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Facile green synthesis of Fe_3O_4 nanoparticles using aqueous leaf extract of *Zanthoxylum armatum* DC. for efficient adsorption of methylene blue

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ABSTRACT

We report a facile and green route for the synthesis of superparamagnetic magnetite nanoparticles (Fe_3O_4 NPs) using aqueous leaf extract of *Zanthoxylum armatum* DC. for efficient adsorption of organic pollutant, methylene blue (MB). The phytochemicals present in the aqueous leaf extract *Zanthoxylum armatum* DC. are not only responsible for the formation of Fe_3O_4 NPs, but also act as capping agent for Fe_3O_4 NPs. The formation of Fe_3O_4 NPs was confirmed by a range of spectroscopy and microscopy techniques such as UV-visible spectroscopy, Fourier transform infrared spectroscopy, powder X-ray diffraction (XRD), field emission-scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and vibrating sample magnetometer. The spectroscopic results indicated the successful formation of Fe_3O_4 NPs. FE-SEM and TEM images revealed the spherical shape with particle size of 17 nm. Fe_3O_4 NPs showed superparamagnetism. Green synthesized Fe_3O_4 NPs shows enhanced adsorption efficiency toward MB from contaminated water. The kinetic data of adsorption fitted very well with the pseudo-second order. The adsorption isotherm data fitted well to Langmuir isotherm and it was found to be 10.4712 mg/g adsorption capacity and it implies that the chemisorptions of MB on to Fe_3O_4 NPs.

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KEYWORDS

Green synthesis; plant-mediated synthesis; magnetite nanoparticles; organic dye pollutants; Langmuir isotherm

1. Introduction

During the past decade, there has been increasing concern about the organic pollutants, heavy metals and pathogens in an aquatic environment due to their wide distribution and potential adverse health effects [1]. Especially, the presence of toxic organic dyes in water effluent, even at parts per billion (ppb) levels, is extremely harmful and undesirable. Various treatment approaches for removing organic dyes from contaminated water are available, such as adsorption, bioremediation, precipitation, membrane filtration, reverse osmosis, and photocatalysis [2]. However, these methods have proved to be ineffective for removal of dyes from water effluents due to high chemical stability of dyes, high cost and low efficiency of these processes. Among these chemical and physical methods, the adsorption method is more versatile and efficient, and has been successfully used for removal of dyes from contaminated water due to its simplicity of design, wide adaptability, convenience and ease of operation. Especially, nano-adsorbents offer the possibility of efficient removal of organic dyes owing to smaller size and higher adsorptive surface area. From the past few years, there have been an increased investigations based on iron oxide nanoparticles such as magnetite nanoparticles (Fe_3O_4 NPs), maghemite ($\gamma\text{-Fe}_2\text{O}_3$ NPs), etc., for the removal of organic and inorganic contaminants. Among all magnetic nanoparticles, Fe_3O_4 NPs have emerged as potential candidate for

technological applications such as magnetic fluids, high-density magnetic storage, environmental remediation, cancer therapy, MRI contrast enhancement, drug delivery, tissue repair engineering, antibacterial, catalysis, lithium-ion battery due to their small size, biocompatibility, low toxicity and high saturation magnetism [1–7].

Numerous methods have been reported for synthesis of Fe_3O_4 NPs such as co-precipitation, thermal decomposition of organic iron precursor, sol-gel method, Polyol method, surfactant- or polymer-assisted precipitation including reverse micelle, co-polymer templates-assisted synthesis, solvothermal synthesis and hydrothermal synthesis [8–18]. All these synthetic methods have employed the chemicals such as sodium borohydride, dimethyl formamide, hydrazine and carbon monoxide as reducing agents and also they are highly reactive and have both biological and environmental negative effects. Therefore, it is highly desirable to prepare Fe_3O_4 NPs via green synthesis approach using non-toxic, environmentally benign materials, which offers numerous benefits of eco-friendliness and compatibility for pharmaceutical, biotechnological and biological applications [19]. More recently, plant-mediated green synthesis of nanoparticles has attracted much attention due to cost effective, environmentally friendly alternative to chemical and physical methods. There are successful reports for plant-mediated synthesis of Fe_3O_4 NPs using various plant extracts such as seed extract of *Grape proanthocyanidin* [20],

leaf extract of *Tridaxprocumbens* [21], seaweed of *Kappaphycusalvarezii* [22], *Caricaya papaya* [23], peel extract of *plantain* [24], and seaweed of *Sargassummuticum* [25]. However, no literature reports are available for the synthesis of Fe_3O_4 NPs using aqueous leaf extract of *Zanthoxylum armatum* DC. The plant *Zanthoxylum armatum* DC. belongs to rutaceae family and is extensively used in traditional medicinal practices of the Khasi tribe in North-Eastern India and in neighboring regions including South-East Asia. The *Zanthoxylum armatum* DC. is an important medicinal plant used for anti-helminthic, controlling hyperglycaemia and also used for treatment of cholera, tonic for fever, remedy for skin diseases, diseases of the mouth and teeth; and possesses antioxidant, antidiabetic, antifungal and antimicrobial activities [26,27].

In this paper, for the first time, we report a simple and environmentally friendly method for the preparation of Fe_3O_4 NPs using the aqueous leaf extract of *Zanthoxylum armatum* DC. for the adsorption of organic dye, methylene blue (MB). The synthesized Fe_3O_4 NPs have been characterized by using UV–visible (UV-vis) spectroscopy, X-ray diffraction (XRD), Fourier transforms infrared (FTIR) spectroscopy, field emission-scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and vibrating sample magnetometer (VSM). Furthermore, as synthesized Fe_3O_4 NPs were investigated for removal of organic dye, MB, from contaminated water. Finally, to find the optimum adsorption conditions of Fe_3O_4 NPs for removal of MB dye, adsorption isotherms and kinetic studies were extensively investigated.

2. Experimental

2.1. Materials

Iron(II)sulfate-hepta-hydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), iron(III) chloride-hexa-hydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ammonia (NH_3) solution and MB were purchased from Merck (Mumbai, India) and used without further purification. The leaves of *Zanthoxylum armatum* DC. were collected from forest of Chintapalli, Andhra Pradesh, India, in May 2015. Botanical aspects of collected plant materials were identified and authenticated by plant taxonomist **Dr. S.B. Padal**, Associate Professor, Department of Botany, Andhra University, Visakhapatnam, India. Milli-Q water (Visakhapatnam, India) was used throughout the synthesis process.

2.2. Preparation of plant extract

The fresh leaves of *Zanthoxylum armatum* DC. were washed thoroughly with water and followed by Milli-Q water to remove the dust particles and then shade dried for 15 days to remove the moisture. Then the

dried leaves were cut into small pieces and powdered using blender. 5 g of powder was transferred to an Erlenmeyer flask containing 100 ml of Milli-Q water, and boiled for 20 min at 60°C . Then, the resultant extract was filtered by Whatman No. 1 filter paper and the filtrate was stored at 4°C for further use.

2.3. Synthesis of Fe_3O_4 NPs

Fe_3O_4 NPs were synthesized based on co-precipitation method in the presence of aqueous leaf extract of *Zanthoxylum armatum* DC. as a reducing and capping agent. In a typical procedure, 2:1 molar ratio of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.11 g) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.556 g), respectively, were mixed with 85 mL Milli-Q water with the assistance of ultrasonication in 250 mL Erlenmeyer flask. Then, the reaction was allowed for 60 min at 80°C with constant stirring under nitrogen atmosphere. After that, 10 mL of 5% aqueous extract of *Zanthoxylum armatum* DC. leaf was quickly added into the reaction mixture. After 30 min of refluxing, 5 mL of 25% NH_3 was added drop wise to the reaction mixture to adjust the pH to 10. Then black precipitate, Fe_3O_4 NPs, was obtained and filtered by using bar magnet. The product was washed with Milli-Q water for three times and once with ethanol and dried in the vacuum at room temperature for further use.

2.4. Characterization

UV–vis spectra of synthesized Fe_3O_4 NPs were recorded by Shimadzu (2450 – SHIMADZUCorporation, Tokyo, Japan) spectrometer. By using SHIMADZU-IR PRESTIGE-2 Spectrometer, FTIR spectra were recorded in the range of $400\text{--}4000\text{ cm}^{-1}$. The powder XRD patterns were recorded by PANalyticalX'pert pro diffractometer at $0.02^\circ/\text{s}$ scan rate with $\text{Cu-K}\alpha_1$ radiation ($1.5406\text{ \AA}$, 45 kV, 40 mA). The morphologies of the samples were characterized using FE-SEM (Zeiss Ultra-60, Carl Zeiss Promenade, Jena, Germany) equipped with X-ray energy dispersive spectroscopy (EDS). TEM images were obtained (TEM model FEI Technai 20 U Twin, ThermoFischer Scientific, Hillsboro, OR, USA) at an accelerating voltages of 120 and 200 kV. In order to study the magnetic behavior of Fe_3O_4 NPs at room temperature, magnetization measurements were recorded using vibrating sample magnetometer (VSM Lakeshore 665, LakeShore CRYOTRONICS, East Lakeshore Drive, USA).

2.5. Batch mode adsorption studies

The absorption behavior of MB at various pHs was studied by measuring the absorbance of MB solutions at 664 nm in primary experiments. To attain maximum

adsorption efficiency, various parameters affecting the MB dye removal were studied and optimized. The adsorption efficiency of synthesized Fe_3O_4 NPs were investigated at room temperature (300 K) using MB as a model water pollutant. Typically, 50 mg of Fe_3O_4 NPs was mixed with 50 mL of known concentration of dye solution. The solution pH was adjusted by HCl (0.1 M) or NaOH (0.1 M). The flasks were stirred for the specified time period and sample from each flask were withdrawn at the desired time of reaction. After the adsorption experiment, Fe_3O_4 NPs were recovered by an external magnet. The residual dye concentration was determined by UV-vis spectrophotometer by measuring the absorbance at a wavelength of maximum ($\lambda_{\text{max}} = 664 \text{ nm}$) absorbance of MB. The following equation was applied to calculate the dye removal efficiency:

$$\text{Dye removal efficiency (\%)} = \frac{C_0 - C_r}{C_0} \quad (1)$$

where C_0 and C_r are the initial and residual concentrations of the dye in the solution (mg L^{-1}), respectively

The amount of adsorbed MB (q) was expressed in mg of dye per gram of synthesized Fe_3O_4 NPs, as shown by Eq. (2):

$$q = (C_0 - C) \times V/m \quad (2)$$

where q is adsorption capacity of MB in (mg/g) at time t , C_0 represents the initial MB concentration in mg/L , C is the concentration of MB in solution after adsorption in mg/L , V is the volume of the aqueous

solution in L, and m is the mass of synthesized Fe_3O_4 NPs in grams. The mechanism of adsorption and kinetics were correlated by adsorption isotherms and kinetic models, respectively.

3. Result and discussion

3.1. Characterization

Phytochemical qualitative analysis of aqueous leaf extract of *Zanthoxylum armatum* DC. was listed in Table S1. The aqueous leaf extract of *Zanthoxylum armatum* DC. contains phenolic, tannins, alkaloids, flavonoid, terpenoids, and their glucosides and benzenoids, fatty acids, amino acids, lignins, coumarins and sterols [28–34], which are responsible for synthesis and capping of Fe_3O_4 NPs. The UV-vis absorption spectra of synthesized Fe_3O_4 NPs and aqueous leaf extract of *Zanthoxylum armatum* DC. were depicted in Figure 1. The aqueous leaf extract of *Zanthoxylum armatum* DC. has a strong absorption bands at 260 and 335 nm, which are attributed to the presence of alkaloids, phenolic acid, flavonoid, tannins, terpenoids and carbohydrates in aqueous extract. The characteristic absorption band at 370 nm indicates the formation of Fe_3O_4 NPs [35,36] which is primarily due to the absorption and scattering of light by Fe_3O_4 NPs. Moreover, the absence of the *Zanthoxylum armatum* DC. leaf extract peak at 260 and 335 nm in the Fe_3O_4 NPs spectrum, clearly indicates alkaloids, phenolic acid, flavonoid, tannins, terpenoids and carbohydrates phytochemicals acting as reducing

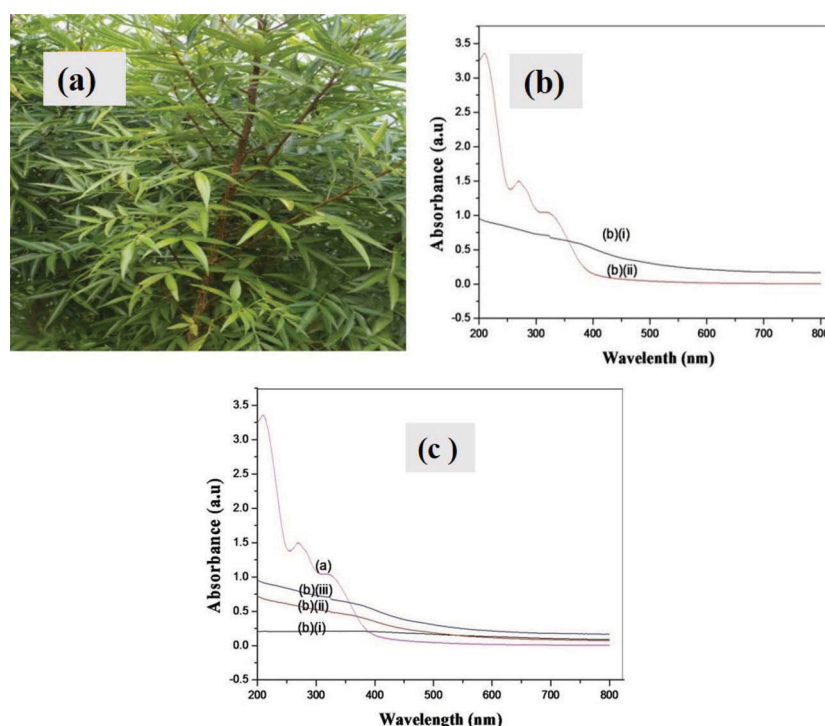


Figure 1. (a) Image of fresh leaves of *Zanthoxylum armatum* DC. (b) The UV-vis spectra of (i) Fe_3O_4 NPs synthesized using aqueous leaf extract of *Zanthoxylum armatum* DC. and (ii) 5% aqueous leaf extract of *Zanthoxylum armatum* DC. (c) The UV-vis spectra of synthesized Fe_3O_4 NPs using different concentrations of *Zanthoxylum armatum* DC. leaf extract at 350 K, and pH 10.

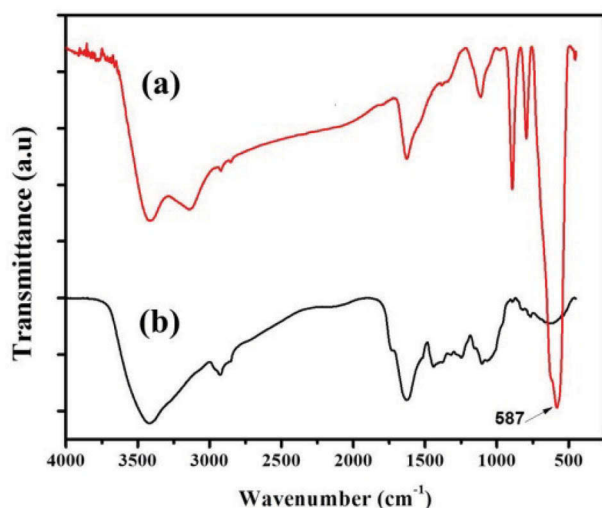


Figure 2. FTIR spectra of (a) Fe_3O_4 NPs synthesized using aqueous leaf extract of *Zanthoxylum armatum* DC. and (b) aqueous leaf extract of *Zanthoxylum armatum* DC.

and capping agent for the synthesis of Fe_3O_4 NPs. The FTIR spectra of aqueous leaf extract of *Zanthoxylum armatum* DC. and Fe_3O_4 NPs were presented in Figure 2. The FTIR spectrum of the aqueous leaf extract of *Zanthoxylum armatum* DC. exhibited characteristic bands at 3417, 2925, 1631, 1441, 1243, 1105 and 617 cm^{-1} . The bands at 3417, 2925, 1631 and 1441 cm^{-1} are ascribed to the presence of O–H group of phenolic compound, C–H group of alkane, C=O group of carboxylic acids, and C=C group of aromatic compound, respectively. In case of Fe_3O_4 NPs (Figure 2 (b)), the characteristic band due to O–H group of phenol shifted from 3417 to 3408 cm^{-1} indicating that O–H group of phenol acts as reducing agent in the formation of Fe_3O_4 NPs. The band due to C=O group of carboxylic acid (1631–1626 cm^{-1}), the bands associated to C=C group of aromatic compounds (1441–1401 cm^{-1}) and also C–O stretching frequency of phenolic group (1105–1130 cm^{-1}) were shifted compared to aqueous leaf extract of *Zanthoxylum armatum* DC. indicating that the carboxyl group (–COOH) present in leaf extract acts as capping agent for Fe_3O_4 NPs. The strong additional band at 587 cm^{-1} was observed for Fe_3O_4 NPs which is ascribed to the stretching vibration of Fe–O [36]. FTIR spectrum indicates that the phyto-constituents present in aqueous leaf extract of *Zanthoxylum armatum* DC. were efficiently acting as reducing and capping agent for the formation of Fe_3O_4 NPs [28].

The phase purity and crystalline nature of Fe_3O_4 NPs were confirmed using powder XRD. The XRD patterns of as prepared Fe_3O_4 NPs using aqueous leaf extract of *Zanthoxylum armatum* DC. were shown in Figure 3. The Bragg reflection peaks were observed at 2θ values of 30.3°, 35.7°, 43.3°, 53.7°, 57.3°, 62.9° and 74.4° which could be indexed to (220), (311), (400), (422), (511), (440) and (533) planes. From Figure 3,

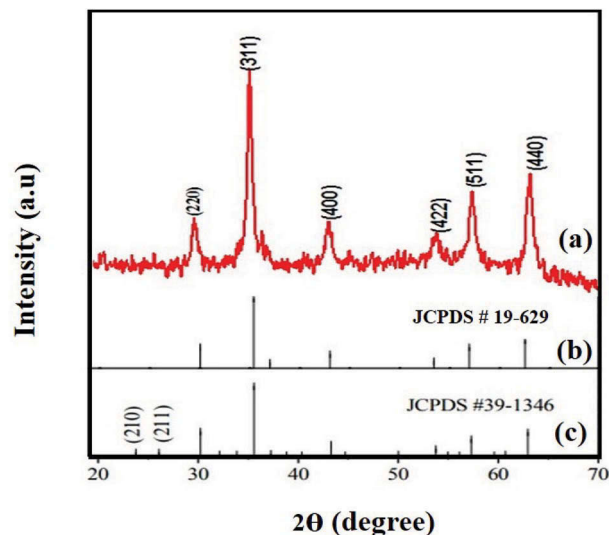


Figure 3. (a) XRD patterns of Fe_3O_4 NPs synthesized using aqueous leaf extract of *Zanthoxylum armatum* DC. (b) JCPDS No. 19-629. (c) JCPDS No. 39-1346.

we have found that the XRD patterns of the synthesized Fe_3O_4 NPs and pure Fe_3O_4 NPs of the Joint Committee on Powder Diffraction Standards (JCPDS No. 19-0629) exactly matched. Although the main XRD peaks of $\gamma\text{-Fe}_2\text{O}_3$ NPs (maghemite nanoparticles) (JCPDS No. 39-1346) are similar to the synthesized Fe_3O_4 NPs ones, the notable $\gamma\text{-Fe}_2\text{O}_3$ peaks ranging from 20° to 30° are absent in XRD pattern of as synthesized Fe_3O_4 NPs. Hence it was confirmed that the prepared Fe_3O_4 NPs have pure Fe_3O_4 inverse cubic spinel phase.

The intense reflection at (311) plane in contrast to the other planes may specify the growth direction of the Fe_3O_4 NPs. The average crystallite sizes of the Fe_3O_4 NPs was calculated from the full width at half-maximum (FWHM = 0.466) of the (311) reflection by the Debye–Scherrer's equation [37].

$$D = k\lambda/\beta \cos \theta \quad (3)$$

where D is particle diameter size, k is a constant equals 1, λ is wavelength of X-ray source (0.1541 nm), β is the FWHM and θ is the diffraction angle corresponding to the lattice plane. The average crystallite size of Fe_3O_4 NPs according to Scherrer equation with the width of (311) plane is found to be 20.7 nm.

Morphology of as synthesized Fe_3O_4 NPs was investigated by FE-SEM and TEM. The representative FE-SEM images of Fe_3O_4 NPs synthesized using aqueous leaf extract of *Zanthoxylum armatum* DC. are depicted in Figure 4. FE-SEM images of Fe_3O_4 NPs clearly reveal spherical shape. Figure 4(d) show the EDS spectrum of Fe_3O_4 NPs synthesized using *Zanthoxylum armatum* DC. leaf extract and it shows Fe, C and O elemental composition. The presence of carbon shows Fe_3O_4 NPs was capped by the

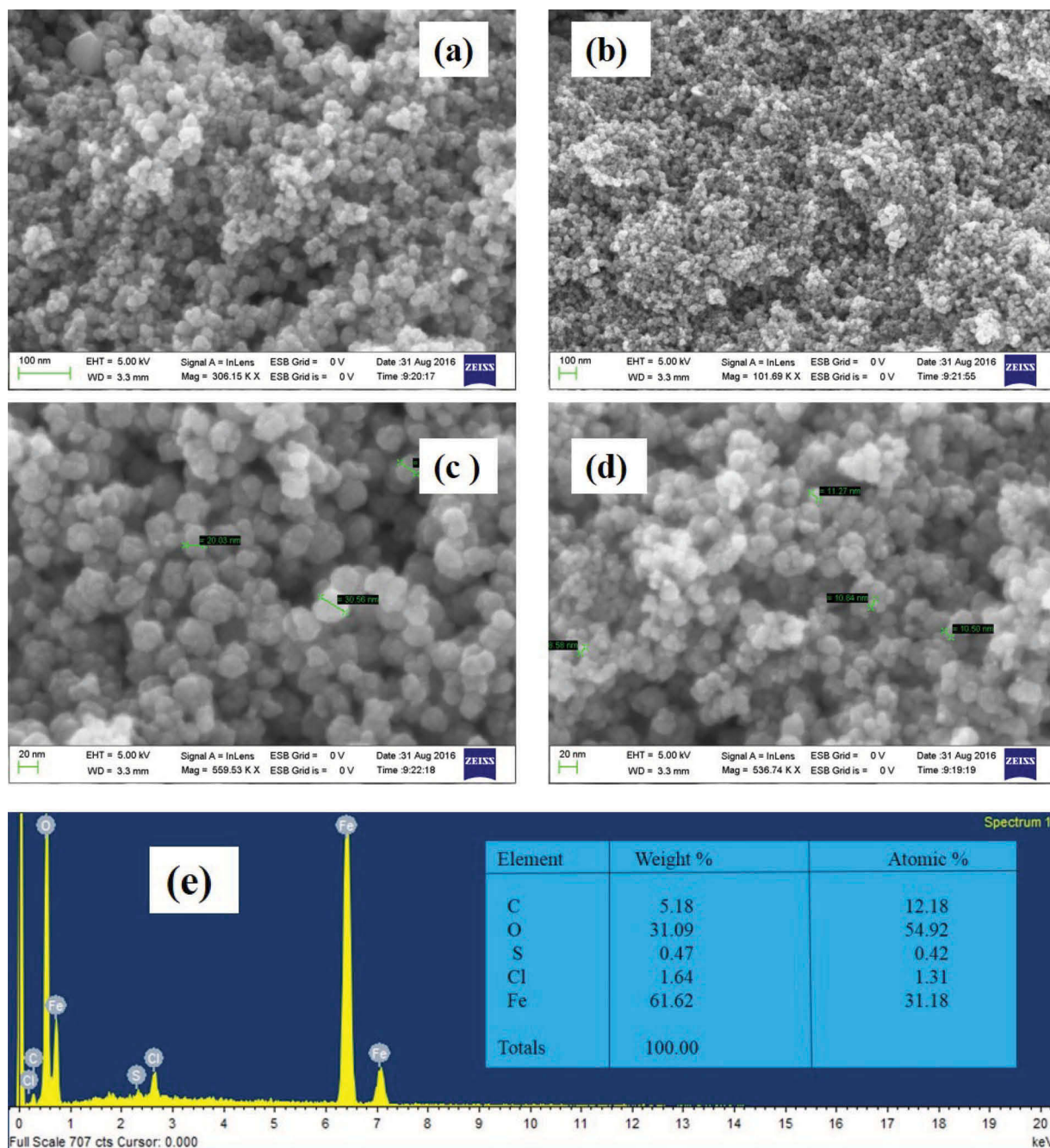


Figure 4. Representative FE-SEM images with (a, b) 100 nm scale resolution, (c, d) 20 nm scale resolution and (e) energy dispersive X-ray spectroscopy (EDS) of Fe_3O_4 NPs synthesized using aqueous leaf extract of *Zanthoxylum armatum* DC.

phyto-constituents of aqueous leaf extract of *Zanthoxylum armatum* DC.

TEM images of synthesized Fe_3O_4 NPs using aqueous leaf extract of *Zanthoxylum armatum* DC. are presented in Figure 5. TEM images clearly reveal the spherical shape of Fe_3O_4 NPs. Average particle size of synthesized Fe_3O_4 NPs measured by image J software (National Institute of Health, Bethesda, MD, USA) was 17 nm by taking more than 200 magnetite nanoparticles. The selected area electron diffraction pattern of the Fe_3O_4 NPs shows (Figure 5(c)) the ring-like diffraction pattern indicating the polycrystalline nature of Fe_3O_4 NPs.

Magnetic behavior of synthesized Fe_3O_4 NPs was investigated by a VSM at room temperature. The magnetization curve of the synthesized Fe_3O_4 NPs is presented in Figure 6. The magnetization curve reveals that the sigmoidal shape without hysteresis loop demonstration of superparamagnetic behavior with the saturation magnetization (M_s) value 128 emu/g at room temperature [36]. The higher saturation magnetization is correlated with the previous literature [38]. The magnetization of synthesized Fe_3O_4 NPs is strong enough that they can be easily concentrated and separated by applying a small magnet from the solution.

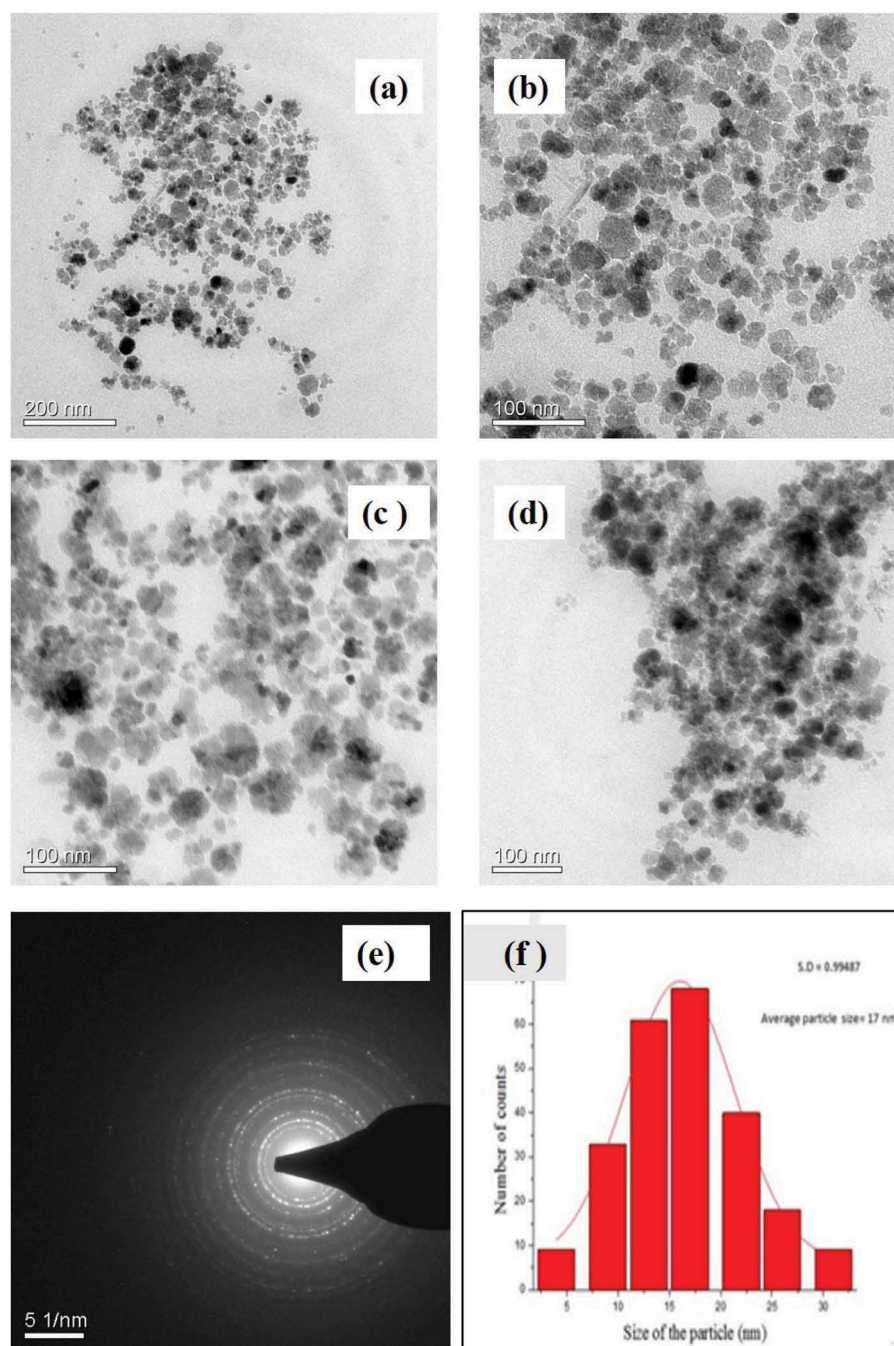


Figure 5. Representative TEM images with (a) 200 nm resolution, (b–d) 100 nm resolution, (e) selected area electron diffraction patterns and (f) size distribution histogram of Fe₃O₄ NPs synthesized using aqueous leaf extract of *Zanthoxylum armatum* DC.

3.2. Plausible mechanism for synthesis of Fe₃O₄ NPs using aqueous leaf extract of *Zanthoxylum armatum* DC

A possible formation mechanism of Fe₃O₄ NPs by using aqueous leaf extract of *Zanthoxylum armatum* DC. is presented in Figure 7. The reaction mixture consists of aqueous leaf extract of *Zanthoxylum armatum* DC., ferric chloride (FeCl₃·6H₂O) and ferrous chloride (FeCl₂·4H₂O) in one aqueous phase. The aqueous leaf extract of *Zanthoxylum armatum* DC. contains alkaloids, phenolic acid, flavonoid, tannins, terpenoids and carbohydrates. It is reported that the gallic acid is a major phytochemical present in aqueous leaf extract of

Zanthoxylum armatum DC. [28]. Moreover, the FTIR results also (Figure 2) supported the presence of carboxylic group in aqueous leaf extract and C=O of carboxylic group (gallic acid) in leaf extract form complex with Fe³⁺ and Fe²⁺. As the reaction was carried out at 80° C, OH[−] of NH₄OH would be involved in the reaction and thus, a competition between of COO[−]...Fe³⁺ and COO[−]...Fe²⁺ bonds and the formation of HO[−]...Fe³⁺ and OH[−]...Fe²⁺ bonds would occur; thereby, resulting in the formation of ferric hydroxide [Fe(OH)₃] and ferrous hydroxide [Fe(OH)₂]. Finally, Fe₃O₄ NPs were formed by dehydration (−H₂O) from ferric hydroxide and ferrous hydroxide in the reaction mixture.

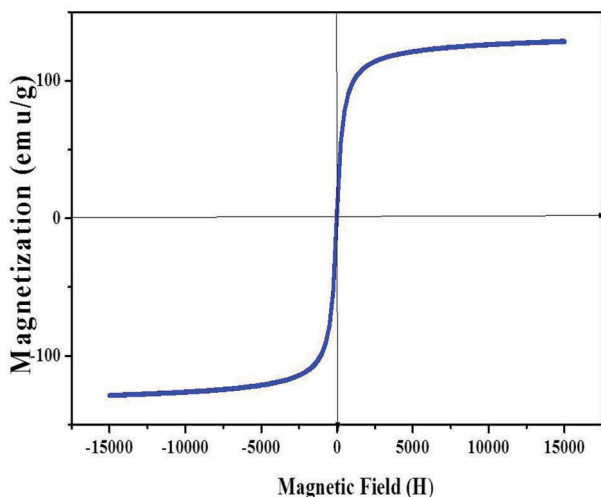


Figure 6. The room temperature magnetization curve of Fe_3O_4 NPs synthesized using aqueous leaf extract of *Zanthoxylum armatum* DC.

3.3. Adsorption studies

The UV–vis absorption spectra of unadsorbed MB in the solution at time “ t ” after the adsorption by *Zanthoxylum*

armatum DC. synthesized Fe_3O_4 NPs is shown in **Figure 8**. When the adsorption was progressed, 71% MB (5 mg L^{-1}) dye removal efficiency was obtained at the end of 180 min. The adsorption after 180 min was not brought further adsorption of MB and which ascribed to adsorption equilibrium was attained at the end of 180 min. **Figure 9(a,b)** depicts that at the adsorption equilibrium (180 min), adsorption of Fe_3O_4 NPs for MB [at 300 K, pH 11] was found to be 71%, 62.1%, and 48.4% for the concentration of 5 mg L^{-1} , 10 mg L^{-1} , and 15 mg L^{-1} MB, respectively.

3.3.1. Adsorption kinetics

Adsorption kinetics gives the valuable information for designing adsorption process for practical application. Hence, in this study, the adsorption kinetics of MB on synthesized Fe_3O_4 NPs was conducted at different concentration of MB. **Figure 9(a,b)** shows that the adsorption rate of MB on to synthesized Fe_3O_4 NPs at different initial concentrations of 5, 10, and 15 mg L^{-1} of MB (at pH 11 and 300 K). The dye removal efficiency is highly dependent on the initial dye concentration. The time variation plot

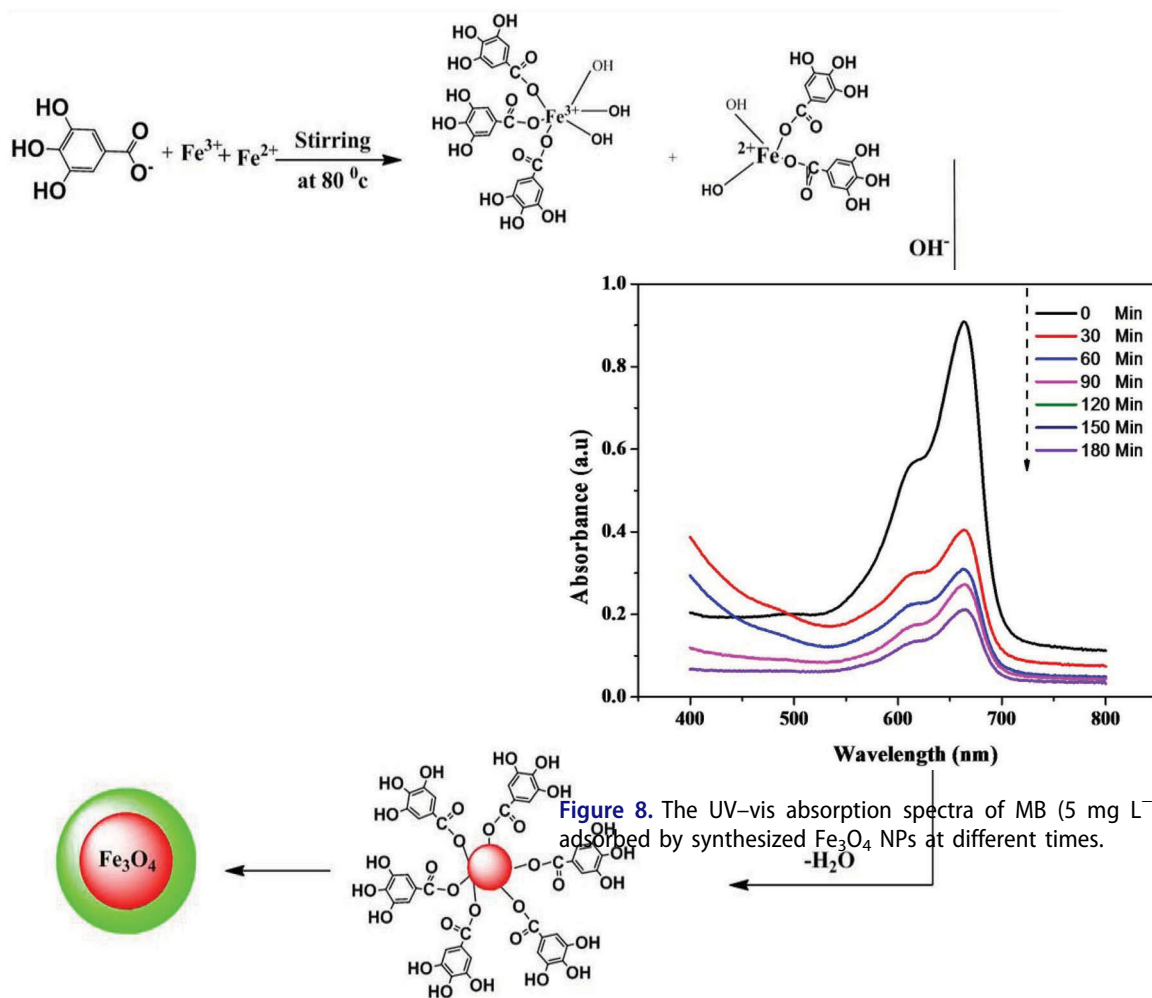


Figure 8. The UV–vis absorption spectra of MB (5 mg L^{-1}) adsorbed by synthesized Fe_3O_4 NPs at different times.

Figure 7. A schematic illustration of the formation mechanism of Fe_3O_4 NPs using the aqueous leaf extract of *Zanthoxylum armatum* DC.

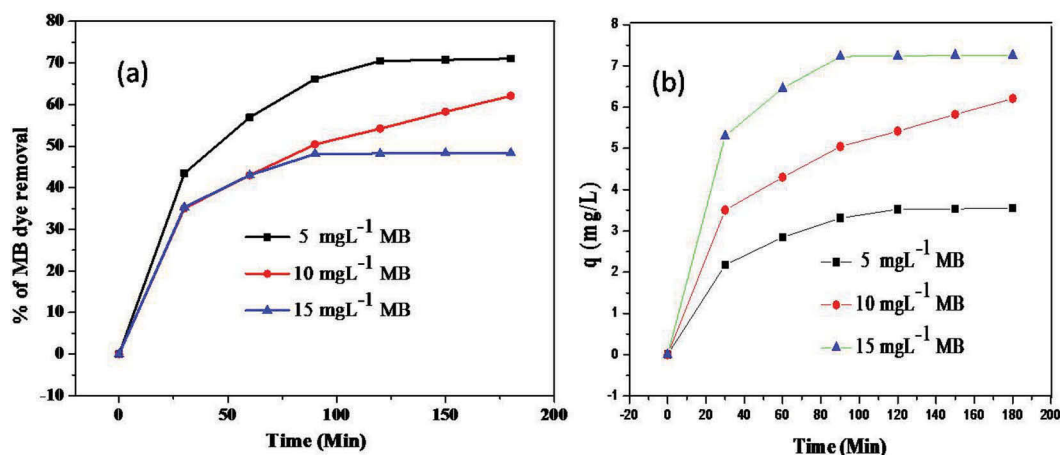


Figure 9. (a) The percent (%) of dye adsorption removal and (b) the amount of MB dye adsorbed (q in mg L^{-1}) at various concentration of MB onto Fe_3O_4 NPs.

specifies that the removal of dye is rapid in preliminary stages but when it approaches equilibrium, it slows down gradually. This may be due to the availability of vacant surface sites during the initial stage of adsorption, and after a certain time period the vacant sites get occupied by dye molecules which create a repulsive force between the adsorbate (MB dye) on the adsorbent surface. When the initial dye concentration increased from 5 to 15 mg/L at 300 K and pH 11, the adsorption capacity increased from

3.5524 to 7.2587 mg/g while the removal percentage of dye decreased from 71% to 48%. At a low dye concentration there will be more unoccupied surface sites on the adsorbent, and when the initial dye concentration increases, there will be insufficient sites for the adsorption of dye molecules, thus decreasing the dye removal efficiency [39]. In contrast, the increase in initial dye concentration will cause an increase in the loading capacity of the adsorbent and this may be due to the high-driving force for mass transfer at a

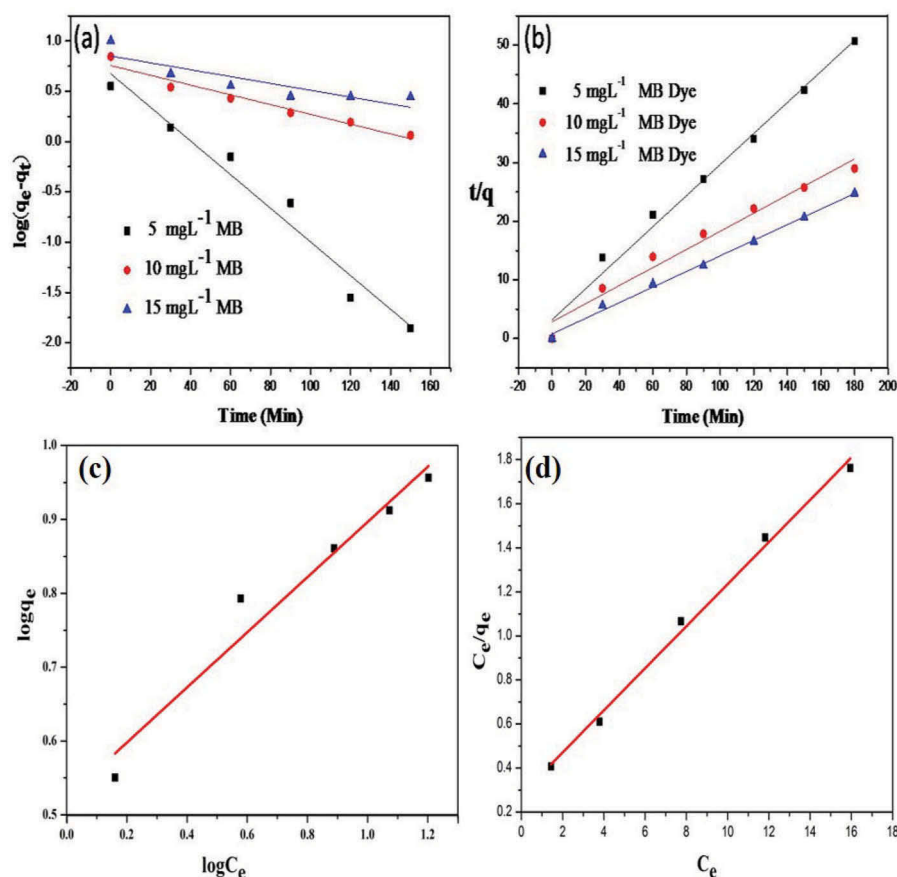


Figure 10. (a) Pseudo-first-order, (b) pseudo-second-order kinetics plots, (c) Freundlich and (d) Langmuir adsorption isotherm plots of MB adsorption to synthesized Fe_3O_4 NPs.

high initial dye concentration [40]. As shown in Figure 9(b), the adsorption process is rapid in the first 30 min and gradually reached to equilibrium at the end of 180 min. The kinetics of adsorption of MB on synthesized Fe_3O_4 NPs was investigated by pseudo-first-order [41] Eq. (4) and the pseudo-second-order Eq. (5) kinetic models. The pseudo-first-order kinetic model is described by the equation:

$$\log(q_e - q_t) = \log q_e - (k_1/2.303) \times t \quad (4)$$

where k_1 (min^{-1}) is the pseudo-first-order rate constant of adsorption, and q_t (mg/g) and q_e (mg/g) are the amount of the MB adsorbed at time t and at equilibrium, respectively. k_1 (min^{-1}) was determined from the slope of the plot of $\log(q_e - q_t)$ vs t (Figure 10(a)) and it was obtained that the correlation coefficient value (R^2) is 0.9660. Moreover, to validate the kinetic of adsorption of MB pseudo-second-order kinetic model was also investigated.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) \times t \quad (5)$$

where k_2 (g/mg min^{-1}) is the pseudo-second-order rate constant, and q_t (mg/g) and q_e (mg/g) are the amount of the MB adsorbed at time t and at equilibrium, respectively. The values of q_e and k_2 can be calculated from the slope and intercept of a plot of t/q_t vs t (Figure 10(b)). For this plot, correlation coefficient value (R^2) was found to be 0.9849. It is concluded that the adsorption of MB on synthesized Fe_3O_4 NPs was found to be pseudo-second-order kinetic model; this implies that the adsorption process will more likely proceed through electrostatic interaction of MB and surface of synthesized Fe_3O_4 NPs, and this process is called as chemisorption process [42].

3.3.2. Adsorption isotherm

Adsorption isotherm analyses are used to investigate the plausible adsorption mechanism and determine the maximum adsorption capacity of synthesized Fe_3O_4 NPs. The equilibrium adsorption isotherm parameters of MB on synthesized Fe_3O_4 NPs were analyzed using Langmuir and Freundlich isotherm models [43,44]. The Langmuir equation can be expressed as (Eq. 6):

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_0 b_L} \quad (6)$$

where q_e (mg/g) is the equilibrium adsorption capacity of MB on the adsorbent, C_e (mg/L) is the equilibrium concentration of MB in the solution, Q_0 (mg/g) is the maximum capacity of adsorbent, and b (L/mg) is the equilibrium constant relating to the enthalpy of process. Figure 10(c) shows that the experimental data well-fitted to the Langmuir

adsorption isotherm and it was found to be 10.4712 mg/g maximum adsorption capacity. As shown in ESI Table 7, the correlation coefficient (R^2) and equilibrium constant (b_L) values were found to be 0.9932 and 0.3416, respectively. Besides, dimension-less factor (R_L) of the Langmuir adsorption isotherm parameter was calculated using Eq. (7). In this study, the R_L value obtained was 0.3693, which is in between 0 and 1. This indicates that the adsorption of MB on Fe_3O_4 NPs is thermodynamically favorable.

$$R_L = \frac{1}{(1 + b_L \times C_0)} \quad (7)$$

where C_0 (mg/g) is initial MB concentration and b_L (L/mg) is the Langmuir constant. For unfavorable sorption, $R_L > 1$; for favorable sorption, $0 < R_L < 1$; for irreversible sorption $R_L < 0$; and for linear sorption, $R_L < 1$

The Freundlich isotherm (Eq. 7) can be expressed as:

$$\log q_e = \log k_f + 1/n \log C_e \quad (8)$$

where q_e (mg/g) is the equilibrium adsorption capacity of MB on the synthesized Fe_3O_4 NPs; k_f (mg/g) and $1/n$ are Freundlich constants representing the adsorption capacity (adsorption coefficient) at unit equilibrium concentration and adsorption intensity, respectively. The value of Freundlich constant “ n ” is 2.6781. For this adsorption, $n > 1$ indicating that MB favorably adsorbed on synthesized Fe_3O_4 NPs. However, as shown in ESI Table 7, the correlation coefficient values of Langmuir model ($R^2 = 0.9932$) were much closer to unity than Freundlich model ($R^2 = 0.9492$), which indicates that the experimental data best fit with the Langmuir isotherm. The monolayer adsorption maximum adsorption capacity (Q_0) of synthesized Fe_3O_4 NPs was found to be 10.4712 mg/g. This figure indicates that *Zanthoxylum armatum* DC. extract-assisted synthesized Fe_3O_4 NP has comparative adsorption efficiency toward organic dyes (ESI, Tables 4 and 8).

4. Conclusion

In conclusion, the Fe_3O_4 NPs was successfully synthesized using aqueous leaf extract of *Zanthoxylum armatum* DC. via green route method. The phytochemical present in aqueous leaf extract of *Zanthoxylum armatum* DC. can act as reducing and capping agent for the formation of Fe_3O_4 NPs. The spherical morphology was observed for Fe_3O_4 NPs with average particle size of 17 nm. The room temperature magnetization curve reveals superparamagnetic behavior of Fe_3O_4 NPs. Furthermore, the obtained Fe_3O_4 NPs has been used as an efficient adsorbent for the removal of MB. The adsorption

kinetics of Fe₃O₄ NPs toward MB followed a pseudo-second-order model, suggesting chemisorptions process. The adsorption mechanism best fit to Langmuir model which indicates the formation of a monolayer covering of the adsorbate at the outer surface of the Fe₃O₄ NPs.

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Disclosure statement

No potential conflict of interest was reported by the authors.
Supplementary can be accessed here.

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