Engineering and Technology Journal
Journal homepage: engtechjournal.org

Green Synthesis of Iron Nanoparticles Using Black Tea Leaves Extract as Adsorbent for Removing Eriochrome Blue-Black B Dye

Dalal Ghanim [a*], Ghayda Y. Al-Kindi [b], Ahmed Kh. Hassan [c]

[a] Sanitary and Environmental Branch, Civil Engineering Department, University of Technology, Baghdad, Iraq. dalalghanim80@yahoo.com

[b] Sanitary and Environmental Branch, Civil Engineering Department, University of Technology, Baghdad, Iraq.

[c] Environment and Water Directorate, Ministry of Science and Technology, Baghdad.

*Corresponding author.

Submitted: 13/11/2019 Accepted: 31/12/2019 Published: 25/10/2020

KEYWORDS

Bentonite; black tea leaves; SEM; synthesizing Nanoparticles.

ABSTRACT

Recently, the world has directed to find environmentally friendly and clean materials to be used to treat wastes difficult to treat in the traditional way such as dyes. The object of this study was to synthesize iron nanoparticles using black tea extracts in an environmentally sustainable method. Also, it was developed by supporting with bentonite, used to remove Eriochrome blue-black B dyes from synthesis wastewater of textile factory. From the results, it was noted that black tea leaf extract has reduced iron ions to iron nanoparticles at room temperature. Composite iron nanoparticles were characterized using Scanning Electron Microscope (SEM), and Atomic force microscopy (AFM) studies where the diameter of iron nanoparticles was less than 70 nm. This research shows that ferrous nanoparticles can be manufactured using black tea leaf extract as a reducing agent. It also shows better-supported nanoparticles than unsupported. The decolorization efficiency catalyzed BT-NZVI, B-BT-NZVI increased from (14%, 42%) to (48%, 68%) at 180 min of batch processes when the NZVI concentration was increased from 0.5 g/L to 2 g/L respectively.

How to cite this article: D. Ghanim, Gh. Y. Al-Kindi and A. Kh. Hassan, “Green synthesis of iron nanoparticles using black tea leaves extract as adsorbent for removing eriochrome blue-black B dye,” Engineering and Technology Journal, Vol. 38, Part A, No. 10, pp. 1558-1569, 2020.
DOI: https://doi.org/10.30684/etj.v38i10A.1225

1. INTRODUCTION

Dye pollutants are the major sources of environmental pollution caused by various industries especially textile, cosmetic, leather, printing, paper, chemical paint, pharmaceutical, food and varnish industries [1]. Discharge of textile wastewater into the streams does not only affect the aquatic lives being having various metals and chlorides but also it seems that the presence of very small amounts less than 1 ppm for some dyes in water is undesirable for any use [2]. The stable and complicated structure of dyes makes a greater difficulty in the process of degradation of these dyes when present all kind of a complex matrix not only in textile wastewater but also in all industry wastewater [3]. This reduces the penetration of light into the water and increases the turbidity, that make the aquatic plants are the most affected as they are not able to carry on the photosynthesis [4]. It also endangers other aquatic life forms and this leads to a disorder of the aquatic ecosystem [5]. There are numerous methods to treat polluted water of textile industry effluent. To minimize the treatment cost of the polluted water to be utilized for drinking, it should not have colors or toxic components. So, before the discharge of textile wastewater into the river, several processes for treatment are used including physical, chemical, biochemical, and hybrid treatment processes developed to treat such pollution in an efficient and economical way [6]. All of these methods have their own advantages and disadvantages. These methods have their limitations where none of them are succeeded in removing or degrading the colors from wastewater [7]. The most popular among these methods is adsorption because of effectiveness and the simplicity of the process [8]. Recently, special attention has been appeared for the use of the available-in-nature and eco-friendly sorbents to replace the expensive and conventional adsorbents. The adsorbent widely used by dye manufacturing factories to remove dyes is activated carbon. But, its difficulty in its regeneration and high price limits the application for decolorization, has increased the interesting in synthesizing Nanoparticles in an easy and environmentally friendly way [9]. The conventional processes such as physical and chemical are used for the synthesis of Nanoparticles, however, due to limitations of these methods, the focus of researchers has been to move towards the development of clean and eco-friendly synthesis protocols. The green synthesis of iron nanoparticles is achieved using acceptable environmental plant extract. Nanoscale iron particles have earned great interest in environmental treating circles. Zero valent iron can be used as a Fenton-like catalyst for the removing of organic pollutants from aqueous solutes. The nanoscale measure provides a high surface reactivity and high surface area. Sodium borohydride, NaBH4, are used as a reducing agent to produce synthesized Iron nanoparticles [10]. Green synthesis of iron nanoparticles is a method that would help beating the concerns related to using sodium borohydride as a capping agent in routine synthesis reported so far.

In this work, iron nanoparticles were synthesized using black tea leaf extracts B-FeNPs. Tea contains polyphenols that act both as a capping and reducing agent. In addition, syntheses the iron nanoparticles was supported with bentonite BT-FeNPs. The produced BT-FeNPs was characterized using Atomic Force Microscopy (AFM) and Scanning Electron Microscope (SEM). The iron nanoparticles and iron nanoparticles supported with bentonite were used as adsorbent to removal Eriochrome Blue-Black Bdye from syntheses Textile wastewater, Furthermore, kinetic and equilibrium models have been used to match experimental data.

2. EXPERIMENTAL WORK

I. Preparation of BT-nZVI

The BT-nZVI nanoparticles were prepared using a similar procedure described in previous studies [11] with some modification:

The synthesis of iron nanoparticles was done by using black tea leaves (Ahmed brand). Extracts were prepared by heating 20.0 g of black tea in 200 mL of deionized water for 30 min at 85 °C on hot plate. The extract was filtered by using filter paper of 0.45 µm pore size.

As a source of Fe (III) a solution of 0.10 M FeCl3was prepared by adding 3.15 g of solid FeCl3 in 200 mL of deionized water as shown in Figure 1. This solution was filtered by using filter paper of 0.45 µm pore size.

The tea extract was mixed with solution of 0.10 M FeCl3 by adding it thoroughly for 15 min. The color immediately was change after the addition of black tea extract to the Ferric chloride solution as shown in Figure 2.

The black iron particles was separated by filter paper of 0.45μm pore size and then left to dry it overnight in oven at 65°C.The dried nanoparticles were ground to fine powder as shown in Figure 3.

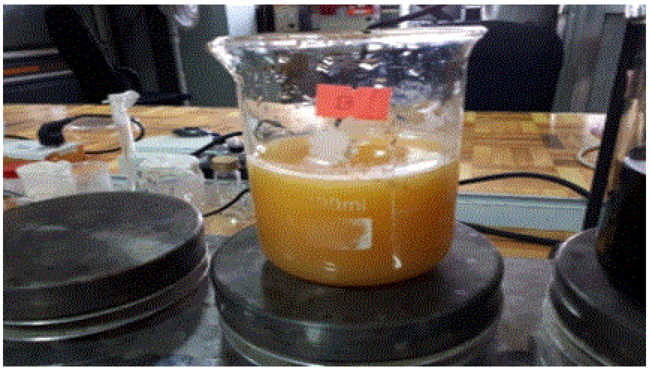

Figure 1: 0.1 M ferric chloride

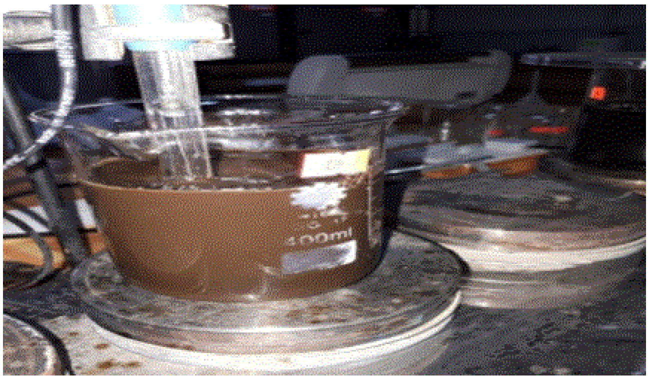

Figure 2: Synthesized iron nanoparticles

Figure 3: Iron particles separated by filter paper of 0.45μm pore size

II. The B-BT-nZVI nanoparticles were prepared using the following steps

2.0 g of bentonite and 150 mL of high purity water were placed in a beaker for 60 min at room temperature of ultrasonic vibration bath. The solution of 0.10 M FeCl3 was prepared by adding 2.5 g solid FeCl3 in 150 mL deionized water. After complete dissolving, this solution was filtered using a 0.45 μm membrane filter to remove any impurities. This solution was added into the bentonite solution, and stirred for 60 min of ultrasonic vibration bath. The black tea extract was prepared by mixing 10.0 g of tea in 100 mL of deionized water and prepared according to the above procedure. Then, the tea extract was added to the mixture of ferric chloride and bentonite by adding it slowly for 15 min at room temperature, and constantly stirred following the same procedure used above. Figure 4 shows BT-nZVI and B-BT-nZVI particles.

Figure 4: B-nZVI and B-BT-nZVI particles

III. Characterization of nanoparticles

By using scanning electron microscope (SEM), morphology and distribution of nanoparticles were determined. The zeta potential test evaluates the stability of nanofluids through the monitoring of electrophoretic behavior of the fluid [12].

IV. Adsorption experiments

NZVI) and (B-BT-NZVI) was conducted in the batch system. A 1000 mL Eriochrome blue-black B solution (0.5g/L) was placed in a conical flask and stirred at 200 rpm at room temperature. The batch processes were done for 180 min under fixed pH condition (2.5) during each run at regular time intervals, the samples were withdrawn, Filtered by filter syringe to separate the dye solution from (BT-NZVI) and (B-BT-NZVI), and evaluated for the degradation efficiencies.

UV–visible spectrophotometer was used to determine Eriochrome blue-black B absorbance with quartz cell at each wavelength. The Figure 5 shows the calibration graph of Eriochrome blue-black B.

The capacity of adsorption qt and removal efficiency of Eriochrome blue-black B dye were calculated from the equations (1) and (2).

$$qt = (Co - Ct)\, V / w \;\ldots.\; (1)$$

$$\text{Colour removal efficiency\%} = [(Co - Ct)/ Co] \times 100\% \;\ldots.\; (2)$$

Where qt is the adsorption capacity at specific time t (mg/g) is the RB 238dye amount adsorbed per unit mass of adsorbent; Co (mg/L) and Ct (m/L) are RB 238concentrations at initial and time t; V is the volume of solution (L) and W is the mass of the adsorbent (g).

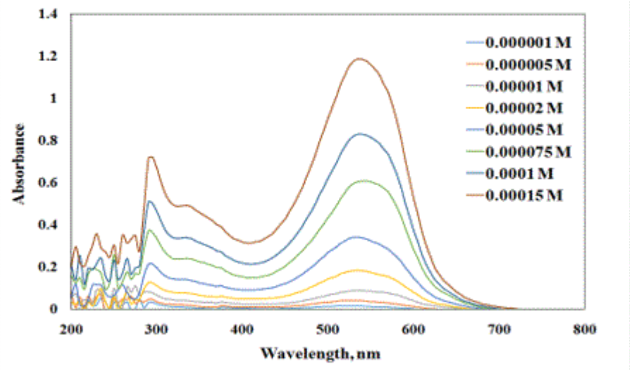

Figure 5: UV-Vis absorption spectra of Eriochrome blue-black B dye solutions

V. Adsorption kinetics

To understand the technique and rate of the adsorption procedure, data produced from adsorption experiment were evaluated by first-order and second-order counterfeit Kinetics. The pseudo-first-order model is given by Eq. (3) [13]:

$$\text{Log}(qe - qt) = \log qe - k1\ t / 2.303 \quad .... (3)$$

Where qt is the adsorption capacity at specific time t (mg/g), qe is the adsorption capacity at equilibrium (mg/g) and k1 (min-1) is the rate constant of the pseudo-first-order model. The pseudo-second-order [14] equation is defined by Eq. (4):

$$t/q = 1 / k2\ q2 + t/q \quad .... (4)$$

k2 (L/mg min) is the rate constant of the pseudo-second-order model.

VI. The models of adsorption isotherm

Solute adsorbed (dye) per unit weight of adsorbent (BT-NZVI or B-BT-NZVI) as a function of the equilibrium concentration in the bulk solution at a fixed temperature know as the adsorption isotherm [14,15,16]. There are many isotherm models such as: Langmuir, Freundlich, KHarkin–Jura, Temkin and Dubinin–Radushkevich. The most commonly used for the description of adsorption data are Langmuir and Freundlich's models [17,18] . The Langmuir isotherm can be expressed as in Eq. (5):

$$Ce/qe = 1/qmKL + Ce/qm \quad ....(5)$$

qe is the adsorption capacity at equilibrium (mg/g), Ce concentration of adsorbates remaining in solution at equilibrium (mg/L) and qm is the monolayer adsorption capacity (mg/g). The KL and qm can be determined by the intercept and the slope of the linear plot of Ce/qe vs. Ce, respectively.

Freundlich equation can be express as in Eq. (6):

$$\text{Log}\ qe = \log KF + 1/n \log Ce \quad ....(6)$$

Ce : the equilibrium concentration in the solution (mg /L)

qe : the amount of dye ions adsorbed (mg /g)

KF : the adsorption coefficient which is related to adsorption capacity of the adsorbent ((mg g-1)(mg L-1)n).

1/n : the surface heterogeneity factor.

KF determined by the intercept of lnqe vs. lnCe, respectively.

3. RESULTS AND DISCUSSION

I. Reduction mechanism of black tea

The iron nanoparticles were synthesized in an eco-friendly and easy way using the black tea leaves extract as a capping agent because tea contains enough amount of polyphenols and other organic groups in it.

II. Characterization of nanoparticles

The size and morphology are verified by characterizing the synthesis BT-NZVI, B-BT-NZVI samples by scanning electron microscope SEM and Atomic Force Microscopy AFM analysis for seeking the diameter of the nanoparticles as shown in Figure 6 A, B represented, the SEM images of synthesized iron nanoparticles by black tea, black tea supported bentonite, respectively. From the SEM images, it can be seen that the nanoparticle an irregular square particles were formed in solution. In Figure 7 A and B particle size distribution of synthesized iron, nanoparticles show size diameter within the average less than 70 nm [19]. The stability of the Nano fluids was characterized by zeta potential analysis technique which showed that zeta potential had values -22.05 for BT-NZVI, -27.22 for B-BT-NZVI Figure 8A and B shows the poor degree of coagulation to both materials [20].

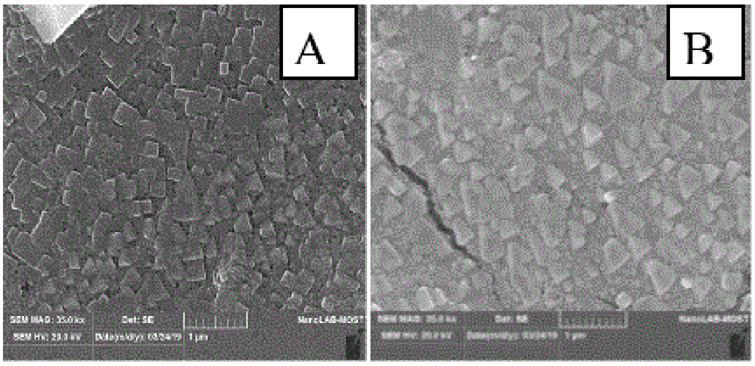

Figure 6: Scanning electron microscope (SEM) images of A) BT-NZVI, B) B-BT-NZVI

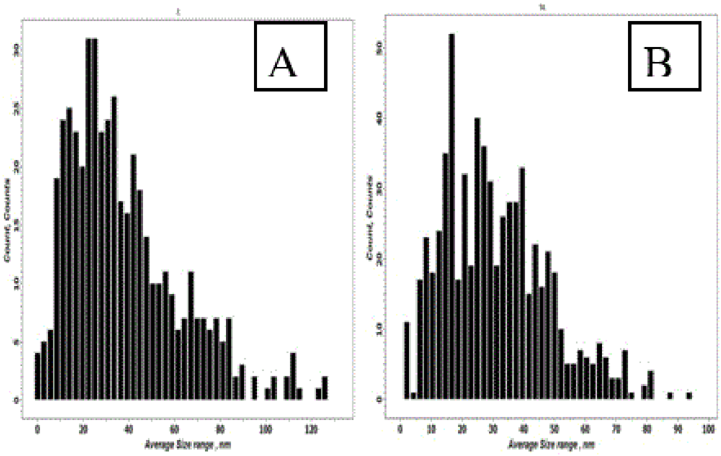

Figure 7: Atomic Force Microscopy (AFM) images of A) BT-NZVI, B) B-BT-NZVI

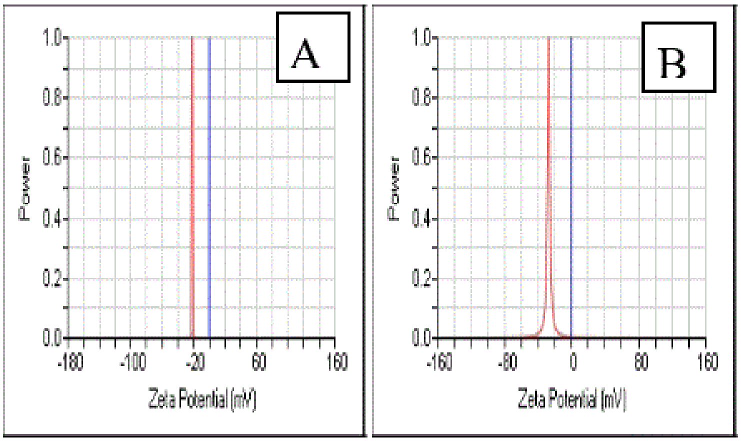

Figure 8: Zeta potential(mV) graph of A) BT-NZVI B) B-BT-NZVI

The results of BET are presented in Table 1. These results of the zero valent nanoparticles iron supported with Bentoniteshowed an improvement in nanoparticle structure, because the presence of Bentonite leads to an increase in the surface area, which is one of the important things to achieve the high performance of the catalyst, where the surface area of the porous material is one of the most importantparameters to determine its properties. Pore volume of synthesized nanomaterials supported with Bentonite also was increased. The International Union of Pure and Applied Chemistry (IUPAC) sorting of pore size (Å) as macropore (≥ 500); mesopore (20 to 500); supermicropore (7-20) and ultramicropore (≤ 7) [21]. From the results it seems that there is no presence of mesopores in all synthesized nanoparticles the pore size is in micropore.

TABLE I: BET isotherm studies and parameter

Parameter	BT-NZVI	B-BT-NZVI
BET (m^2/g)	1.3851	21.2709
pore volume (cm3/g)	0.000794	0.044451
Pore size (nm)	2.29256	8.35910
Langmuir surface area (m^2/g)	2.8372	31.7776

III. Adsorption studies of of Eriochrome blue-black B

1) The batch processes

The effect of BT-NZVI, B-BT-NZVI(adsorbent) concentration on the removal of Eriochrome blue-black B dye was examined by using the various NZVI concentrations from 0.5 g/L to 2 g/L. The batch processes were done for 180 min under fixed pH condition (2.5) with constant dye dose of 0.5 g/L stirred at 200 rpm at room temperature. At regular time intervals the samples were withdrawn, filtered by filter syringe to separate the dye solution from BT-NZVI or B-BT-NZVI, and estimated for the removal efficiencies. As can be observed in Figure 9, the removal rate of Eriochrome blue-black B was enhanced by increasing the NZVI concentration from 0.5 to 2 g/L. The main reason for this enhancement in the removal efficiencies is due to more surface sites ready to reacting with reactive dye to accelerate its removal rate [22] As well as the number of free electron producing active sites was increased with the amount of iron powder, leading to an improvement of the removal efficiency [23] according to the following reactions:

$$\mathrm{Fe0 \rightarrow Fe2+ + 2e\text{-}....\ (1)}$$

$$\mathrm{Fe0 + 2H2O \rightarrow Fe2+ + H2 + 2OH\text{-}...(2)}$$

$$\mathrm{2Fe0 + O2 + 2H2O \rightarrow 2Fe2+ + 4OH\text{-}...\ (3)}$$

$$\mathrm{2Fe0 \rightarrow 2Fe3+ + 6e\text{-}...\ (4)}$$

$$\mathrm{Fe2+ + 1/4O2+ 2.5H2O \rightarrow Fe(OH)3\ (s) + 2H+...\ (5)}$$

For example, the decolorization efficiency catalyzed BT-NZVI, B-BT-NZVI was increased from (14%, 42%) to (48%, 68%) at 180 min of batch processes when the NZVI concentration increased from 0.5 g/L to 2 g/L respectively and the resulted adsorption isotherm of this batch experiment was displyed in Table 2.

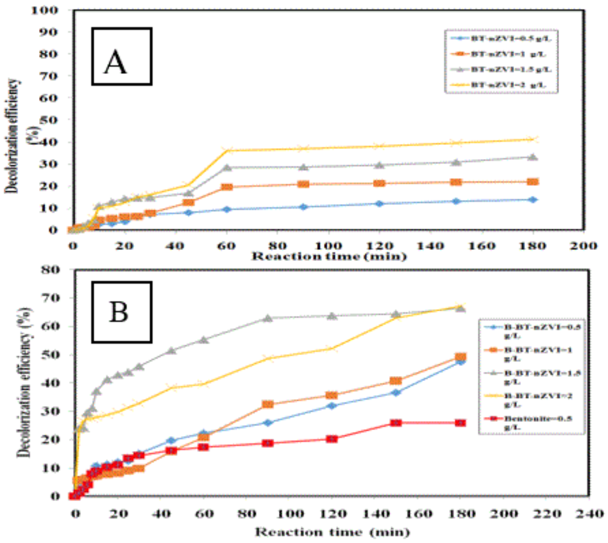

Figure 9: Effect of adsorption on the removal efficiency of Eriochrome blue-black Bdye, A)BT-NZVI, B)B-BT-NZVI

TABLE II: Decolorization efficiency at varying NZVI dosages Experimental conditions: [EBB] = 0.05 mM, pH=2.5, and room temperature

NZVI type	NZVI (g/L)	DE, % after 180 min	Ce (mg/L)	qe (mg/g)
BT-NZVI	0.5	14	71.846	18.307
	1	22	64.486	16.713
	1.5	33.2	62.241	16.547
	2	42	55.381	15.591
B-BT-NZVI	0.5	48	67.480	35.419
	1	49.3	53.884	28.315
	1.5	66.3	38.417	24.608
	2	68	33.303	22.248

2) The adsorption isotherm processes

were done for 180 min under fixed pH condition (2.5) with constant dye dose of 0.5 g/L at room temperature appears in Figure 10 and 11. In the Table 3 the amount of qmax, KF, KL, n and the correlation coefficients for Freundlich and Langmuir are given. Based on the correlation coefficients; equation Freundlich performs a better fit of data than Langmuir for GT-NZVI and B-GT-NZVI.

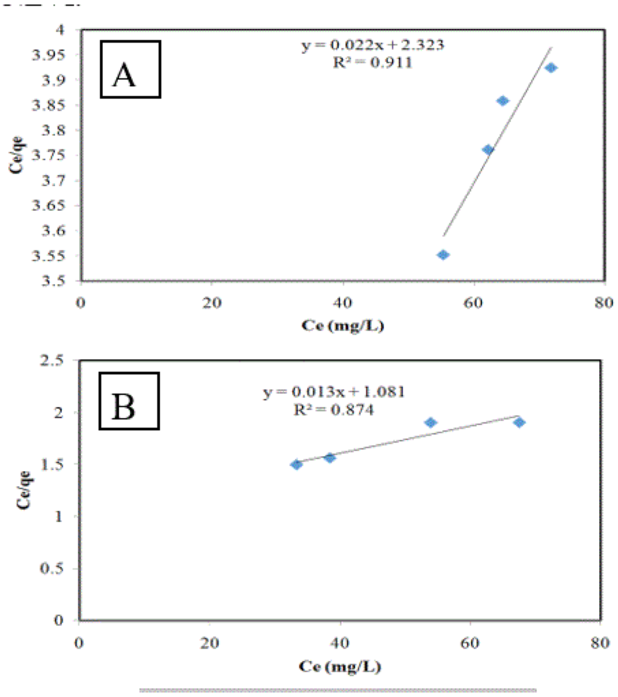

Figure 10: Langmuir adsorption isotherm of Eriochrome blue-black Bdye adsorption onto A)BT-NZVI,B) B-BT-NZVI

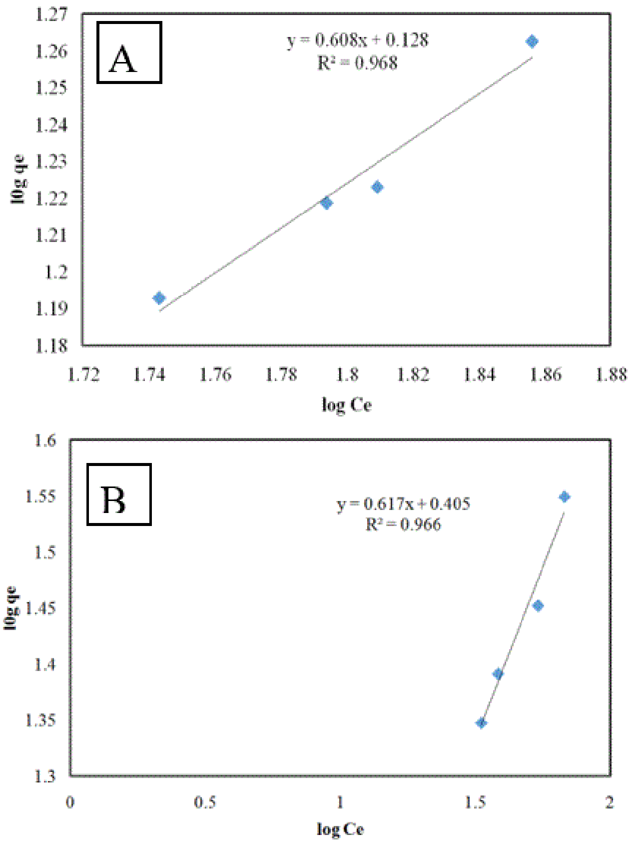

Figure 11: Freundlich adsorption isotherm of Eriochrome blue-black Bdye adsorption onto A)BT-NZVI,B) B-BT-NZVI

TABLE III: Adsorption parameters for of Eriochrome blue-black Bdye onto BT-NZVI, B-BT-NZVI

Group no.	Beam designation	shear cracking load (kN)	Ultimate load (kN)
BT-NZVI	Langmuir	$q_{max.}$(mg/g)	45.45
		K_L	0.073
		R^2	0.911
	Freundlich	K_F	1.34
		n	1.64
		R^2	0.968
B-BT-NZVI	Langmuir	$q_{max.}$(mg/g)	76.92
		K_L	0.014
		R^2	0.874
	Freundlich	K_F	2.54
		n	1.62
		R^2	0.966

3) Adsorption kinetics

The kinetics data gained by utilizing the pseudo-first and second model are shown in Figure 12. The parameters k, qe and R2 were calculated from the slope and intersect of linearization from the equations (3) and (4); k, qe and R2 of each model are shown in Table 4. The R2 of the pseudo-first-order model for Bentonite, B-BT-NZVI was higher than those of the pseudo-second-order model for the same materials; for BT-NZVI the R2 of the pseudo-second-order model higher than those of the pseudo-first-order model and the calculated qe was much close to the qe, exp (experimental values).

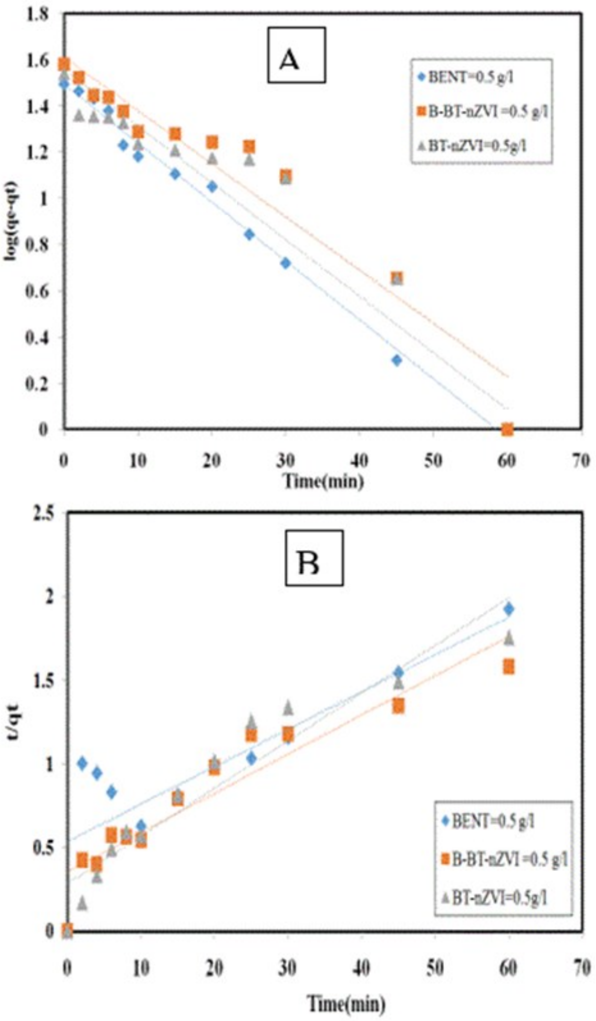

Figure 12: A) The plots of pseudo-first-order kinetics for the adsorption of Eriochrome blue-black B dye onto bentonite, B-BT-NZVI and BT-NZVI; B)The plots of pseudo-second-order kinetics for the adsorption of Eriochrome blue-black B dye onto bentonite, B-BT-NZVI and BT-NZVI. Experimental condition: [NZVI] = 0.5 g/L, [EBB]= 0.05M, pH=2.5 and room temperature

TABLE IV: The kinetics parameters (pseudo-first-order and pseudo-second-order) for the adsorption of Eriochrome blue-black B dye onto BT-NZVI, B-BT-NZVI at specific dosages. Experimental conditions: [EBB] = 0.05 mM, pH = 2.5 and room temperature

NZVI TYPE	NZVI (g/L)	qe,exp(mgg^{-1})	Pseudo-first-order			Pseudo-second-order		
			Qe (mgg^{-1})	k_1 (min^1)	R^2	qe (mgg^1)	k_2 (M^{-1} min^{-1})	R^2
Bentonite	0.5	31.18	31.26	0.057	0.992	19.3	0.0009	0.746
B-BT-NZVI	0.5	37.91	40.73	0.052	0.928	47.4	0.0014	0.882
BT-NZVI	0.5	34.19	36.05	0.055	0.862	35.71	0.0027	0.903

4. CONCLUSIONS

The traditional methods of developing Nanoparticles are costly and produce toxic products, so the need to reduce the risk of toxicity in the environment from the different chemicals used in chemical and physical methods is recommended. The alternative approach found to develop Nanoparticles is "green synthesis". As an outcome of this study, green Synthesis of Iron Nanoparticles by using a non-toxic and cost-effective reducing agent (black tea and black tea support on bentonite) and less time consuming, was a successful method to remove the blue dye from the residues of the textile- factory, The decolorization efficiency catalyzed BT-NZVI, B-BT-NZVI was increased to (42%, 68%) in the operation condition.

References

[1] A. Pokharia, & S. S. Ahluwalia, "Biodecolorization and degradation of xenobiotic azo dye-Basic Red 46 by Staphylococcus epidermidis MTCC 1062," Int. J. Res. Biosciences, 5, 2, 10-23, 2016.

[2] E. S. Önal, T. Yatkin, M. Ergüt, & A. Özer, "Green synthesis of iron nanoparticles by aqueous extract of eriobotrya japonica leaves as a heterogeneous fenton-like catalyst: degradation of basic red 46, 2017.

[3] S. Ding, Z. Li, & R. Wang, "Overview of dyeing wastewater treatment technology," Water ResourProt, 26, 73-78, 2010.

[4] N. Rahman, Z. Abedin, Z., & M. A. Hossain, "Rapid degradation of azo dyes using nano-scale zero valent iron," American Journal of Environmental Sciences, 10, 2, 157, 2014.

[5] F. M. D. Chequer, D.J. Dorta and D.P. de Oliveira, "Azo Dyes and their metabolites: does the discharge of the azo dye into water bodies represent human and ecological risks?," In: Advances in Treating Textile Effluent, Hauser, P. (Ed.), ISBN-10: 978-953-307-704-8, pp: 27-48, 2011.

[6] M. T. Yagub, T. K. Sen, S. Afroze, & H. M. Ang, "Dye and its removal from aqueous solution by adsorption: a review," Advances in Colloid and Interface Science, 209, 172-184, 2014.

[7] P. Prema, S. Thangapandian, M. Selvarani, S. Subharanjani, & C. Amutha, "Color removal efficiency of dyes using nanozerovalent iron treatment," Toxicological & Environmental Chemistry, 93, 10, 1908-1917, 2011.

[8] K. B. Tan, M. Vakili, B. A. Horri, P. E. Poh, A. Z. Abdullah, & B. Salamatinia, "Adsorption of dyes by nanomaterials: recent developments and adsorption mechanisms," Separation and Purification Technology, 150, 229-242, 2015.

[9] J. Galán, A. Rodríguez, J. M. Gómez, S. J. Allen, & G. M. Walker, "Reactive dye adsorption onto a novel mesoporous carbon," Chemical Engineering Journal, 219, 62-68, 2013.

[10] Y. P. Sun, X.-Q. Li, J. Cao, W.-X. Zhang, H.P. Wang, "Characterization of zerovalent iron nanoparticles," Adv. Colloid Interface Sci. 120, 47–56, 2006.

[11] X. Wang, J. Yang, & M. Zhu, "Effects of PMMA/anisole hybrid coatings on discoloration performance of nanozerovalent iron toward organic dyes," Journal of the Taiwan Institute of Chemical Engineers, 45, 3, 937-946, 2014.

[12] A. Ghadimi, R. Saidur, and H. S. C. Metselaar, "A review of nanofluid stability properties and characterization in stationary conditions," International Journal of Heat and Mass Transfer, 54, 17-18, 4051–4068, 2011.

[13] S. Wang, & H. Wu, "Environmental-benign utilisation of fly ash as low-cost adsorbents," Journal of Hazardous Materials, 136, 3, 482-501, 2006.

[14] O. G. Apul, Q. Wang, Y. Zhou, & T. Karanfil, "Adsorption of aromatic organic contaminants by graphenenanosheets: Comparison with carbon nanotubes and activated carbon," Water Research, 47, 4, 1648-1654, 2013.

[15] T. A. Kurniawan, & W. H. Lo, "Removal of refractory compounds from stabilized landfill leachate using an integrated H_2O_2 oxidation and granular activated carbon (GAC) adsorption treatment," Water Research, 43, 16, 4079-4091, 2009.

[16] S. Agarwal, H. Sadegh, M. Monajjemi, A. S. Hamdy, G. A. Ali, A. O. Memar, & V. K. Gupta, "Efficient removal of toxic bromothymol blue and methylene blue from wastewater by polyvinyl alcohol," Journal of Molecular Liquids, 218, 191-197, 2016.

[17] L. Wang, J. Li, Q. Jiang, & L. Zhao, "Water-soluble Fe_3O_4 nanoparticles with high solubility for removal of heavy-metal ions from waste water," Dalton Transactions, 41, 15, 4544-4551, 2012.

[18] H. H. Abdel Ghafar, G. A. Ali, O. A. Fouad, & S. A. Makhlouf, "Enhancement of adsorption efficiency of methylene blue on Co3O4/SiO2 nanocomposite," Desalination and Water Treatment, 53, 11, 2980-2989, 2015.

[19] L. Huang, F. Luo, Z. Chen, M. Megharaj, & R. Naidu, "Green synthesized conditions impacting on the reactivity of Fe NPs for the degradation of malachite green," Spectrochim. Acta A, 137, 154-159, 2015.

[20] J. D. Cloqston, A. K. Patri, “Zeta potential measurement,” Methods Mol. Biol. 69763-70, 2011.

[21] Nicoleta Platon, ANA-Maria ROSU, Vasilica Alisa ARUS, “Denisa Ileana Nistor, IlieSiminiceanu,” Journal of Engineering Studies and Research, 19, 4, 52-58, 2013.

[22] N. Ahuja, A. Chopra, & A. A. Ansari, “Removal of colour from aqueous solutions by using zero valent iron nanoparticles,” Journal of Environmental Science, Toxicology and Food Technology (IOSR-JESTFT), 10, 1, 4-14, 2016.