



Synthesis, antibacterial activity and adsorption studies of Bentonite-iron nanoparticles in the removal of methyl blue dye

K Shahul Hameed, G Jesline Mary¹, M Jannathul Firdhouse* & S Sivakumar

Department of Chemistry, Hajee Karutha Rowther Howdia College, Uthamapalayam, Tamil Nadu, India

¹Department of Chemistry & Physics, Nadar Saraswathi College of arts and science, Vadaputhupatti, Tamil Nadu, India

E-mail: kfirdhouse@gmail.com

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Green synthesis of bentonite-iron nanoparticles (Be-FeNPs) has been carried out using the leaf extract of *Helicteres isora* and its antibacterial and adsorption capacity for the removal of Methyl Blue (MB) dye have been also studied. The prepared Be-FeNPs and iron nanoparticles (FeNPs) are characterized by UV-visible, FTIR spectroscopic techniques and SEM analysis. The antibacterial activity of Be-FeNPs show good zone of inhibition against *E. coli* and *S. aureus*. Further the prepared composite (Be-FeNPs) and bentonite are used as adsorbents for the removal of Methyl Blue (MB) dye in aqueous solution under various experiment parameters like initial concentration, contact time and pH. The optimum initial pH, adsorbent concentration and time were determined to be 8.1, 45°C, and 100 ppm, 80 min for MB adsorption on to Be-FeNPs. The experimental data for MB adsorption fits well to the Freundlich and Langmuir isotherm models. The kinetic equations like Natarajan-Khalaf, Bhattacharya-Venkobachar and Lagergren equations were found to be applicable. The surface morphology of the Be-FeNPs before and after adsorption of dye revealed that it can be used as an excellent adsorbent for dye removal from dilute industrial effluents.

Keywords: Adsorption, Bentonite, Antibacterial, FTIR, Iron nanoparticles, SEM

Water is the most important in human life and this utility is use in many industries such as food processing, metal producing industry, paper and wood process, chemicals, oil and gases, textile industries, laundry services and other industries. Most of the industries just release the wastewater to the drain or river and the wastewater can induces water pollution. The unique properties of water which make it universal solvent and by virtue of this property have got a much greater tendency to get polluted. Water can be regarded as polluted when it changes its quality or composition either naturally or as a result of human activities, thus becoming not suitable for drinking, domestic, agricultural, industrial, recreational, wildlife and other uses for which it would have been otherwise suitable in its natural or unmodified state. The textile industries consume large volumes of water and dye chemicals for wet processing of textiles. The chemical reagents used are very diverse in chemical composition, ranging from inorganic compounds to polymers and organic products¹⁻³.

Normally colour is visible at a dye concentration higher than 1 mgL⁻¹ and an average concentration of 300 mg L⁻¹ has been reported in effluents from textile

manufacturing processes^{4,5}. Over 7×10⁵ ton and approximately 10,000 different dyes and pigments are produced annually world-wide, about 10% of which may be found in wastewater⁶. Methyl blue (MB) is main basic dye commonly used for colouring paper, temporary hair colorant, dyeing, leather dyeing and other medical purpose^{7,8}. Powder and granular forms of iron have been applied as reactive materials in permeable reactive barriers (PRB) for the removal of different pollutants. Iron nanoparticles established an excellent removal capability towards various organic and inorganic aqueous pollutants by increasing the surface to volume ratios. By incorporating iron nanoparticles specifically with clay minerals might be helpful in overcoming problems such as the agglomeration and the zero point of charge of iron nanoparticles^{9,10}.

The conventional methods for treating dye containing wastewaters are electrochemical treatment, coagulation and flocculation, liquid-liquid extraction and adsorption. In recent years, special emphasis on the preparation of low-cost materials from agricultural by-products has been the growing interest in concerning treatment of wastewater. Researchers have

studied the production of low-cost materials from palm-tree cobs¹¹, plum kernels^{12,13}, cassava peel¹⁴, bagasse¹⁵, jute fibre¹⁶, coconut husk¹⁷, rattan sawdust¹⁸, seed shells¹⁹, cocoa shell²⁰ and Eucalyptus globules bark²¹.

In the present work, the iron nanoparticles were synthesized using *H. isora* leaves extract and incorporated into the bentonite. The prepared Be-FeNPs were characterized by UV-visible, FTIR spectroscopic techniques and SEM analysis. The antibacterial activity and adsorption studies were carried out for the Be-FeNPs nanocomposite and their adsorption capacity was also compared with bentonite.

Experimental Section

Preparation of plant extract

Fresh leaves of *Helicteres isora* was collected from Yercaud, Salem dried under home shade and powdered. The plant powder (2 g) was weighed and boiled with distilled water (100 mL) for 15 min, and then filtered. The prepared extract is used for further process.

Preparation of iron nanoparticles (FeNPs)

Iron (III) chloride (1.07 g) was dissolved in 30 mL of distilled water. The plant extract (50 mL) is mixed with 30 mL of iron solution and stirred continuously for 1 h. After 1h the colour change was observed.

Preparation of Bentonite iron nanocomposite (Be-FeNPs)

Bentonite (22g) was added with 75 mL of prepared iron nanoparticles and doubly distilled water (100 mL) was added and stirred vigorously for 6 h. Thus, the obtained substance was dried in vacuum at 110°C. The powder form obtained is used for further adsorption process¹.

Characterization of the Be-FeNPs

UV-visible spectrum and FTIR of Be-FeNPs were recorded using Double Beam Spectrophotometer-2202 (Sytronics) and FTIR 8400S (Shimadzu), respectively. Scanning Electron Microscope (TESCAN MIRA3) was used to examine the morphology of the FeNPs and Be-FeNPs. The EDAX sometimes called energy dispersive X-ray analysis is an analytical technique used for the elemental analysis or chemical characterization of a sample.

Applications of the synthesized Bentonite iron nanocomposite

The prepared bentonite iron nanocomposite (Be-FeNPs) was analysed for the antibacterial activity and also in the removal of Methyl Blue dye.

Antibacterial activity

Antibacterial activity was determined by agar well diffusion method. In this method, wells of 8 mm diameter were punched into the agar medium and filled with 100 μ L (10 mg/mL) of Be-FeNPs and allowed to diffuse at room temperature for 2 h. The plates were then incubated in the upright position at 37° for 24 h. Wells containing the same volume of DMSO (10%), *E.coli* and *S.aureus* served as negative controls. After incubation, the diameters of the zones of growth inhibition were measured in mm.

Adsorption studies

The various experiments in this adsorption study were carried out by employing the batch adsorption technique. In order to find out optimum experimental conditions for the removal of the dye Methyl blue by Be-FeNPs and bentonite adsorbents, various adsorption experimental parameters were studied as follows: Initial concentration of the dye; Contact time and Initial pH

Preparation of standard curve

A stock solution containing 1000ppm of Methyl blue dye was prepared by dissolving 1g of it in 1 L distilled water. Solutions of various concentrations such as 5, 10, 15, 20, 25, 30, 35, 40, and 45 ppm were prepared separately.

Results and Discussion

The leaf extract of *Helicteres isora* had a brown colour and showed absorption at 290 nm. It indicates that the leaf extract of *H. isora* had free phytochemicals like alkaloids, carbohydrates, polyphenols, saponins, proteins, amino acids and flavonoids²². After the addition of leaf extract of *H. isora* to ferric solution, a black-coloured colloidal solution was formed.

The UV-visible spectrum of the black coloured colloidal solution shows a strong absorption peak at 320 nm confirms the formation of FeNPs. During the synthesis of FeNPs, the reduction of Fe³⁺ ions to Fe⁰ is indicated by the change in colour due to excitation of electrons.

Figure 1 depicts the UV-visible spectra of before and after adsorption of Be-FeNPs, respectively. The SPR band of FeNPs and bentonite shifted to the visible region confirms the formation of Be-FeNPs nanocomposite [Fig. 1(a)]. The broad band obtained in Fig. 1(b) and the disappearance of some of the bands in Fig. 1(a) clearly shows that the adsorption of methyl blue dye onto the Be-FeNPs. This may be due to the binding of the MB dye to the surface of the prepared adsorbent.

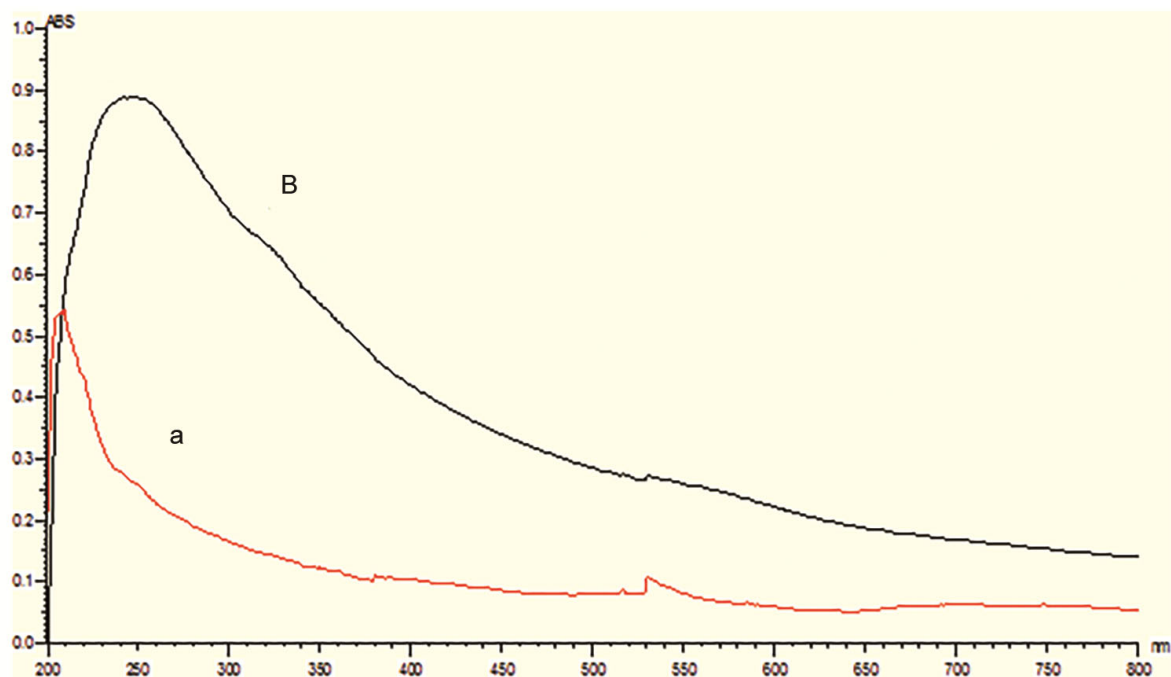


Fig. 1 — UV-visible spectra of before (a) and after (b) adsorption of Be-FeNPs

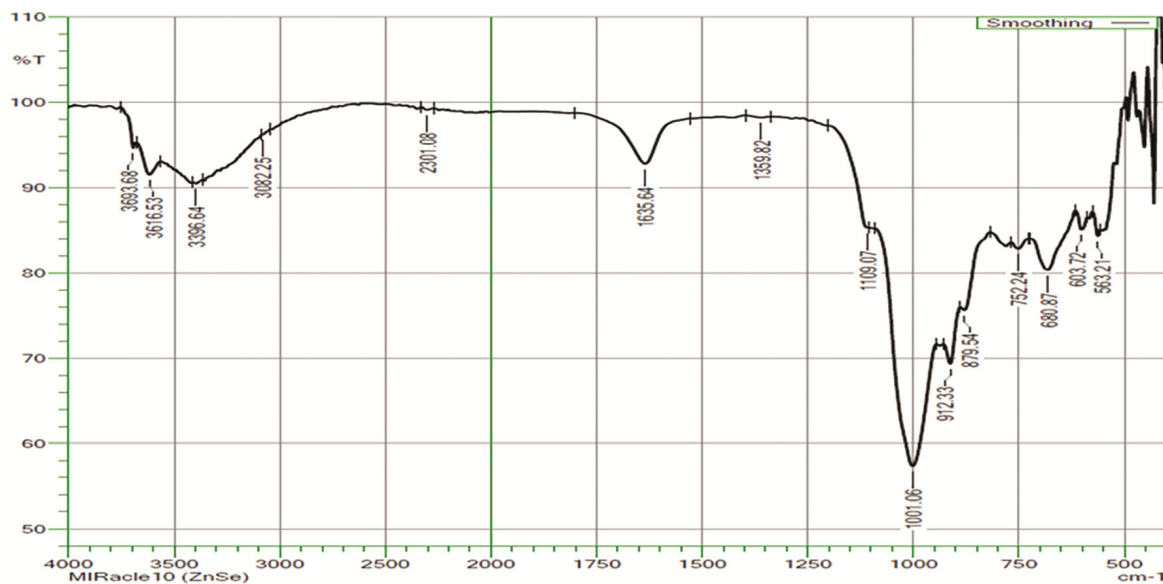


Fig. 2 — FTIR spectra of Be-FeNPs

FTIR spectroscopy for Be-FeNPs

FTIR spectra (Fig. 2) shows that the bands at 3616 and 3396 cm^{-1} were correspond to the O–H vibration for Be-FeNPs. The bands at 1001 and 1109 cm^{-1} attributed to Si–O stretching vibration. In addition, the band at 1635 cm^{-1} for Be-FeNPs may be related to the C=C ring stretching in polyphenols, indicating the formation of the iron–polyphenols co

SEM analysis of Be-FeNPs

Figure 3 revealed the formation of monodispersed FeNPs of size below 10 nm which is embedded onto the bentonite. The scanning electron micrographs clearly revealed the surface texture and morphology of the Be-FeNPs adsorbent at different magnifications. Figure 4 shows that Be-FeNPs tend to possess smooth surface and uneven in size. The SEM micrographs of

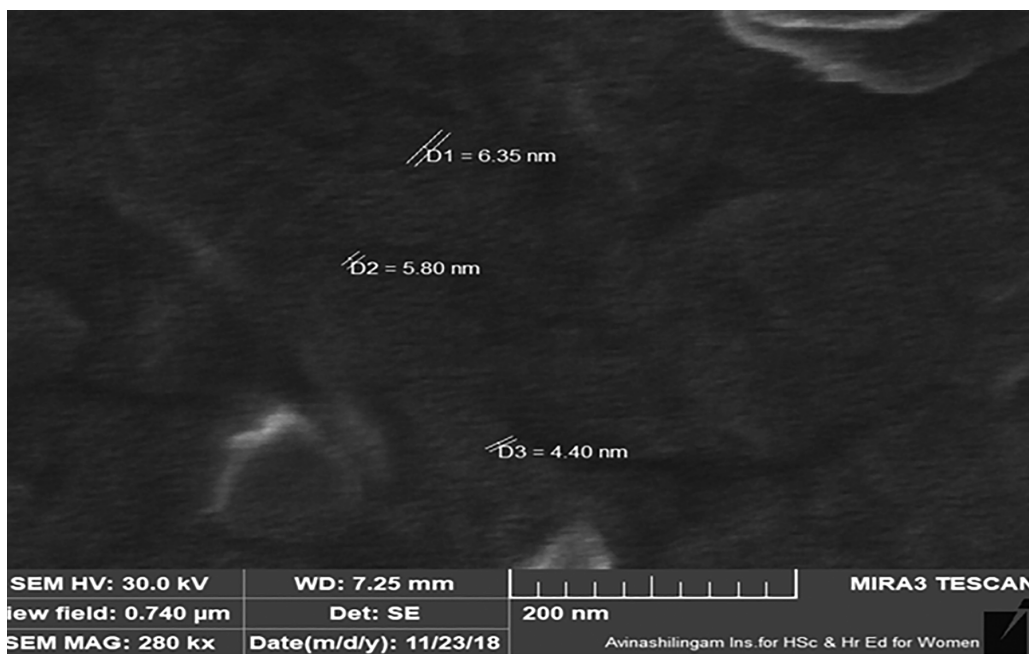


Fig. 3 — SEM micrographs of synthesized FeNPs

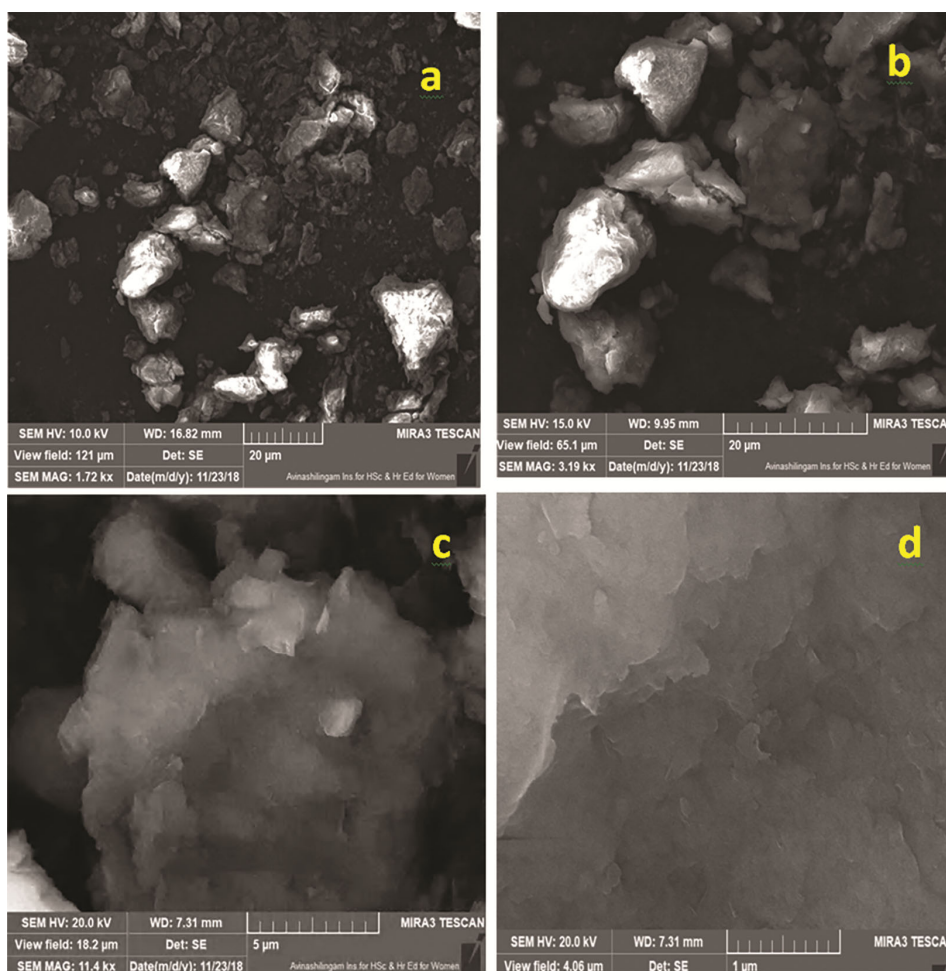


Fig. 4 — SEM micrographs of Be-FeNPs before adsorption at different magnifications

Be-FeNPs after adsorption revealed the agglomeration of particles and rough surface, which may be due to the binding of particles i.e. MB dye onto the Be-FeNPs adsorbent (Fig. 5).

EDAX analysis of Be-FeNPs

Chemical compositions of Be-FeNPs before and after adsorption were analyzed by Energy Dispersive X-ray analyzer (EDAX). The chemical formula of bentonite is $[(\text{Mg,Ca})_x\text{Al}_2\text{O}_3.y\text{SiO}_2.n\text{H}_2\text{O}]$ which indicates the presence of elements like C, O, Na, Ca, Si, and Al. The

EDAX spectrum clearly shows the value composition of C, O, Na, Si and Al is 14.43, 46.19, 2.36, 17.15 and 9.70% respectively, in addition to this 5.89% of Fe confirms the formation of Be-FeNPs [Fig. 6(a)]. The percentage weights of the elements present in the Be-FeNPs before and after adsorption are given in table 1.

The EDAX spectrum of Be-FeNPs [Fig. 6(b)] after adsorption clearly revealed that the percentage weights of some elements like C, O and Al were increased to 19.93, 56.99 and 13.92% compared to the composition

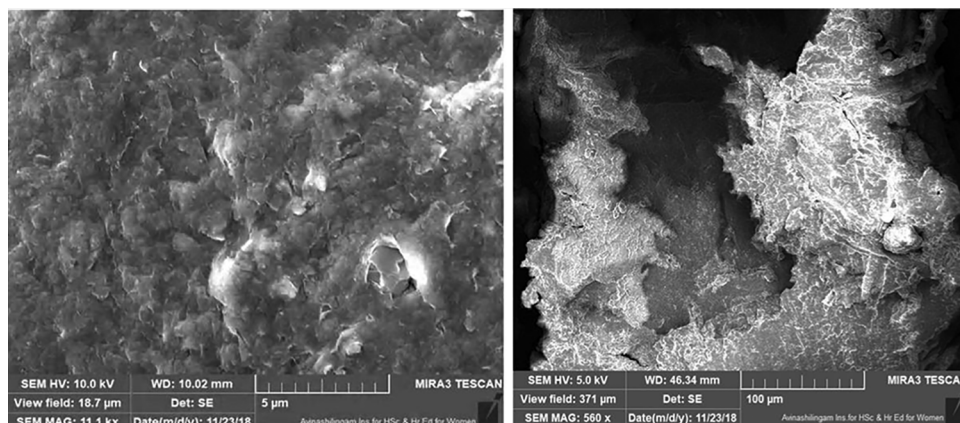


Fig. 5 — SEM micrographs of Be-FeNPs after adsorption at different magnifications

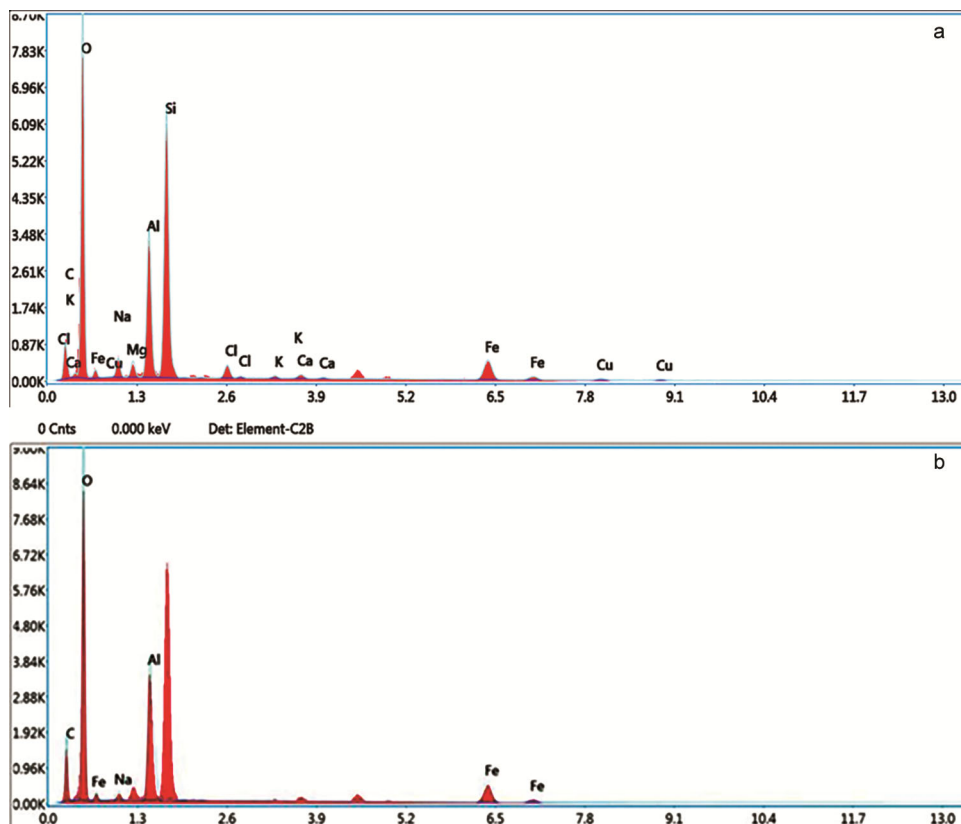


Fig. 6 — (a-b) EDAX analysis of Be-FeNPs; (b) – EDAX analysis of Be-FeNPs after adsorption

of the nanocomposite before adsorption (Table 1). This may be due to the adsorption of the MB dye onto the Be-FeNPs adsorbent.

Antibacterial activity of the prepared Be-FeNPs

The results of the antibacterial activity of the synthesized Be-FeNPs against *E.coli* and *S. aureus* showed good zones of inhibition. Be-FeNPs possessed high zone of inhibition viz. 20 mm and 18 mm against *E.coli* and *S.aureus*, respectively (Table 2). The good antibacterial activity of the synthesized Be-FeNPs may also use as an adsorbent for the removal of the aforesaid bacteria.

Adsorption studies of Be-FeNPs and Bentonite onto MB dye

Effect of initial concentration

Studies on the removal of MB dye by Be-FeNPs and bentonite were carried out at different initial concentration of the dye at fixed dose of Be-FeNPs and bentonite (50 mg for Be-FeNPs and 100mg for bentonite) and constant time (30 min). The percentage removal of dye was found to increase with decrease of initial concentration of dye [Fig. 7(a)]. At an optimum initial concentration of dye 100ppm for Be-FeNPs and 150 ppm for bentonite of MB. For lower concentrations, the total removal was caused by the large number of vacant sites available for the lower number of dye molecules, therefore, the thrust of the concentration gradient between adsorbate in solution and adsorbent is increased^{23,24}.

Table 1 — Elemental analysis of Be-FeNPs before and after adsorption

Be-FeNPs			Be-FeNPs after adsorption		
Element	Weight %	Atomic %	Element	Weight %	Atomic %
CK	14.73	22.67	CK	19.93	27.95
OK	46.19	53.39	OK	56.99	59.98
Nak	2.36	1.90	NaK	1.44	1.06
MgK	1.21	0.92	AIK	13.92	8.69
AIK	9.70	6.65	FeK	7.72	2.33
SiK	17.15	11.30			
CIK	1.21	0.63			
KK	0.29	0.14			
CaK	0.52	0.24			
FeK	5.85	1.94			
CuK	0.80	0.23			

Table 2 — Antibacterial activity of the prepared Be-FeNPs

Nanocomposite	Bacteria	Zone of inhibition (mm)
Be-FeNPs	<i>E.Coli (Gram Negative)</i>	20
	<i>S. aureus (Gram positive)</i>	18

Effect of contact time

In the adsorption system, contact time plays a vital role irrespective of the other experimental parameters affecting the adsorption kinetics. In order to study the kinetics and dynamics of adsorption of MB dye on Be-FeNPs and bentonite, adsorption experiments were carried out at different contact time (10-80 min) at constant optimum initial concentration of dye (100ppm for Be-FeNPs and 150ppm for bentonite) with 1 gL⁻¹ of Be-FeNPs and bentonite Fig. 7 (b).

Effect of initial pH

The initial pH plays a vital role in the adsorption of dye MB on Be-FeNPs and Bentonite. The effect of initial pH of dye solution was studied at different pH values (range from pH 4.9 to 8.1 for Be-FeNPs and

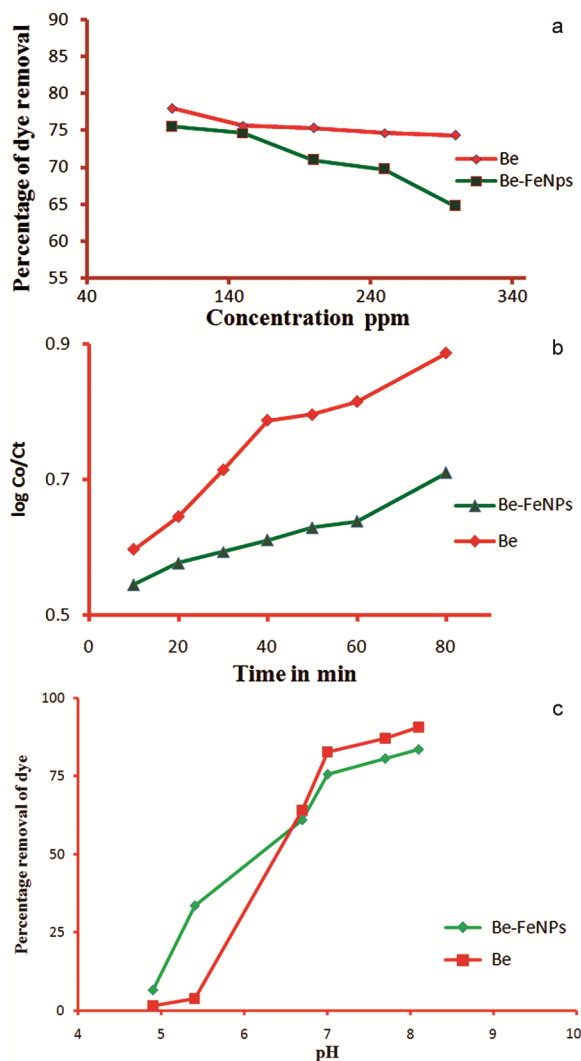


Fig. 7 — (a) Effect of initial concentration on the percentage removal of dye; (b) Effect of contact time on the percentage removal of dye Adsorption isotherm and (c) Effect of pH on the percentage removal of dye

4.9 to 8.5 for bentonite). The percentage removal was found to increase with increase in pH for adsorption of dye MB on Be-FeNPs and Bentonite [Fig. 7(c)]. The adsorptions of this dye on Be-FeNPs and bentonite were found to be highly pH dependent.

Figure 7(c) represents the effect of pH on dye uptake using Be-FeNPs and bentonite adsorbent. In the case of MB, as pH increased from 4 to 10, uptake of dye increased from 6.50 % to 83.50% for Be-FeNPs and 1.6% to 90.66% for bentonite. It is evident that percentage removal of dye was increased consistently with pH .

Adsorption isotherm

Adsorption isotherms are essential for the explanation of how adsorbate will cooperate with an adsorbent and are serious in optimizing the use of adsorbent. Two legendary isotherm equations, the Langmuir, Freundlich isotherm, were employed for additional elucidation of the obtained adsorption data^{25,26}. The Langmuir adsorption isotherm has been successfully used to explain the adsorption of dyes from aqueous solutions¹⁴. The equilibrium data for the removal of MB dye on Be-FeNPs and bentonite were used.

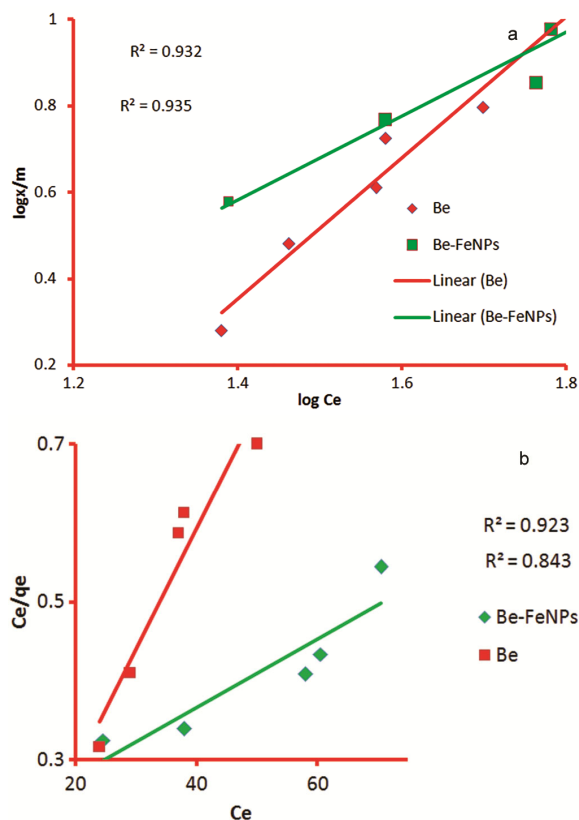


Fig. 8 — (a) Freundlich adsorption isotherm; (b) Langmuir Adsorption Isotherm

$$\text{Freundlich isotherm: } \log(x/m) = \log K + (1/n)\log C_e \quad \dots (1)$$

$$\text{Langmuir isotherm: } (C_e/q_e) = (1/Q_0b) + (C_e/Q_0) \quad \dots (2)$$

The data obtained from the adsorption experiments were fitted into Freundlich and Langmuir isotherms respectively by plotting $\log x/m$ against $\log C_e$ and (C_e/q_e) against C_e , the two isotherm plots are shown in Fig. 8 (a) and (b). The values are correlated with one another. The results indicated the applicability of these adsorption isotherms for the removal of dye MB by Be-FeNPs and bentonite. The 'r' values computed along with isotherm constants are given in Table 3.

Kinetics and Dynamics of adsorption of MB on Be-FeNPs and bentonite

The optimum equilibrium contact time is fixed as 30 min at which the maximum extent of removal of dye occurs. The following kinetics equations were employed to study the kinetics and dynamics of adsorption of dye under the correlation of first order kinetics.

$$\text{Natarajan – Khalaf equation: } k = (2.303/t) \log (C_0/C_t) \quad \dots (4)$$

$$\text{Lagergren equation: } \log (q_e - q_t) = \log q_e - (k/2.303) \quad \dots (5)$$

$$\text{Bhattacharya – Venkobachar equation: } \log [1 - U(t)] = -(k/2.303) \quad \dots (6)$$

$$\text{Where, } U(t) = [(C_0 - C_t) / (C_0 - C_e)]$$

C_0 = Initial concentration of dye solution (in ppm)

C_t = Concentration of dye solution at various time (in ppm)

K = First order rate constant for adsorption of dyes (in min^{-1})

Table 3 — Correlation analysis for the adsorption of MB dye on Be-FeNPs and Bentonite

Parameters	MB on Be-FeNPs	MB on Bentonite
Freundlich isotherm		
Slope 1/n	0.8978	0.9024
Intercept	0.6658	0.5553
Correlation Coefficient(r)	0.9748	0.9827
Langmuir isotherm		
Slope(1/Q ₀)	0.0043	0.0151
Intercept (1/Q ₀ b)	0.1901	0.0261
Correlation Coefficient(r)	0.9207	0.8965
Q ₀ (mg g ⁻¹)	230.88	64.95
b(gL ⁻¹)	0.0228	0.5894
R _L	0.4673	0.0167

q_e = Amount of dye adsorbed per unit mass of adsorbent (gL^{-1})

Q_t = Amount of dye adsorbed per unit mass of adsorbent (gL^{-1})

C_e = Concentration at equilibrium time

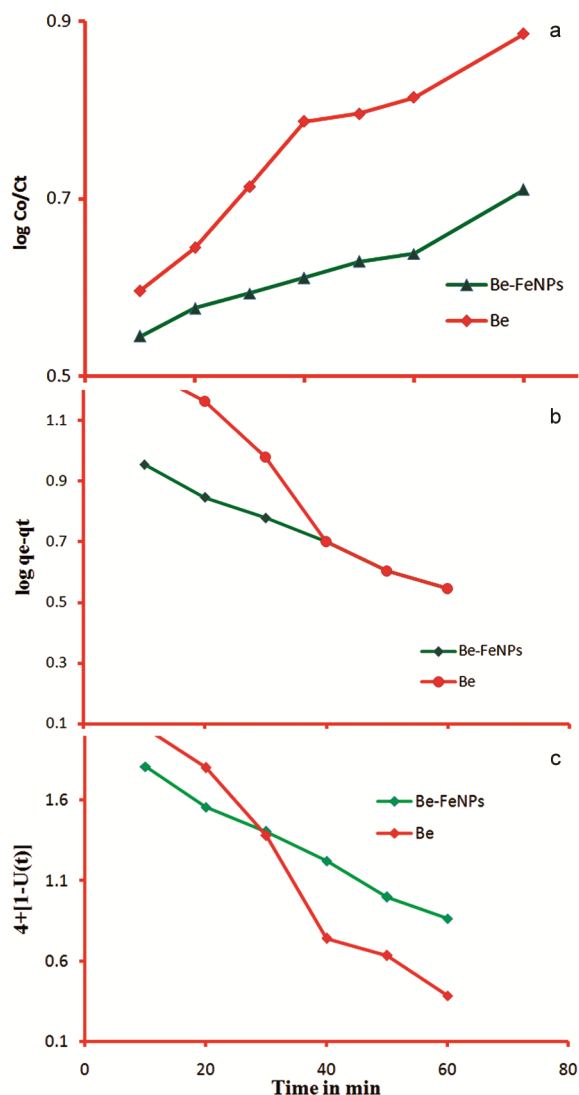


Fig. 9 — (a) Natarajan Khalafplot; (b) Lagergren plot and (c) Bhattacharya – Venkobachar Plot

Table 4 — Kinetics and dynamics of adsorption of Methyl Blue dye on Be-FeNPs and bentonite

S. No	Parameters	MB on Be-FeNPs	MB on Bentonite clay
Natarajan Khalaf equation			
1.	Correlation Coefficient(r)	0.9868	0.9707
Lagergren equation			
2.	Correlation Coefficient(r)	0.9452	0.9764
Bhattacharya-Venkobachar equation			
3.	Correlation Coefficient (r)	0.9456	0.9813

The values of $\log (C_0 - C_t)$, $\log (q_e - q_t)$ and $\log [1-U(t)]$ were plotted against time and the kinetics plots are found to be linear [Fig. 9(a-c)]. These values are also noted to be linearly correlated to each other as evidenced from the values of correlation coefficients (r values) close to unity (Table 3 and 4). The results indicate the applicability of these kinetics equation and first order nature of adsorption kinetics.

Conclusion

The present investigation deals with synthesis and characterization of FeNPs and Be-FeNPs. The synthesized Be-FeNPs was analysed for its antibacterial activity and adsorption studies on the removal of dye MB and compared with commercially available Bentonite clay. The UV-visible spectrum of the black coloured colloidal solution shows a strong absorption peak at 320 nm confirms the formation of FeNPs. The SPR band of FeNPs and bentonite shifted to the visible region confirms the formation of Be-FeNPs nanocomposite. The results of the antibacterial activity of the synthesized Be-FeNPs against *E.coli* and *S. aureus* showed good zones of inhibition. Be-FeNPs possessed high zone of inhibition viz. 20 mm and 18 mm against *E.coli* and *S. aureus*, respectively. The batch experiment conducted with the adsorption demonstrated that the Be-FeNPs adsorbent and bentonite exhibited the potential removal of methyl blue dye from aqueous solution.

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Conflict of interest

The authors declare no conflict of interest.

References

- Mishra G & Tripathy M, *Colourage*, 40 (1993) 35.
- Banatl M, Nigam P, Singh D & Marchant R, *Bioresour Technol*, 58 (1996) 217.
- Juang R S, Tseng R L, Wu F C & Lin S J, *J Environ Sci Health A*, 31 (1996) 325.
- Goncalves I, Gomes A, Bras R, Ferra M I A & Amorim M T P, *J Coloration Technol*, 116 (2000) 393.
- Neill C, Freda R H, Dennis L H, Nidia D L & Helena M P, *J Chem Technol Biotechnol*, 74 (1999) 1009.
- Deveci T, Unyayar A & Mazmanci M A, *J Mol Catal B:Enzyme*, 30 (2004) 25.
- Hameed B H, Din A T M & Ahmad A L, *J Hazard Mater*, 141 (2007) 819.
- Coşkun R, Yıldız A & Delibaş A, *J Mater Environ Sci*, 8 (2017) 398.

- 9 Karabelli D, Uzum C, Shahwan T, Eroglu A E, Scott T, Hallam K R & Lieberwirth I, *Ind Eng Chem Res*, 47 (2008) 4758.
- 10 Li L, Fan M, Brown R C, Leeuwen J V, Wang J, Wang W, Song Y & Zhang P, *Crit Rev Environ Sci Technol*, 36 (2006) 405.
- 11 Avom J, Ketcha J, Noubactep C & Germain P, *Carbon*, 35(1997) 365.
- 12 Wu F, Tseng R & Juang R, *J Hazard Mater*, 69 (1999) 287.
- 13 Tseng R, *J Hazard Mater*, 147 (2007) 1020.
- 14 Schwantes D, Gonçalves A, Coelho G, Campagnolo M, Dragunski D, Tarley C, Miola A & Leismann E, *J Chem*, (2016) 1.
- 15 Ezeonuegbu B A, Machido D A, Whong C M Z, Japhet W S, Alexiou A, Elazab S T, Qusty N, Yaro C A & El-Saber Batiha G, *Biotechnol Rep*, 30 (2021) 00614.
- 16 Roy A, Chakraborty S, Kundu S, Adhikari B & Majumder S, *J Appl Polym Sci*, 129 (2013) 10.
- 17 Hasfalina C B M, Akinbile C O & Jun C X, *Bio Res*, 10 (2015) 2859.
- 18 Osma J, Saravia V, Toca-Herrera J & Rodriguez-Couto S, *J Hazard Mater*, 147 (2007) 900.
- 19 Rodríguez-Arellano G, Barajas-Fernández J, García-Alamilla R, Lagunes-Gálvez L M, Lara-Rivera A H & García-Alamilla P, *Materials*, 14 (2021) 2763.
- 20 Hameed B & El-Khaiary M I, *J Hazard Mater*, 159 (2008) 574.
- 21 Fabre E, Vale C, Pereira E & Silva C M, *Int J Mol Sci*, 20 (2019) 5973.
- 22 Kumar N & Singh A K, *Asian Pac J Trop Biomed*, 4 (2014) 22.
- 23 Igwegbe C A, Umembamalu C J, Osuagwu E U, Oba S N & Emembolu L N, *Eur J Sustain Dev Res*, 5 (2021) 0145.
- 24 AL-Tufaily M & Al-Qadi Z, *Babylon Univ Eng Sci J*, 24 (2016) 700.
- 25 Laysandra L, Sari M W M K, Soetaredjo F E, Foe K, Putro J N & Kurniawan A, *Heliyon*, 3 (2017) 00488.
- 26 Mousavi S A, Kamarehie B & Almasi A, *Biomass Conv Bioref*, (2021).