ZnFe₂O₄@SiO₂@Tragacanth gum nanocomposite: synthesis and its application for the removal of methylene blue dye from aqueous solution

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Abstract

In this study, the ZnFe₂O₄@SiO₂@Tragacanth gum magnetic nanocomposite as a novel adsorbent was synthesized and was confirmed by FTIR, XRD, TEM, TGA and VSM methods. Then, the prepared nanocomposite has been tested for the removal of methylene blue dye from aqueous solution for adsorption process, and the effect of various parameters including pH (2–12), adsorbent dosage (0.2–2 g/L), temperature (15–45 °C), initial dye concentration (10–60 mg/L) and contact time (5–120 min), also its isotherms and kinetics has been studied. The results showed that the optimum pH, contact time, initial dye concentration, adsorbent dosage and maximum adsorption capacity were 8, 60 min, 60 mg/L, 0.2 g/L and 109.37 mg/g, respectively. Furthermore, the experimental data determined that the adsorption of methylene blue dye interpreted the Freundlich isotherm ($R^2=0.979$) and the pseudo-second-order kinetics model ($R^2=0.998$). Also, the thermodynamic parameters of the absorption system, such as changes in enthalpy ($\Delta H=+9.36$ kJ/mol), entropy ($\Delta S=+40.72$ J/mol k) and Gibbs free energy ($\Delta G=-3.5$ kJ/mol), were measured and showed that adsorption process of ZnFe₂O₄@SiO₂@Tragacanth gum magnetic nanocomposite was endothermic and spontaneous process. As a result, due to high adsorption capacity, environment friendly, low cost, rapid extraction and non-toxicity, the ZnFe₂O₄@SiO₂@TG magnetic nanocomposite can be used as an effective adsorbent for methylene blue removal from aqueous solutions.

Keywords ZnFe₂O₄ · SiO₂ · Nanocomposite · Removal · Methylene blue (MB) · Tragacanth gum (TG) · Nanoparticles (Np_s) · Nanocomposite (NC_s)

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Introduction

In recent years, industrial development has led to an ever-increasing rise in industrial wastewater and environmental pollution [1]. Dyes are one of the most important pollutants in various industries such as textiles, paper, plastics, cosmetics and hygiene [2]. Synthetic dyes used in the industry are compounds with complex molecular structure and persist to light, heat and microbial degradation [3]. The discharge of dyed wastewater into the environment, in addition to messing up the beautiful face of nature, disrupts the function of photosynthesis and extirpates the aquatic plants and animals [1]. Also, they may also be carcinogenic or mutagenic [4]. Methylene blue (MB) is a cationic dye that is widely used in the textile industry and is usually toxic and carcinogenic [5, 6]. Burning eyes, nausea, diarrhea and vomiting are also side effects of contact with containing MB sewage [7]. Many techniques, such as coagulation and filtration, ion exchange, filter membranes, adsorption, advanced oxidation and photocatalytic processes, have been widely used for dyes removal. Among these methods, surface adsorption has been widely used due to various advantages such as low cost, easy design and high efficiency [8–16]. Many studies have been carried out on the absorption of methylene blue by various adsorbents that can be cited in studies by authors Andreas, Fan, Alehyen Omidi Khaniabadi and Altıntig such as orange peel [17], tea waste [18], fly ash-based geopolymers [19], aloe vera wastes [5] and magnetic loaded activated carbon adsorbents [6] in 2016–2018.

In recent years, the use of nanoparticles, especially magnetic nanoparticles, as adsorbents for the removal of various pollutants, due to the important properties, including easy separation by an external magnetic field, easy synthesis of nanoparticles, high surface area and ease of enhancement, has been found [12, 20–23]. Recently, many studies have been conducted on ferrite nanoparticles (NP_f) due to important properties such as high surface-to-volume ratio, high stability, recyclability and biocompatibility [24]. Oxidation potential in ferrite NP_f is high. For this purpose, it is necessary to modify the surface of ferrite NP_f using organic or mineral substances [25]. SiO_2 is a non-toxic, water-dispersible and biocompatible substance for coating ferrite NP_f [26]. Recently, magnetic NP_f have been combined with biopolymers to increase adsorption capacity and have been used for various purposes [27–30]. Tragacanth gum (TG) as a magnetic biosorbent and porous hydrogel beads is a non-toxic, low-cost, abundant, affordable and biocompatible biopolymer which can be utilized as a thickening agent as well as a binder and even stabilizer [29, 31]. The presence of various functional groups such as primary and secondary hydroxyl groups, carboxylic acid and epoxy group in the catalyst structure provides favorable conditions for reaction with reactants containing functional groups [31]. Iran is the largest producer of quality tragacanth gum [32]. The molecular structure of TG is shown in Fig. 1 [33].

In the present study, the zinc ferrite NP_f were synthesized and then a silica layer was fixed on the NP_f . Further, the surface of the magnetic NC_s was modified with natural TG biocompatible polymer and the application of synthesized magnetic NC_s in MB removal was studied. In the present study, the $\text{ZnFe}_2\text{O}_4@$

Fig. 1 The chemical structure of TG

SiO₂@Tragacanth gum magnetic nanocomposite as a novel adsorbent was synthesized and was confirmed by FTIR, XRD, TEM, TGA and VSM methods. This novel adsorbent has different advantages such as biocompatibility, low toxicity, low cost, high performance in removal, easy availability and easy separation and synthesis.

New nanocomposite due to high absorption capacity compared to some of the above sorbents (Table 1), biocompatibility, easy separation with an external magnetic field, low toxicity, low cost, easy availability and environment friendly of tragacanth (Iran's largest producer of high-quality tragacanth) is a good adsorbent for methylene blue removal.

Parameters such as pH, contact time, initial dye concentration, absorbance dosage, temperature and thermodynamics of the adsorption process were tested. In addition, four isotherm models (Langmuir, Freundlich, Temkin and Dubinin–Radushkevich) and two models of adsorption kinetics (pseudo-first and pseudo-second order) were analyzed. Different techniques such as TEM, XRD, TGA, FTIR and VSM were used to identify NP_S.

Table 1 Comparison of the adsorption capacities of various adsorbents for methylene blue dye

Adsorbent	$q_{\max}$ (mg g ⁻¹)	References
ZnAPSO-34	14.49	[66]
γ -Fe ₂ O ₃ /SiO ₂	116.09	[67]
Carbon nanotube-biochar	6.2	[68]
Magnetic modified Fe ₃ O ₄	90.9	[69]
Magnetic carboxyl functional nanoporous	57.74	[70]
ZnFe ₂ O ₄ @SiO ₂ @Tragacanth gum	109.37	Present study

Materials and methods

Material and Devices

Zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), ethylene diamine (ED), sodium hydroxide (NaOH), ammonia solution 25%, tetraethyl orthosilicate (TEOS), ethanol (EtOH), potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), methyl methacrylate (MMA), ascorbic acid (AA), acetone and methylene blue colored powder were purchased from Merck company and used without purification. Tragacanth gum (TG) was prepared residential natural resources. Stock solution of MB dye was given by dissolving a certain amount of MB in distilled water. $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$ magnetic NC_s was characterized by FTIR, XRD, TEM, TGA and VSM patterns. Transmission electron microscopy (TEM) model Zeiss-EM10C-100 kV Germany, Fourier transform infrared spectroscopy (FTIR) model AVATAR370 made in USA, the X-ray diffraction device (XRD) model X' Pert Pro PANalytical company, UV–Vis spectrophotometer model (UV–Vis spectrophotometer T80+, PG Instrument Ltd), vibration test sample magnetometer (VSM) model 7400, thermogravimetric analysis (TGA) model STA1500 from Rheumatic scientific company were used as technical devices.

Preparation of the Adsorbent

Synthesis of $\text{ZnFe}_2\text{O}_4 \text{ NP}_s$

4.9 g of zinc nitrate $\text{Zn}(\text{NO}_3)_2$ and 13.4 g of iron (III) nitrate $\text{Fe}(\text{NO}_3)_3$ were dissolved in 50 mL deionized water (first solution). In the other balloon, 4.2 g of NaOH was dissolved in 70 mL distilled water and 3 mL ethylene diamine (ED) (second solution). Afterward, the first solution was added into the second solution. The solution was heated about 60 min at 90 °C. Then, the solution was washed several times by distilled water and ethanol. Synthesized $\text{ZnFe}_2\text{O}_4 \text{ NP}_s$ were put in the vacuum oven, for 7 h and in 80 °C. The powder was calcined for 1 h at 600 °C with a heating rate of 10 °C/min [34].

Synthesis of $\text{ZnFe}_2\text{O}_4@\text{SiO}_2 \text{ NP}_s$

0.5 g of $\text{ZnFe}_2\text{O}_4 \text{ NP}_s$ was added into 20 mL distilled water, 60 mL ethanol and 1 mL ammonia 25%. The mixture obtained was dispersed for 30 min in an ultrasonic bath. 0.5 mL of tetraethyl orthosilicate (TEOS) was mixed with 10 mL ethanol and was added dropwise to the solution of containing NP_s . The resulted solution was mixed up for 24 h at room temperature. At last, the solution was washed several times by distilled water and ethanol and NP_s were separated by magnet and they were dried in a vacuum oven at 80 °C and for 7 h [25].

Synthesis of $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$ magnetic NCs

Firstly, 1 g of TG was dissolved in 250 mL distilled water at 70 °C in a glass beaker. Then, 2 g of $\text{ZnFe}_2\text{O}_4@\text{SiO}_2$ NP_s was added to the solution under stirring at 1200 rpm. Afterward, 6 mL of methyl methacrylate (MMA) and 1.35 g of ascorbic acid (AA) were added, and the solution was mixed up for 30 min. Then, 1.35 g of $\text{K}_2\text{S}_2\text{O}_8$ was added to the solution and the solution was mixed up for another 1 h at room temperature. Finally, the sample was washed by acetone for several times and modified NP_s were separated by magnet. The sample was dried under vacuum at 60 °C for 6 h [29] (Fig. 2).

Adsorption experiments

All adsorption experiments were performed in laboratory scale and batch system in 250-mL Erlenmeyer flasks containing adsorbents and 50 ml of MB dye with different initial concentrations on a shaker with a stirring speed of 180 rpm. The effect of different parameters such as initial pH of the solution (2–12), initial concentration of dye (10–60 mg/L), contact time (5–120 min), adsorbent dose (0.2–2 g/L) and temperature (15–45 °C) on the removal efficiency and adsorption capacity by $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$ magnetic NC_s was studied. At the end of each experiment, the magnetic NC_s was separated by an external magnetic field and the remaining dye concentration was measured using UV/Vis spectrophotometer at a wavelength of 665 nm.

Efficiency and capacity of adsorption were calculated by Eqs. (1) and (2):

Fig. 2 Schema of synthesis of the methylene blue adsorption on $\text{ZnFe}_2\text{O}_4/\text{SiO}_2/\text{Tragacanth gum}$ magnetic nanocomposite

$$\% \text{ Removal} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{C_0 - C_e}{m} \times V \quad (2)$$

where C_0 and C_e are, respectively, the initial concentration and equilibrium in mg/L, q_e is the capacity of dye adsorption in mg/g, m is the mass of adsorbent in g and V is the volume of solution in L [35].

Determination of pH_{ZPC} of $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$ magnetic NCs

Fifty milliliters of deionized water was added to Erlenmeyer flasks, and then pH of deionized water in the range of 2 to 12 was set by HCL and NaOH 0.1 N. Afterward, 0.025 g of $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$ magnetic NCs was added to each one of Erlenmeyer flasks and was put on the shaker with 200 rpm for 24 h. After passing 24 h, the final pH of the solution was measured by pH meter. A pH at a point where the initial pH of the solution crossovers the final pH equilibrated by an amount of an adsorbent is related to as the pH_{ZPC} .

Results and Discussion

Characteristics of adsorbent

FTIR analysis

Figure 3 shows the FTIR spectra of ZnFe_2O_4 , $\text{ZnFe}_2\text{O}_4@\text{SiO}_2$ NPs and $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$ magnetic NCs. In the FTIR spectrum of ZnFe_2O_4 NPs (Fig. 3a), peaks

Fig. 3 FTIR spectra of (a) ZnFe_2O_4 , (b) $\text{ZnFe}_2\text{O}_4@\text{SiO}_2$, (c) $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$

appeared at wavelengths 453 and 562 cm^{-1} are, respectively, related to tensile vibrations of Zn–O and Fe–O. As well as, created vibrations in 3405 cm^{-1} are related to the tensile vibrations of O–H [36, 37]. Furthermore, vibrational peaks in 1087 and 959, respectively, are related to Si–O–Si and Si–OH [38, 39], showing the silica coating on ZnFe_2O_4 NP_S (Fig. 3b). In the FTIR spectra related to $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$ magnetic NC_S (Fig. 3c), in addition to listed vibrational peaks, other main vibrational peaks in 2945, 1746 and 1638 cm^{-1} are, respectively, related to tensile vibrations C–H, C=O and C=C. The adsorption peaks in wavelengths of 1228 and 1138 cm^{-1} are related to tensile vibrations of C–O [40]. Vibrational bands in (2945, 1746, 1638, 1228 and 1138 cm^{-1}) are reason to fixation of TG cover on $\text{ZnFe}_2\text{O}_4@\text{SiO}_2$ magnetic NC_S.

XRD analysis

Figure 4 shows the XRD patterns of ZnFe_2O_4 , $\text{ZnFe}_2\text{O}_4@\text{SiO}_2$ NP_S and $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$ magnetic NC_S. Figure 4a shows the cubic spinel structure of ZnFe_2O_4 with Fd-3m space group. The medium ZnFe_2O_4 NP_S size was calculated to be about 12 nm according to characteristics of the main peak (311) and using Scherer equation. The XRD pattern of $\text{ZnFe}_2\text{O}_4@\text{SiO}_2$ NP_S (Fig. 4b) showed a broad peak in $2\theta=20\text{--}27$ which is related to the amorphous of SiO_2 shells [26]. Also, the medium $\text{ZnFe}_2\text{O}_4@\text{SiO}_2$ NP_S size was calculated to be about 15 nm. In the XRD pattern of $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$ magnetic NC_S (Fig. 4c) presence 2θ in angle of 30.88 relate to amorphous of TG [41]. The medium $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$ magnetic NC_S size was calculated to be about 24 nm.

TEM analysis

Figure 5 shows the TEM image of ZnFe_2O_4 , $\text{ZnFe}_2\text{O}_4@\text{SiO}_2$ NP_S and $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$ magnetic NC_S with the average size of 13, 17 and 25 nm, respectively, which is similar to the XRD results. Also, the successful coatings of SiO_2 and TG

Fig. 4 XRD pattern of (a) ZnFe_2O_4 , (b) $\text{ZnFe}_2\text{O}_4@\text{SiO}_2$, (c) $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$

Fig. 5 TEM images of (a) ZnFe_2O_4 , (b) $\text{ZnFe}_2\text{O}_4@\text{SiO}_2$, (c) $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$

on the surface of NP_S and cube structure of ZnFe_2O_4 NP_S and branched structure of TG are shown.

VSM analysis

Figure 6 shows the VSM pattern of ZnFe_2O_4 , $\text{ZnFe}_2\text{O}_4@\text{SiO}_2$ NP_S and $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$ magnetic NC_S . The VSM patterns of ZnFe_2O_4 nanoparticle (Fig. 6a) show that these NP_S have paramagnetic behavior at room temperature and can be separated with a magnet. Amount of saturated magnetism for ZnFe_2O_4 NP_S equals 19.325 emu/g. With surface modification of ZnFe_2O_4 NP_S by silica (Fig. 6b), yet these NP_S at the room temperature show paramagnetic behavior and can be separated with an external magnet. The amount of saturated magnetism for $\text{ZnFe}_2\text{O}_4@\text{SiO}_2$ NP_S equals 15.363 emu/g. Also, the amount of saturated magnetism of $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$ magnetic NC_S equals 6.1657 emu/g (Fig. 6c). Although the amount of saturated magnetism has dropped in this magnetic NC_S but, this magnetic NC_S shows paramagnetic behavior at room temperature and can easily be separated by an external magnet.

Fig. 6 VSM pattern of (a) ZnFe_2O_4 , (b) $\text{ZnFe}_2\text{O}_4@\text{SiO}_2$, (c) $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$

TGA analysis

The TGA thermograms of ZnFe_2O_4 , $\text{ZnFe}_2\text{O}_4@\text{SiO}_2$ NP_s and $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$ magnetic NC_s are shown in Fig. 7. The TGA of ZnFe_2O_4 NP_s (Fig. 7a) shows a weight loss at 25 to 434 °C of about 1.97% due to evaporation of ethanol, water and crystal structure of ZnFe_2O_4 NP_s [26, 42]. Significant weight loss was observed in the temperature range of 434 to 800 °C. The TGA thermogram of the $\text{ZnFe}_2\text{O}_4@\text{SiO}_2$ NP_s (Fig. 7b) shows the weight loss in two stages. The first weight loss stage in the temperature ranges from 25 to 155 of about (1.45%) due to loss of water present on the surface of the NP_s [43]. The two weight loss step ranges between 155 and 450 °C of about 1.25% due to the evaporation water molecules and additional compounds [44]. Significant weight loss was observed in the temperature range of 450 to 800 °C. The thermogram of $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$ magnetic NC_s (Fig. 7c) shows the weight loss in four steps. The first weight loss is between 25 and 193 of about 3.2%, due to loss of water, methyl methacrylate and the remaining solvent [28]. Most weight loss in the second stage is between 193 and 390 °C of about 22.37%, due to TG link and methyl methacrylate decomposition [29, 31]. The third step of weight loss is due to decomposition of TG branched structure about 4.55% between 390 and 606 °C [31]. The fourth stage of the weight loss is about 10.43 in the range of 606–800 °C that probably is due to the oxidation of metal oxides [43].

Effect of pH on adsorption

pH is one of the basic parameters that should be considered in analyzing sorbate–sorbent systems and determining the mechanisms of adsorption process, because it affects both the water chemistry and the adsorbent binding sites [45]. In the present study, the effect of pH on the removal of MB dye was investigated in the range of pH = 2–12 with an initial dye concentration of 10 mg/L and adsorbent mass of 0.02 g in 50 mL of coloring solution for 60 min (Fig. 8). With increasing pH from 2 to 8, the efficiency and adsorption capacity increase, so that at pH = 8, the highest removal efficiency and adsorption capacity are observed

Fig. 7 TGA spectra of (a) ZnFe_2O_4 , (b) $\text{ZnFe}_2\text{O}_4@\text{SiO}_2$, (c) $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$

Fig. 8 Effect of pH on the removal of MB using $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$ ($v=50$ mL, adsorbent mass 0.02 g, $C_0=10$ mg/L, $t=60$ min)

and after $\text{pH}=8$, the efficiency and adsorption capacity remain almost constant. The reason for this is related to the adsorbent pH_{zpc} , pK_{a} and the MB dye cationic structure. pH_{zpc} is one of the parameters that can be used in the adsorption process. In the present study pH_{zpc} of $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$ magnetic NC_S was determined to be 6.86 (Fig. 9). MB is a cationic dye with pK_{a} equal to 3.8 [46]. The increase in efficiency in alkaline pH is due to increased hydroxyl (OH^-) ions and increasing electrostatic gravity between the positive and negative charges of adsorption sites [47]. On the other hand, considering that $\text{pH} > \text{pK}_{\text{MB}}$ and $\text{pH} > \text{pH}_{\text{zpc}}$, consequently, the dominant surface charge on the MB dye surface is positive and the surface load of $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$ magnetic NC_S is negative at pH values higher than pH_{zpc} . Therefore, due to the cationic nature of MB dye, the electrostatic gravity of the adsorbent and pollutant increases and the removal efficiency and adsorption capacity increase. In contrast, at pH less than pH_{zpc} adsorbent surface charge and MB dye is positive and by increasing electrostatic repulsion force between the adsorbent and the contaminants removed and adsorption capacity decreases [46, 48]. The results of this study are consistent with the results of studies conducted by Mulugeta and Coskun in 2013 and 2017 [49, 50].

Fig. 9 pH_{zpc} curve of $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$ ($V=50$ mL, adsorbent mass 0.025 g, time 24 h)

Effects of contact time and concentration on the removal of dye

The effect of contact time on the MB dye adsorption in the range of 5 to 120 min at pH=8 and 50 mL of MB colored solution with an adsorbent mass of 0.02 g at 10, 20, 30, 40, 50 and 60 mg/L concentrations was tested (Fig. 10). According to the results, with increasing initial dye concentration, the dye adsorption decreases, but the adsorption capacity increases in such a way that the adsorption of MB by $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$ magnetic NC_s after 60 min reaches at all concentrations equilibrium. This is due to an increase in the number of dye molecules to bind to existing positions on the surface of the adsorbent and to reduce the inter-particle penetration and to increase the effective collision of MB molecules and adsorbent particles [51]. On the other hand, the adsorption of MB in the early stages of the reaction is rapid, and then it is slowed down near equilibrium, which is due to the abundance of empty surface sites in the early stages of adsorption. With the passage of time, the occupancy of the remaining vacant sites increases due to the repulsive forces between the MB and the adsorbent molecules and, as a result, adsorption decreases [52]. Similar results were observed in 2015 by Seidmohammadi and et al. [47].

Effect of Adsorbent dosage on adsorption

Figure 11 shows the effect of adsorbent dosage on the adsorption capacity and efficiency of MB dye indicated by $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$ magnetic NC_s. Increasing the adsorbent dosage from 0.2 to 2 g/L increased the removal of MB because increasing the adsorbent dosage increases the available and active adsorption sites for the interaction between sorbate and sorbent. Also, increasing the amount of adsorbents from 0.2 to 2 g/L led to a decrease in absorbed capacity, because with increasing adsorbent dose, unsaturated residual adsorption sites reduce adsorption capacity during adsorption [53]. The results of studies conducted by Seidmohammadi et al. in 2015 and Gupta et al in 2014 are consistent with the result of study [47, 54].

Fig. 10 Effect of contact time and initial concentration on the adsorption of MB using $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$ (pH=5, V=50 mL, adsorbent mass=0.02 g)

Fig. 11 Effect of adsorbent dosage on the removal and adsorption capacity of MB using $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$ (pH=5, $V=50$ mL, time=90 min, $C_0=60$ mg/L)

Adsorption Isotherms

The adsorption isotherms of $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$ magnetic NCs MB dye were investigated, and the data were analyzed by Langmuir and Freundlich, Temkin and Dubinin–Radushkevich equations.

Theoretical Langmuir isotherm describes monolayer adsorption of adsorbate onto a homogeneous adsorbent surface [1]. The linear equation of Langmuir is defined in Eq. (3):

$$\frac{C_e}{q_e} = \frac{1}{K_1 q_m} + \frac{C_e}{q_m} \quad (3)$$

where C_e is the equilibrium concentration of adsorbate (mg/L), q_e is the amount of absorbed matter in equilibrium time (mg/g), K_1 is the Langmuir constant (L/mg) and q_m is the maximum amount of adsorption of amount of adsorbed dye in mg/g monolayer (mg/L).

The main feature of Langmuir equation is separation factor (R_L) that is defined in Eq. (4)

$$R_L = \frac{1}{1 + bC_0} \quad (4)$$

where b is Langmuir constant (L/mg), R_L indicates type of isotherm—favorable adsorption $0 < R_L < 1$, unfavorable adsorption $R_L > 1$, linear adsorption $R_L = 1$ and irreversible adsorption $R_L = 0$ [3].

The Freundlich isotherm model is based on heterogeneous surface that has unequal energies [55]. Its empirical equation is defined in Eq. (5):

$$\log q_e = \log K_f + 1/n \log C_e \quad (5)$$

where n is the indicator of the desirability extent of adsorption process and K_f is the amount of capacity of adsorbent adsorption in (mg/g (L/mg) $^{1/n}$) [35].

In order to estimation of porosity and free energy used to of adsorption, Dubinin Radushkovich model was investigated [56]. The linear equation of this model is defined in Eq. (6):

$$\ln(q_e) = \ln(q_m) - \beta \epsilon^2 \quad (6)$$

where q_m is the maximum amount of adsorption (mg/g), β (constant of the equation) porosity factor and ϵ Polanyi potential that is defined by Eq. (7):

$$\epsilon = RT \ln \left[1 + \frac{1}{C_e} \right] \quad (7)$$

where R is the global constant of gas ($R = 8.3144 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the temperature (in Kelvin).

The Temkin isotherm model shows between adsorbate/adsorbate interactions, and linear form of Temkin isotherm is given in Eq. (8):

$$q_e = B \ln A_T + B \ln C_e \quad (8)$$

where B is the constant of Temkin (KJ/mol) and A_T is the connection constant of Temkin equation (L/g) [56, 57].

According to the isothermal charts (Fig. 12) and the results obtained from Table 1, Freundlich isotherm shows the best interpretation of the MB adsorption using $\text{ZnFe}_2\text{O}_4/\text{SiO}_2/\text{TG}$ magnetic NCs. Therefore, the results indicate that the adsorbent level is non-homogeneous or heterogeneous and has unequal and

Fig. 12 Adsorption isotherm models of MB adsorption using $\text{ZnFe}_2\text{O}_4/\text{SiO}_2/\text{TG}$. **a** Langmuir, **b** Freundlich, **c** Temkin, **d** Dubinin–Radushkevich

non-uniform energies. The parameter $1/n$ and n in the Freundlich equation can determine the desirability of the adsorption process. If $1/n$ is less than 1 and n is between 1 and 10, it indicates that the adsorption process is desirable by Freundlich isotherm model [58]. According to Table 2, the value of n is between 1 and 10; also, the value of $1/n$ is less than 1, which indicates the desired adsorption of MB using $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$ magnetic NCs. The results of studies conducted by some researchers in 2017 are consistent with the present study [59, 60].

Adsorption kinetics models

Kinetic models are used to define the speed of the adsorption process and how this speed controls the equilibrium time. Two kinetic models were studied: pseudo-first order and pseudo-second order. These models are the most used to describe dye (Fig. 13). The pseudo-first-order kinetic model is used more for lower concentrations of solute. The linear forms of pseudo-first-order and pseudo-second-order kinetics are defined in Eqs. (9) and (10):

$$\log(q_e - q_t) = \log q_e - K_1/2.303 \quad (9)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e} + \frac{t}{q_e} \quad (10)$$

where q_e is the amount of adsorbed MB at equilibrium time (mg/g), q_t is the amount of adsorbed MB at time (mg/g), K_1 (1/min) is the constant of pseudo-first-order kinetic and K_2 (g/mg min) is the constant of pseudo-second-order kinetics [2, 61].

In this study, two kinetic adsorption pseudo-first-order and pseudo-second-order kinetic models have been investigated by kinetics study in different initial concentrations of adsorbent material MB dye using $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$ magnetic NCs. The comparison of the R^2 coefficients in the two kinetic models studied shows that the MB dye adsorption process is matched using $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$ magnetic NCs from the pseudo-second-order equation. Also, according to the results obtained (Table 2), the adsorption capacity, which is calculated by considering the kinetic equations ($q_{e, \text{cal}}$), is closer to the adsorption capacity obtained from the adsorption experiment ($q_{e, \text{exp}}$)

Table 2 Coefficients of isotherm models of MB adsorption using $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$

Models	Isotherm constants		Models	Isotherm constants	
Langmuir	q_{max} (mg/g)	97.087	Temkin	A_T (L/mg)	0.74
	K_L (L/mg)	0.072		B_T (J/mol)	20.99
	R_L	0.303		R^2	0.973
	R^2	0.972	Dubinin–Radushkevich	B (mol ² /kJ ²)	− 13.77
Freundlich	K_f	2.797		E (kJ/mol)	0.19
	$1/n$	0.549		R^2	0.87
	n_F	1.821			
	R^2	0.979

Fig. 13 Adsorption kinetic models of MB adsorption using ZnFe₂O₄@SiO₂@TG. **a** Pseudo-first-order kinetics model, **b** pseudo-second-order kinetics model

in the pseudo-second-order kinetic model. This also confirms the adherence of the adsorption process to the pseudo-second-order kinetic model. Therefore, chemical adsorption is a process-limiting step which is suggested to evaluate the reaction speed of this model. In studies conducted in 2017, various researchers reported similar results [62, 63].

The effect of temperature and thermodynamics on adsorption

The experiment with keeping constant of optimal parameters (pH, contact time, adsorbent dosage and dye concentration) was performed at temperatures of 15, 25, 35 and 45 °C. Thermodynamic parameters related to the adsorption process, Gibb's free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) are determined by Eqs. (11) to (13):

$$\Delta G = \Delta H - T\Delta S \quad (11)$$

$$\Delta G = -RT\ln(K) \quad (12)$$

Fig. 14 Effect of temperature and thermodynamic on MB dye adsorption using $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$

Table 3 Kinetic constants for MB dye adsorption

C_0 mg/L	$q_{e, \text{exp}}$ mg/g	Pseudo-first-order kinetic			Pseudo-second-order kinetic		
		K_1 min^{-1}	$q_{e, \text{cal}}$ mg/g	R^2	K_2 $\text{g mg}^{-1} \text{min}^{-1}$	$q_{e, \text{cal}}$ mg/g	R^2
10	17.74	-0.004	0.47	0.13	-0.12	15.8	0.991
20	33.92	-0.017	0.90	0.54	0.02	33.4	0.994
30	42.21	-0.008	0.83	0.23	-0.03	39.5	0.994
40	53.87	-0.012	1.14	0.58	0.01	54	0.998
50	62.11	-0.009	1.10	0.45	0.03	60.2	0.998
60	70.33	-0.014	1.31	0.61	0.01	69.9	0.998

$$\text{Ln}(K) = \frac{\Delta S}{R} - \frac{\Delta H}{R} \times \frac{1}{T} \quad (13)$$

where K indicates the equilibrium adsorption constants of the isotherm fits, R is the universal gas constant ($R = 8.3144 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the absolute temperature in Kelvin [53].

Figure 14a shows the effect of temperature on the MB dye adsorption capacity using $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$ magnetic NCs. Based on the results, when the temperature rises from 14 to 45, the adsorption capacity increases, which may be due to increased solubility of the dye with increasing temperature; in addition, it increases the collision between adsorbents and agglomerate and increases the size. The pores are absorbed by the surface and thus increase the adsorption capacity [47].

Thermodynamic parameters including Gibbs free energy (ΔG , kJ/mol), enthalpy (ΔH , KJ/mol) and entropy (ΔS , $\text{J.mol}^{-1} \text{ K}^{-1}$) were investigated to describe and confirm the mechanism of absorbing the MB dye using $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$ magnetic NCs (Fig. 14b and Table 3). According to Table 3, ΔG is negative at all temperatures, which indicates self-sustaining adsorption processes.

Table 4 Thermodynamic parameters of MB adsorption using $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$

	ΔG (KJ/mol)				ΔH KJ/mol	ΔS J mol ⁻¹ K ⁻¹
Temperature K	288	298	308	318		
	-2.4	-2.7	-3.3	-3.5	9.36	40.72

In addition, increasing free energy with increasing temperature indicates that the process is more favorable at higher temperatures. The amount of free energy can also determine the type of physical or chemical adsorption process. If ΔG rate is between 0 and -20 kJ/mol, the adsorption process is a physical type, but if ΔG is between 80 and -400 kJ/mol, the adsorption process is a chemical type. When ΔG is less than -20 kJ/mol, the adsorption process is a physical type. The positive amount of enthalpy also shows that the MB adsorption reaction on the adsorbent is physical and endothermic. If $\Delta H < 25$ kJ/mol, the adsorption reaction is physical and if $\Delta H > 40$ kJ/mol, the adsorption reaction is chemical. Positive entropy values indicate that the disorder of the dye molecules and the adsorbent in the solution increases during the adsorption process of MB on the adsorbent [64, 65] (Table 4).

Conclusion

In this study, $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$ magnetic NC_s was synthesized and identified using various methods such as FTIR, XRD, TEM, VSM and TGA. Then, the efficiency of the synthesized magnetic NC_s was investigated in the removal of MB from aqueous solutions. Various variables including pH, initial concentration of dye, adsorption dosage, temperature and contact time were tested, and optimum conditions were determined. Under optimal conditions—the pH=8, the contact time of 60 min, the initial radiation dose of 60 mg/L and the absorbance dose of 0.2 g/L, the maximum adsorption capacity was 109.37 mg/g. In the following, four isotherm models (Langmuir, Freundlich, Temkin and Dubinin–Radushkevich) were investigated in the adsorption of MB using $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$ magnetic NC_s , and the balance data were Langmuir isotherm model. The kinetic adsorption analysis showed that pseudo-second-order reactions can be used to predict adsorption kinetics. Thermodynamic parameters showed that the adsorption of MB is self-sustaining. As a result, due to the high absorption capacity of the nanocomposites compared with some absorbents and environment friendly, low cost, rapid extraction and non-toxicity, $\text{ZnFe}_2\text{O}_4@\text{SiO}_2@\text{TG}$ magnetic NC_s can be used as an effective adsorbent to remove MB from aqueous solutions.

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