= 10 mg, [H₂O₂]=1 ml(10%) under atmospheric pressure, 8 mL methyl orange (25 mg/L) | Decolourisation efficiency was calculated to be 95% in a 6 h process for methyl orange removal | Ebrahiminezhad et al. (2018) |
| Magenta dye  | Oak leaves                                     | [dye]= 180 mg/L, [NZVI]= 60 mg/L[H₂O₂]= 11 ml pH= 2, Working volume 250 cm3 | For a 180 mg/L⁻¹ initial dye concentration of Magenta dye, a removal efficiency of 94% was observed after the 60 min | Kecić et al. (2018) |

The green synthesis method has been used to synthesize iron nanoparticles in the field of nanotechnology, which is characterized by high efficiency, especially in industrial production, and is low in cost (Beheshtkhooet, 2018). In this study, black tea paper was used to synthesis iron nanoparticles (FeNPs) in a simple way to be used as a reducing and stabilizing agent.

2. Material and Experimental work
All chemicals from the analytical reagent grade were used in this study, and deionised water was used to prepare the chemicals. The locally available dry black tea leaves (Ahmad brand) were used. Hydrogen peroxide (H₂SO₄) at a concentration of 30% w/w H₂SO₄. Ferric chloride (III) (FeCl₃), sodium hydroxide (NaOH) and sulfuric acid (H₂SO₄) purchased from AppliChem (GmbH) were used to adjust the pH.

2.1 Dyes Used
The Reactive blue 238 dyes were used, which were brought from Waist Textile Factory. The maximum wavelength λ (nm) was measured using a spectrophotometer (UV/VIS, Model SP-3000 OPTIMA). The characteristics of the dye were shown that Molecular formula (C₁₂H₁₆N₆Na₄O₂₈S₆), Molar Mass (992 g/mol).
2.2. Preparation of NZVI particles

BT-NZVI nanoparticles were prepared using the method mentioned in the study (Wang, 2014) with some modifications. 20.0 grams of black tea (Ahmad brand) was weighed in 200 ml of Deionised water. Preheat the solution at 85 °C for 30 minutes on a hot plate. Use 0.45μm filter paper to filter and remove suspended tea particles. To keep them from spoiling, and for more than one use, store the extract in the refrigerator at 4 °C. Prepare a solution of FeCl₃ (0.1 M), adding 3.25 g of solid FeCl₃ in 200 ml of deionised water. Mix well to fully dissolve, filter the solution with a 0.45μm membrane to remove any impurities. Mix the solution frequently. After the addition, the colour of the solution changes from yellow to black due to the reduction of iron (III) ions to iron (0). Nanoparticles. Add 1.0 M NaOH solution drop by drop to set the pH at 6.0 and continue mixing for 15 minutes (Shahwan, 2011). Collect the black precipitate of iron particles by vacuum filtration using filter paper with a pore size of 0.45 microns and washing it several times with water and ethanol.

2.3 Preparation of the B-NZVI particle.

The same method was used by (Wu, 2015) to prepare B-BT-NZVI nanoparticles. Add 2.0 g of bentonite to 150 ml of high purity water in a beaker and place it in an ultrasound vibration bath. For 60 minutes at room temperature. To prepare a solution of 0.10M FeCl₃ to add 2.5 g of solid FeCl₃ in 150 ml of deionised water. Mix to completely dissolve, filter with a 0.45μm membrane filter to remove any impurities. Add it to the bentonite solution and mix it for 60 minutes of an ultrasonic vibration bath. As previously mentioned, black tea extract was prepared by adding 10.0 grams of tea to 100 ml of deionised water. Add the tea extract to the mixture of ferric chloride and bentonite by adding it slowly for 15 minutes at room temperature with continuous mixing and following the same method mentioned previously, prepare B-NZVI, NZVI particle, and B-NZVI.

2.4 Characterisation of titration schemes for building nanoparticles

Eight solutions of dyes (RB 238) at concentrations of (1.5x10⁻⁴, 1.0x10⁻⁴, 7.5x10⁻⁵, 5.0x10⁻⁵, 2.0x10⁻⁵, 1.0x10⁻⁵, 5.0x10⁻⁶ and 1.0x10⁻⁶ mol/L) respectively was Prepared. Wavelengths determined the absorbance and a linear relationship was drawn between absorbance and each dye concentration at each λ_max wavelength (605, 540). Repeat the process several times to obtain absorption factors to estimate unknown dyes' concentration (Azadeh, 2018). UV Vis absorption spectra for each of the dye shown in Figures 1.

![Figure 1: UV-Vis absorption spectra of solutions](image_url)

2.5 Zeta Potential Analysis

The zeta potential analysis depends on the observation of the liquid's electrostatic behaviour in assessing the stability of the nanoparticles (Singh, 2018). In any nanoparticles, the zeta potential ranges from the cation to the low pH, to the negative zeta potentials at higher pH. The zeta potential value of > ± 60 mV has excellent stability, ± (40 to 60) mV has good stability, ± (30 to 40) mV is considered stable, and < ± 30 mV is highly agglomerated.
2.6 Another requirements analysis
The Scanning Electron Microscope (SEM) was used to investigate the morphology and Distribution of GT-NZVI nanoparticles. According to the (ASTM F1375) Atomic force microscopy (AFM) was used to measure the surface morphology of nanoparticles (Daniel, 2013). Atomic force microscopy (AFM) measures the contact force between the tip and surface. The Blumenauer-Emmer-Teller (BET) method can measure the size of open porosities in the range of 0.4 to 50 nm. According to ASTMD 3908 method.

2.7 Degradation of dyes in batch experiments
In this work, batch experiments were performed to evaluate dyestuff removal efficiency according to the following procedure: In Fenton-like experiments, the effects of [NZVI] doses in the range of 0.1 - 1.5 g / L of a 1 L synthetic solution were studied with 0.05 mM or 49.6 mg / L of dyes at a concentration of 5 mM H2O2 and a pH of 3.5. The concentration of the dyes was monitored during the Fenton-like oxidation, 10 mL of the sample was withdrawn at set intervals and transferred to a glass vial containing 200 mL of 1 M Na2SO3 to stop the reaction (Hassan, 2019). While the effect of H2O2 concentration was evaluated in the range of 0.64-10 mmM when removing 0.05 mmM or 49.6 mg / L of dyestuff solution under optimum dose [NZVI] 0.5 g / L at pH 3.5. Experiments were conducted at a pH ranging from 2.0 to 9.0 to find the best pH for degradation.

2.8 Continuous Experiments (Up Flow Mode)
The packed bed reactor is used in the Up-flow mode operation, from studies that are more suitable for the process than other reactor types. A packed-bed reactor has made from glass tub (35cm) length and diameter (2.2cm). The Glass wool has been used to prevent missing of the bed's materials, the reactor consist of equipment shown in Figure (2).

2.9 experimental procedures
The packed bed reactor was operated depending on the results obtained from a batch reactor such as pH, temperature, and dye concentration. Various parameters were studied in packed bed reactor (continuous experiments) including (bed height of adsorbent (black tea Nano zero-valent iron supported bentonite (B-BT-NZVI)) was (0.5- 1 - 1.5 cm), flow rate (1- 1.5- 2 L/hr) and hydrogen peroxide doses (2.5- 5- 10 L/hr). The dyes solution were measured using a scale. UV-Vis spectrophotometer and decolourisation efficiency were determined

3. Results and Discussion
3.1 Characterisation of the Synthesised NZVI Particles
The size and morphology were verified by characterising the synthesis iron nanoparticles by black tea extracts. Black tea supported bentonite samples (BT-NZVI, B-BT-NZVI) by scanning electron microscope (SEM) and Atomic Force Microscopy (AFM) analysis for studying the diameter of the Nanoparticles.
A, B represented the SEM images of synthesised iron nanoparticles (BT-NZVI, B-BT-NZVI). From SEM images observed the morphology of these materials. The Irregular rectangular shapes were seen in nanoparticles. This issue may be due to the presence of polyphenols on the nanoparticles’ surface. These results were agreed with the results of preparation NZVI using the tree leaf extracts, black tea extracts (Machado, 2015). Other research indicates iron nanoparticles’ production as an irregular spherical particle formed in solution. This issue depending on polyphenols and caffeine percentage present in the extract that can react differently, and promoting the growth of the NZVI nanoparticles, producing different sizes and shapes of iron nanoparticles (Machado, 2015). Figure 4 A and B, the particle size distribution of synthesised iron nanoparticles show size diameter within the average less than 50 nm with no obvious agglomeration. Figure (4) C represents the BT-NZVI after up-flow treatment.

Figure 3: Scanning electron microscope (SEM) images of A) BT-NZVI, B) B-BT-NZVI and C) BT-NZVI after treatment.

Figure 4: Atomic Force Microscopy (AFM) images of A) BT-NZVI and B) B-BT-NZVI

Using the zeta potential analysis technique, the nanofluids' stability can be distinguished as shown in Figure (5) A, B, a negative zeta potential values -22.05 for BT-NZVI 27.22 for B-BT-NZVI which shows that the four nanoparticles were more agglomerative.

Figure 5: Zeta potential (mV) graph of A) BT-NZVI and B) B-BT-NZVI

The results obtained from Blumenauer-Emmer-Teller (BET) showed that the unequal iron nanoparticle supported by bentonite had improved the structure of the nanoparticles because of the fineness of the
bentonite. This result leads to an increase in the surface area, and an improvement in the structure of the nanoparticles, the surface area of the porous material most important parameters for determined the catalyst. For the pores' size, the mesopores do not find the synthesised nanoparticles, the supermicropore and ultramicropore only presented as The International Union of Pure and Applied Chemistry (IUPAC) classification; these results were shown in Table (2). The plugging efficiency (P.E.) was calculated by equation (1).

\[ P. \ E. \% = \left( \frac{\text{BET before treatment} - \text{BET after treatment}}{\text{BET before treatment}} \right) \times 100\% \]

Table 2: BET isotherm studies and parameter.

| Parameter          | BT-NZVI  | B-BT-NZVI |
|--------------------|----------|-----------|
| BET (m²/g)         | 1.3851   | 21.2709   |
| Pore volume (cm³/g)| 0.000794 | 0.044451  |
| Pore size(nm)      | 2.29256  | 8.35910   |
| Langmuir surface area(m²/g) | 2.8372 | 31.7776 |

3.2 The RB 238 Dye Degradation in Aqueous Media

3.2.1 Effect of hydrogen peroxide (H₂O₂). Effect of hydrogen peroxide (H₂O₂). For blank experiments conducted in the presence of peroxide, no degradation or colour removal of RB 238. but the increase in decolourisation efficiency by increasing hydrogen peroxide from 0.64 mM to 2.5 mM for BT-NZVI catalyst. This result is due to the increased production of free radicals hydroxyl (OH●). The decolourisation efficiency decreases with increasing the hydrogen peroxide concentration from 0.64 mM to 10 mM for the catalysed B-BT-NZVI, as shown in (Figure (6)). An increase of more than 2.5 mm causes a decrease in the removal efficiency of BT-NZVI. Where the hydroxyl radical is scanned, due to the recycling of the hydroxide radical with H₂O₂, which can be illustrated by formula (1) (AL-Kindi, 2019a: Hassan , 2019: Shih, 2012):

\[ H₂O₂ + OH → H₂O + HO₂● \]

A concentration of 2.5 mM for BT-NZVI and 0.64 mM B-BT-NZVI of hydrogen peroxide was considered suitable and ideal for use in the rest of the experiments.

Figure (6): The Decolorization efficiency of RB 238 with constant variables: [RB 238] = 0.05 mM, pH = 3.5, [NZVI] = 0.5 g / L and room temperature. With different concentrations of H₂O₂ catalyzed by A) BT-NZVI and B) B-BT-NZVI.

3.2.2 Effect of NZVI Amount. To determine the amount of BT-NZVI and B-BT-NZVI needed for active treatment. Several experiments were conducted to determine the concentration of RB 238 and used a solution pH of 0.05 mM and 3.5, respectively. H₂O₂ concentration was stabilised at 2.5 mM and 0.64 mM for BT-NZVI and B-BT-NZVI, respectively.
The results found that the optimal doses are (0.1 g / L) for BT-NZVI and B-BT-NZVI, as shown in Figure (7) A and B, respectively. RB 238 dye solutions' removal efficiency was at higher doses of BT-NZVI or B-BT-NZVI to decrease dye degradation. Due to the presence polyphenols of tea in the surface of iron nanoparticles and when increasing the amount of BT-NZVI or B-BT-NZVI, this may increase polyphenols in the aqueous solution of the dye and thereby scavenge the OH● free radicals (Wu, 2015).

3.2.3 Effects of pH value. The decolourisation efficiency of RB 238 is affected by the initial pH value of solutions from 2 to 7 using BT-NZVI or B-BT-NZVI. The highest pH value was 7, and pH 9 was not used because of this value. It leads to an acceptable result in previous experiments. As the pH decreased, the decolourisation efficiency increased from RB 238 using BT-NZVI and B-BT-NZVI. This behaviour may be attributed to the inhibition of ferrous hydroxide on the surface of iron nanostructures when BT-NZVI or B-BT-NZVI is oxidised at low pH solutions (Satapanajaru, 2011). The best pH value was verified at pH 2.5 with 93.5%, 95%, 90.5% and 87.5% of RB 238 catalysed decolourisation efficiency by BT-NZVI B-BT-NZVI, respectively, after 60 minutes of Fenton-like oxidation reaction as It is shown in Table (3). Apparently, from Figure (8), the solution's pH had a strong effect on the rate of decolourisation.

3.2.4 Effects of RB 238 aqueous dye solution. Figure 9 shows the effect of initial dye concentration on 238-inch RB degradation. The decolorization efficiency decreased from (93.5%, 95.1%, 90.5%, 87.5%) to
When the initial RB 238 dye concentration increased from 0.05 mmol to 0.25 mmol. For BT-NZVI and B-BT-NZVI respectively. The optimum condition of the dye-based aqueous media RB 238 and room temperature is shown in Table 3. The decrease in the dye concentration reveals an increase in the dyes' decolourisation efficiency due to the small dye particles available for cleaning by the hydroxyl radicals (Hassan, 2018).

Table 3: optimum condition for RB 238 dye aqueous solution at room temperature.

| NZVI TYPE | \( \text{H}_2\text{O}_2 \text{ mM} \) | \( [\text{NZVI}] \text{ g/l} \) | pH | \( [\text{RB 238}] \text{, mM} \) |
|-----------|----------------|----------------|----|------------------|
| BT-NZVI   | 2.5            | 0.1            | 2.5| 0.05             |
| B-BT-NZVI | 0.64           | 0.1            | 2.5| 0.05             |

Figure 9: The removal efficiency of RB 238 at different concentrations of dye catalyzed by, A) BT-NZVI and B) B-BT-NZVI. Experimental constant condition: pH = 2.5, \( \text{[H}_2\text{O}_2\text{]} \text{ = 2.5 Mm for C, 0.64 Mm for [BT-NZVI] or [B-BT-NZVI] = 0.1 g/l and room temperature.} \)

3.2.5 Temperature Effects. The oxidation reaction effect at different temperature levels from 20 °C to 50 °C on the decolourisation efficiency of RB 238 dye solution (0.05 mM) was studied. From Figure (10), raising the temperature positively affects the degradation of RB 238. from results were observed an increase in decolourisation efficiency within 10 minutes of the reaction from (39 % To 93.3%) and (36.6% to 92.5%) by using BT-NZVI and B-BT-NZVI as a catalyst, respectively, by increasing the temperature from 20 °C to 50 °C. This issue is because the higher the temperature increases the oxidation reactions between the catalyst and H2O2, increasing the production rate of free radicals of hydroxyl (OH ⋅) or highly valued iron species (Demirezen, 2019). The higher temperature may increase the reactant molecules' energy to overcome the reactive energy (AL-Kindi, 2019b).
3.3 The kinetic study

The kinetic study is an important step in all the processes. (Wang, 2019) was studied using the pseudo-zero, pseudo-first and pseudo-second-order for kinetic models which are described by the linear Equations (2) (Emami, 2010).

\[
\text{(Second-order)} \quad \frac{1}{C_t} = \frac{1}{C_0} + k_2 * t
\]  

Where, C0 the initial dye concentrations (mol/l) and Ct is the dye concentration (mol/l) at any time of the reaction, t is the time of Fenton process (min), k2 is the rate constant for second-order oxidation reaction respectively. From the batch reactor results, The kinetic study depended on the high R2 in this study for The effect of NZVI Amount on the Degradation of RB 238 dye Aqueous Media. At the higher dosages of BT-NZVI or B-BT-NZVI, RB 238 dye solutions' removal efficiency results in decreased degradation. Because the iron nanoparticles contain tea polyphenols in the surface and increased the amount of BT-NZVI or B-BT-NZVI, that may lead to more polyphenols discharge to the aqueous solution of dye and scavenged the OH\textsuperscript{●} free radicals (Wu, 2015). From experimental data, the best fit with the second-order model as shown in Table (4) and Figure (11)A, B  the decolourisation efficiencies for the oxidation reaction on BT-NZVI or B-BT-NZVI catalysed were shown after 60 min, and 180 min of reaction.

![Figure 11: Linear plots of kinetics data of the second-order model at a various dosage of green catalyst, A) BT-NZVI and B) B-BT-NZVI.](image)

**Table 4:** Zero-order, First-order and second-order kinetic models constants, regression coefficients and decolorization efficiency at varying green catalyst dosages of Fenton-like oxidation. Experimental conditions: [RB 238] = 0.05 mM, pH = 3.5, [H\textsubscript{2}O\textsubscript{2}] = 2.5 mM for BT-NZVI, 0.64 mM for B-BT-NZVI and room temperature.

| NZVI TYPE | NZVI (g/l) | DE, % after 60 min | DE, % after 180 min | Zero-order | First-order | Second-order |
|-----------|------------|--------------------|--------------------|------------|-------------|--------------|
|           |            | k\textsubscript{0} (M min\textsuperscript{-1}) | R\textsuperscript{2} | k\textsubscript{1} (min\textsuperscript{-1}) | R\textsuperscript{2} | k\textsubscript{2} (M\textsuperscript{-1} min\textsuperscript{-1}) | R\textsuperscript{2} |
| BT-NZVI   | 0.1        | 76.3               | 92.2               | 7.00E-07   | 0.955       | 0.023        | 0.998        | 876.6       | 0.962 |
|           | 0.25       | 73.3               | 90.8               | 7.00E-07   | 0.924       | 0.02         | 0.99        | 716.1       | 0.982 |
|           | 0.5        | 57.9               | 84.5               | 5.00E-07   | 0.97        | 0.013        | 0.995       | 368.7       | 0.988 |
|           | 0.75       | 67.5               | 83.5               | 5.00E-07   | 0.883       | 0.014        | 0.956       | 418.6       | 0.993 |
|           | 1          | 60.4               | 77.1               | 6.00E-07   | 0.881       | 0.017        | 0.966       | 567.5       | 0.996 |
|           | 1.5        | 50.3               | 72.7               | 4.00E-07   | 0.908       | 0.01         | 0.959       | 268.9       | 0.989 |
| B-BT-NZVI | 0.1        | 49.0               | 83.6               | 4.00E-07   | 0.947       | 0.01         | 0.981       | 267.1       | 0.997 |
3.4 Packed-bed Reactor in Up Flow mode for RB 238 Dye. The Up flow packed-bed reactor based on sets of experiments were conducted. The optimum parameters from batch experiments for decolorization of RB 238 by B-BT-NZVI in the presence of H2O2 were used, the dose of 0.05 mM or 49.67 mg/L RB 238 aqueous solution, fixed pH 2.5 and room temperature. Using different bed height of B-BT-NZVI, flow rate and concentrations of H2O2 for determination the removal efficiency of RB 238 dye. Sets of experiments were proceed as follows:

3.4.1-Effect of Flow Rate. The effect of using different flow rates (1, 1.5, 2 l/hr) was investigated by keeping other parameters constant, in figure 12 the flow rate increase the removal efficiency decrease. The concentration of RB 238 can explain this phenomenon affected the formation of OH• and their scavengers. This behavior may participate in less scavenging of consisted OH• when initial organic substrate concentration increased without exceeding its optimum value (AL-Kindi, 2019b; Li., 2015) Therefore, 1l/hr is within the optimal period for degradation, which will avoid speeding up hydroxyl radical's scavengers.

\[
\begin{array}{ccccccccc}
0.25 & 47.7 & 81.5 & 4.00E-07 & 0.959 & 0.01 & 0.987 & 252.7 & 0.998 \\
0.5 & 47.6 & 77.1 & 4.00E-07 & 0.937 & 0.008 & 0.968 & 186.3 & 0.988 \\
0.75 & 41.0 & 70.3 & 4.00E-07 & 0.966 & 0.01 & 0.989 & 240.1 & 0.992 \\
1 & 39.6 & 66.8 & 4.00E-07 & 0.934 & 0.007 & 0.966 & 174.7 & 0.986 \\
\end{array}
\]

Figure (12): Effect of flow rate on decolorization efficiency of RB 238 dye. Experimental condition: bed height = 1 cm, [H2O2] = 0.25 M, [RB 238] = 0.05 M, pH = 2.5 and room temperature.

3.4.2 Effect of Bed Height of B-BT-NZVI. Three experiments were made to study the effect of varying the bed height of the B-BT-NZVI (1, 1.5, 2 cm). The Effect of bed height of B-BT-NZVI on the removal efficiency of RB 238 dye using Up-flow packed-bed system with the presence of hydrogen peroxide is presented in figure (13). The greater nanomaterial bed height significantly improved decolorization by providing more surface-active sites to accelerate the initial reaction resulting in more iron ions colliding with dye molecules to remove colour. Also, the high iron loading can lead to NZVI particles agglomeration resulting, again, in decreased removal efficiency. Therefore, the bed height 1 cm was chosen as the optimum concentration and was used in the next set of experiments.

3.4.3 Effect of Hydrogen Peroxide Concentration. The concentration of hydrogen peroxide affects the removal efficiency directly to since it is related to the number of hydroxyl radicals produced in the reaction. Three experiments were conducted to study the effect of varying concentrations of H2O2 1, 0.5, 0.25 M. Figure (14) shows the effect of H2O2 concentration on the decolorization efficiency of RB 238 dye. When the H2O2 concentration increased to 1 M, decolorization efficiency of RB 238 dye decreased rapidly, that may be because the generation of hydroxyl radicals is vassal on hydrogen peroxide concentration, and scavenging of hydroxyl radicals will occur. [H2O2] =0.5 M was chosen as the optimum concentration.
Figure (13): Effect of bed height of B-BT-NZVI on the decolorization efficiency of RB 238 dye. Experimental condition: flow rate = 1 l/hr, [H₂O₂] = 0.25 M, [RB 238] = 0.05 M, pH = 2.5 and room temperature.

Figure 14: Effect of [H₂O₂] on the decolorization efficiency of RB 238 dye. Experimental condition: flow rate = 1 l/hr, bed height = 1 cm, [RB 238] = 0.05 M, pH = 2.5 and room temperature.

4. Conclusions

Black tea is a plant with high application qualifications as a green reducing or gapping agent with no additional agents. Iron nanoparticles with a size diameter of less than 50 nm were formed and provides high efficiency for catalytic or adsorption purposes. Under the optimum conditions, the high decolourisation efficiencies of RB 238 dye after 60 min were (90.5%, 87.5%) using BT-NZVI and B-BT-NZVI catalyzed the Fenton-like oxidation, respectively. The temperature effect was between 30°C and 40°C, and more than 97% was degraded after 60 min. The maximum removal efficiency of RB 238 dyes by using an up-flow packed-bed reactor with the presence of the H2O2 technique at optimal conditions is 97%. The removal efficiency of RB 238 dyes increases with decreasing the flow rate.

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