IRON-TANNIC ACID NANOCOMPLEXES: FACILE SYNTHESIS AND APPLICATION FOR REMOVAL OF METHYLENE BLUE FROM AQUEOUS SOLUTION

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In this study, iron-tannic acid nanocomplexes (iron-TA) was synthesized by a simple precipitation method and were used as novel adsorbents for the removal of Methylene blue (MB) dye from water. The structure, crystallinity and surface functionality of as-prepared nanocomplexes were characterized by X-ray diffractometer (XRD) and Fourier transform infrared spectroscopy (FTIR). The effects of various parameters such as pH, adsorbent dosage, contact time, ionic strength, and temperature on MB adsorption were investigated. Results showed that the adsorption of MB on iron-TA was found to be dependent on pH and temperature, while increasing ionic strength decreased the adsorption of MB on iron-TA. Adsorption equilibrium was achieved in 4 h and the adsorption kinetics of MB was found to follow a pseudo-second-order kinetic model. Equilibrium data for MB adsorption were fitted well by Sips isotherm model. The maximum adsorption capacity for MB was estimated to be 67.41 mg/g at 313 K. Furthermore, thermodynamic parameters exhibited the feasibility, spontaneity and endothermic nature of the adsorption process. FTIR study revealed that the hydroxyl groups of iron-TA might be involved into electrostatic interaction with MB. The results suggested that the iron-TA would be an excellent alternative for the removal of MB by adsorption process.

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1. Introduction

Dyes are colour organic compounds which can colorize the other substances. It is estimated that the annual dye production in the world exceeds 700,000 tons and more than 10,000 commercially available dyes of different chemical and physical properties are being used [1]. These dyes are widely used in many industries such as the textile, leather, food, dyeing, cosmetics and paper, which can generate a large amount of coloured wastewater [2]. Because many organic dyes are harmful to human beings and hazardous to aquatic organisms, removal of dyestuffs from wastewater has received considerable attention over the past decades. Methylene blue (MB) is a cationic dye that can be widely used in medical science, coloring paper, dying cotton, wood and silk, etc [3]. Due to its known strong adsorption onto solids, MB often serves as a model

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compound for removing dyes and organic contaminants from aqueous solution [1]. Although MB is not strongly hazardous, MB can have some harmful effects on human beings [4]. Therefore, an increased interest has been focused on the removal of MB from the wastewater.

Numerous approaches have been implemented to treat the dye-containing wastewater, including ion-exchange, coagulation/flocculation, chemical oxidation, ozone treatment, membrane filtration, photocatalysis, adsorption, and so forth [5-7]. However, it is worthwhile to note that the dyes often include a broad spectrum of different chemical structures, primarily based on the substituted aromatic and heterocyclic groups [8]. Due to the complex chemical structure of these dyes, they are resistant to breakdown by chemical, physical and biological treatments. Furthermore, any degradation by physical, chemical or biological treatments may produce small amount of toxic and carcinogenic products [9]. In contrast with other methods, a great deal of attention has been paid to the adsorption method due to its high efficiency, low cost, simplicity of design and ease of operation. In particular, adsorption of MB and other dyes by using clay as low-cost adsorbents gained significant importance in recent years. For example, the adsorption of MB by laponite [10], kaolinite [11], montmorillonite [12], sepiolite [13], and swelling clays [14] have been reported in previous work. Nevertheless, applications of these materials in adsorption dye pollutants are being limited because of their low adsorption capacity. On this basis, several studies have explored the potential of combining conventional adsorbents with humic acid (HA), fulvic acid (FA) and tannic acid (TA) or other natural organic matter (NOM) to enhance the adsorption ability towards MB. Highly efficient adsorption of MB by humic acid (HA) immobilized pillared clay [15], HA-immobilized amine modified polyacrylamide/bentonite composite [16], HA immobilized polymer/bentonite [17], and TA modified super paramagnetic Fe_3O_4 nanoparticles [18], have been intensively studied. In addition, MB removal by peat has also been reported [19]. It is considered that peat contains about 65% of organic matter, and major constituents of peat are lignin, cellulose, HA and FA, which bear a number of polar functional groups, such as alcohols, aldehydes, ketones, carboxylic acids and phenolic hydroxides, which may bond with adsorbed pollutant species [20]. Moreover, it has been reported that the isoelectric point of NOM is around pH 2.0, and thus they carry a net negative charge over the usual pH values [21]. Therefore, it could be concluded that NOM played a positive role in MB adsorption, which should be attributed to the fact that negatively charged NOM had great affinities to cationic MB.

However, as a class of dissolved NOM, bare HA, FA or TA could not be used directly as adsorbents due its high water solubility in a wide pH range. In order to exploit the full advantages of the NOM in terms of adsorption ability towards MB and other pollutants, there are two basic strategies: either immobilization/modification of NOM on other solid adsorbents [15-18,22-29], or the soluble NOM reacts with polyvalent metal cations to form less soluble metal-NOM complexes [30-35]. Recently, the latter method has received considerable attention since metal-NOM complexes can be prepared in a relatively simple way by a precipitation of NOM with suitable metal compounds. Particularly, precipitation of NOM with iron salts is considered to be one of the most promising technique to produce metal-NOM complexes. For example, a stable form of iron humate has been prepared by the precipitation with an aqueous solution of iron sulfate and used as an efficient adsorbent for the removal of MB from aqueous solution [32]. In our previous work, iron humate was successfully applied as a novel adsorbent for the removal of aqueous p-arsanilic acid [35]. Elmorsi [30] reported the efficient adsorption of crystal violet dye by titanium(III)-tannate nanocomplex. By contrast, the precipitation of TA with iron salts and the utilization of iron-tannic acid (Iron-TA) nanocomplexes in adsorption of contaminants are still limited [31,36].

TA, as a humic substance, is one of the NOM found in surface water as a result of decaying vegetation in soil, gallic acid being the basic building block of the decomposition products [37]. It contains several o-dihydroxy and trihydroxy aromatic rings (polyhydroxy polyphenols), and has attracted much attention because of the antimicrobial and anticorrosive activities in aqueous solution, as well as its specific affinities to various contaminants [26]. Nevertheless, TA is a water-soluble compound and has the disadvantage of being leached by water when used directly as an adsorbent [29]. In contrast, iron-TA nanocomplexes can probably be used

In this study, iron-TA nanocomplexes were prepared by a simple precipitation method and characterized by Fourier transform infrared (FTIR) spectrometry and powder x-ray diffraction (XRD). The objectives of this work are the following: (i) to characterize the surface physical and chemical properties of iron-TA; (ii) to investigate the effects of pH, adsorbent dosage, contact time, ionic strength, and temperature on adsorption of MB by iron-TA; (iii) to analyze the adsorption kinetics and equilibrium isotherms of MB by iron-TA; and (iv) to evaluate the adsorption mechanisms of MB onto iron-TA.

2. Materials and methods

2.1. Materials

For the preparation of HAP iron-TA nanocomplexes, analytical grade iron(III) nitrate nonahydrate and TA ($C_{76}H_{52}O_{46}$, molar mass: 1701.18 g/mol) were purchased from Shanghai Guoyao Chemical Company (China). MB, a cationic dye with molecular formula ($C_{16}H_{18}ClN_3S\cdot 3H_2O$) as shown in Figure 1 was supplied by Sigma-Aldrich (St. Louis, MO, USA), and used as adsorbate without any further purification. Milli-Q water was used throughout this study.



Fig. 1. The molecular formula and UV-visible spectrum of methylene blue.

2.2. Preparation and characterization of iron-TA nanocomplexes

The solid iron-TA used in this study were prepared by a precipitation method according to the previous work with a little modification [30,31]. While a brief description of the experimental procedure is given below. An aqueous TA (100 mL, 0.1 mol/L) solution was added dropwise to a stirred solution of 200 mL 1.0 mol/L iron(III) nitrate at room temperature, then the pH of the mixture was adjusted to 7.0 by using 0.1-0.5 mol/L sodium hydroxide. The suspensions were agitated for 2 h and then centrifuged and the recovered precipitate was washed with deionized water several times. The obtained solid materials were freeze-dried, ground, and stored for future experiments.

The crystal structure of the synthetic iron-TA nanocomplexes was analyzed by XRD (Rigaku D/max-IIIB, Rigaku, Japan) in scan mode with Cu K α (λ =1.5405 Å) radiation in the 2 θ range of 10° to 70°. The functional groups in the synthesized iron-TA were characterized through the analysis of FTIR (Nicolet iS5, Thermofisher, USA) using KBr pellet in the range of 400 to 4000 cm⁻¹.

2.3. Adsorption experiments

Batch adsorption experiments were carried out in a series of conical flasks (250 mL). A given dose of adsorbents (iron-TA nanocomplexes) were added to 100 mL MB solution with given

concentrations and pH values in a thermostatic air bath shaker at shaking rate 180 rpm. HNO₃ (0.1 mol/L) and NaOH (0.1 mol/L) were used to adjust the pH value of working solution. The pH value of the solution was measured with a model 868 pH meter (Orion, USA) using a combined glass electrode. MB concentration was measured by a UV-Vis spectrophotometer (UV-2450, Shimadzu, Japan) at $\lambda_{max} = 663$ nm. The effect of pH on the λ_{max} of MB was also studied in our preliminary experiments, and the maximum absorption peak position of MB did not change with the change in pH. The adsorption time between adsorbents and the MB solution was 4 h, which was considered as the adsorption time of adsorption equilibrium status, then the solid material was separated by centrifugation. The equilibrium adsorption capacity, $q_e (mg/g)$ and removal rate (%), are expressed as follows: $q_e = (C_0 - C_e)V/m$ and removal rate (%) = $(C_0 - C_e)/C_0$, where C_0 and C_e are the initial and equilibrium concentrations of MB (mg/L) in solution; V (L) is the volume of aqueous solution containing MB; and m (g) is the weight of adsorbent. All assays were carried out in triplicate and only mean values were presented.

2.4. Mathematical Models

The modeling of the adsorption kinetics of MB onto iron-TA was investigated by three common models, namely, the Lagergren pseudo-first-order model (Eq. (1)) [38], Ho's pseudo-second-order model (Eq. (2)) [39], and the Elovich model (Eq. (3)) [40]. The pseudo-first-order reaction equation of Lagergren is widely used for the adsorption of liquid/solid system on the basis of solid capacity. This model assumes that the rate of change of surface site concentration is proportional to the amount of surface sites remaining unoccupied [41]. The pseudo-second-order model includes all the steps of adsorption including external film diffusion, adsorption, and internal particle diffusion. This model assumes that the differences between the average solid phase concentration at time t (min), q_t (mg/g), and the equilibrium concentration, q_e (mg/g), are the driving force for adsorption and the overall adsorption rate is proportional to the square of the number of remaining free surface sites [42]. In reactions involving chemisorption of adsorbate on a solid surface without desorption of products, adsorption rate decreases with time due to an increased surface coverage, which can be described by the Elovich equation [43]. These kinetic models are represented by:

$$q_t = q_e (1 - \exp(-k_1 t))$$
(1)

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{2}$$

$$q_t = \frac{1}{\beta} \ln(1 + \alpha \beta t) \tag{3}$$

where $q_t \pmod{g}$ is the amount of MB adsorbed onto adsorbent at time t; $k_1 \pmod{1/\min}$ and $k_2 \binom{g}{(\text{mg} \cdot \text{min})}$ are the rate constants for the pseudo-first-order and pseudo-second-order models, respectively; $q_e \pmod{g}$ is the amount of adsorbate adsorbed per unit adsorbent at equilibrium; α is the initial MB adsorption rate for the Elovich model $(\text{mg}/(\text{g} \cdot \text{min}))$, and β is the desorption constant (g/mg).

The nonlinear Langmuir (4) [44], Freundlich (5) [45] and Sips (6) [46] isotherms are represented by:

$$q_e = \frac{q_{mK_L C_e}}{1 + K_L C_e} \tag{4}$$

$$q_e = K_F C_e^{1/n} \tag{5}$$

$$q_e = \frac{q_m (K_S C_e)^{1/n}}{1 + (K_S C_e)^{1/n}} \tag{6}$$

where K_L (L/mg), K_F [mg/g(L/mg)^{1/n}] and K_S (L/mg) are the equilibrium constants of Langmuir, Freundlich and Sips models, respectively; $q_e(mg/g)$ is the adsorption capacity at equilibrium; C_e (mg/L) is the equilibrium concentration of MB in solution; q_m (mg/g) is the maximum adsorption capacity, and 1/n is the heterogeneity factor.

3. Results and discussion

3.1. Characterization of iron-TA nanocomplexes

The X-ray powder diffractograms of TA and iron-TA nanocomplexes are shown in Fig. 2. No discernible peaks of crystalline phase were observed in the XRD pattern of TA, but characteristic data, $2\theta = 25.2^{\circ}$, indicating the amorphous nature of TA, which was similar with previous work [31]. On the contrary, the XRD pattern of the iron-TA showed slight background between $2\theta = 15^{\circ}$ to 30° , likely attributable mainly to tannate, which suggested the presence of a largely nanocrystalline, tannate phase in the samples. Similar findings have been reported by Elmorsi [30] and Zhang et al. [31] who also indicated that titanium tannate nanocomplexes and ferric tannate had very poor crystallinity. In the present study, however, it was noteworthy that the synthetic iron-TA showed crystalline diffraction peaks at $2\theta = 14.1^{\circ}$, 27.0° , 36.3° , 46.8° , 52.7° and 60.3° were observed clearly. They could be consistently indexed with the (200), (210), (301), (020), (511), and (002) planes of the unit cell of lepidocrocite (γ -FeO(OH), respectively, which revealed that the presence of γ -FeO(OH) (JCPDS # 44-1415) in the iron-TA samples [47-51]. These results showed that the synthetic iron-TA nanocomplexes were probably present as organic-inorganic composites.



Fig. 2. The XRD patterns of TA, prepared iron-TA nanocomplexes and the reference pattern of pure lepidocrocite (JCPDS # 44-1415).

The FTIR spectra of TA, iron-TA nanocomplexes, MB laden iron-TA and MB are shown in Figure 3. It was found that the spectra of TA and iron-TA showed a strong absorption around 3700 and 3000 cm⁻¹ with a wide and strong band centered at 3401 and 3378 cm⁻¹, respectively. These bands were assigned to the hydroxyl (OH) groups stretching vibrations and due to the wide variety of hydrogen bonding between OH [52]. The absorption bands between 1713 and 1447 cm⁻¹ were characteristic of aromatic compounds, which have been reported intensively in literature [53-55]. The adsorption band at 1713 cm⁻¹ was due to the stretching vibration of the carbonyl (C=O) groups. The aromatic C-O symmetrical stretch was located at 1612 cm⁻¹; The bands observed around 1447 and 1532 cm⁻¹ were assigned to the aromatic ring C=C stretching; Various peaks in the range of 1000-1300 cm⁻¹ and smaller peaks between 750 and 900 cm⁻¹ correspond to substituted benzene rings [53]. While the band at 1322 cm⁻¹ exhibited a characteristic bending vibration of C-O in a phenolic hydroxyl group [31,52].



Fig. 3. The FT-IR spectra of TA, prepared iron-TA, MB laden iron-TA and MB.

The FTIR spectrum of iron-TA nanocomplexes was similar to TA showing a broad absorption band between 3700 and 2600 cm⁻¹, which was attributed to the OH stretching for the hydrogen bond with the physical adsorbed water molecules. There were some strong adsorption bands typical of poly(hydroxyl) compounds assigned to OH bending and C-OH stretching vibrations, and several other peaks characteristics of skeletal vibrations, aromatic compounds and substituted benzene rings [56]. However, for the prepared iron-TA nanocomplexes, several of the peaks not only shifted slightly, but reduced in intensity. For instance, the C=O stretching band of the carbonyl group at around 1713 cm⁻¹ (TA) decreased and shift to lower wave numbers at around 1701 cm⁻¹ for iron-TA. The interaction between Fe³⁺ and the phenolic hydroxyl group had an effect on the C-O bond stretching vibration, in which the band was shifted from 1322 cm⁻¹ in the spectrum of TA to 1328 cm⁻¹ in the spectrum of the iron-TA [31]. Moreover, the peaks occurring between 1000 and 1700 cm⁻¹ were very broad in the iron-TA sample due to the amorphous nature of the nanocomplexes [47]. It was considered that these changes in FTIR spectrum of iron-TA could be attributed to the complexation of TA and ferric iron ions. Özacar and Sengil [57] reported that the hydroxyl groups included in TA offered special opportunities for the formation of metal complexes. Iron could form complexes with the phenolics with two adjacent hydroxyls (catechols), and the presence of a third adjacent hydroxyl (pyrogallols) increased the stability of the complex. Similar results have been obtained by Oladoja et al. [58] who revealed an interaction between the OH group of tannin and the metal ions. The possible complexation mechanism of TA with Fe³⁺ is shown in Figure 4. Furthermore, it was worth nothing that two bands at 1024 and 751 cm⁻¹ were ascribed to the bending vibration of OH modes in γ -FeO(OH), which was consistent with the XRD analysis [49,59-61].



Fig. 4. The possible complexation mechanism of TA with Fe^{3+} .

After MB adsorption, most of these characteristic peaks of MB laden iron-TA nanocomplexes remained the same as those of iron-TA (Figure 3). However, a shift of the 1328 cm⁻¹ peak (now at 1325 cm⁻¹) in the spectrum for iron-TA was observed, and the peak sharpen and showed a significant increase in intensity, which indicated that the hydroxyl groups might be involved into interaction with MB. Two new weak and sharp adsorption bands around 1600 and

1384 cm⁻¹ could also be observed and should be assigned to the stretching vibration of aromatic ring and C-N stretching vibrations of the dye heterocycle, respectively, reflecting the evidence for the strong interaction between MB and iron-TA nanocomplexes [62].

3.2. Effect of adsorbent dosage on MB adsorption

In order to investigate the effect of adsorbent dosage on the removal of MB dye by iron-TA nanocomplexes, the adsorption experiments were carried out by varying the adsorbent dosage (0.2-2.0 g/L) at pH 8.0 and initial concentration of 10, 20 and 50 mg/L for 4 h of contact time. The variation in the adsorption amount (q_e) and removal rate (%) with adsorbent dosage is given in Figure 5. The results indicated that the removal rate of 10 mg/L MB by the synthesized iron-TA increased from 61.7% to 99.4% when the amount of adsorbent was increased from 0.2 to 2.0 g/L. A plateau occurred at the adsorbent dosage of 1.0 g/L, which might be attributed to the formation of aggregates at higher solid/liquid ratios or precipitation of particles [63]. The adsorption amount of MB decreased from 30.8 to 5.0 mg/g following the increase of adsorbent dosage from 0.2 to 2.0 g/L. Overall, by increasing the adsorbent dosage, the removal rate increased while the adsorption amount per unit mass decreased. It was readily understood that the number of available adsorption sites increased with an increase in adsorbent dosage and it, therefore resulted in increase in the removal rate of MB [64]. The decrease in adsorption amount might be due to the decrease in the MB concentration gradient per unit mass of adsorbent with the increase in amount of synthesized iron-TA nanocomplexes. The driving force generated from the concentration gradient thus decreased as well [65]. Therefore, less MB diffused though the liquid film and intra-particle channels to the adsorption sites of the iron-TA nanocomplexes, and more sites remained unsaturated. Another reason for this might be due to the particle interaction, such as aggregation, that resulted from high adsorbent concentration. Such aggregation would lead to a decrease in total surface area of the adsorbent and an increase in diffusional path length [66]. Particle interaction might also desorb some of the adsorbate that was only loosely and reversibly bound to the adsorbent surface [64].



Fig. 5. T Effects of adsorbent dosage on MB adsorption on iron-TA. (Adsorption conditions: initial pH = 8.0, contact time = 4 h, and temperature = 298 K).

3.3. Effect of pH on MB adsorption

The pH of the dye solution may influence the degree of ionization of the adsorption material, the surface charge of the adsorbent and the dissociation of functional groups such as carboxyl and hydroxyl groups present on the active sites of the adsorbent [67]. The adsorption experiments of MB on iron-TA nanocomplexes were conducted in different pH range from 3.0 to 10.0, and the results are presented in Figure 6. It was observed that an increase in solution pH from 3.0 to 10.0 caused an obvious increase in the MB adsorption amount for iron-TA from 19.8 to 39.5 mg/g (50 mg/L MB). It could be seen that the MB adsorption was highly pH-dependent and the adsorption of MB on iron-TA was favored at higher pH value. It has been reported that MB was a very weak base and reacted only in the solutions of strong acids to yield low amounts of protonated cations; therefore, it was safe to assume that MB is a positively charged, unprotonated

cation, throughout the pH range investigated [68]. Therefore, when the solution pH was low, functional groups on the adsorbent were protonated. The electrostatic attraction between iron-TA nanocomplexes and MB weakened, as a result, MB adsorption amount decreased. When the solution pH increased gradually, hydroxyl and carboxyl functional groups were deprotonated and positively charged MB could be bound to negatively charged groups by electrostatic attraction. The monotonous increasing trend of MB adsorption-pH relationship has been reported intensely and similar results of pH effect were also reported for the adsorption of MB on TA modified super paramagnetic Fe₃O₄ nanoparticles [18], HA-impregnated biogenic hydroxyapatite [62] and HA-coated magnetic nanoparticles [69].



Fig. 6. *Effects of initial pH on MB adsorption on iron-TA. (Adsorption conditions: adsorbent dosage = 1.0 g/L, contact time = 4 h, and temperature = 298 K).*

3.4. Effect of contact time on MB adsorption and adsorption kinetics

Contact time is an important parameter because it can determine the time required to attain thermodynamic equilibrium for the adsorption system and predict the feasibility of an adsorbent for its use in wastewater treatment. In addition to a high adsorption capacity, a fast adsorption rate is also essential for practical application [70]. Experiments were performed at three different initial MB concentrations, and data were collected within the time period 0-300 min. Results obtained are depicted in Figure 7, where the solid dots showed experimental q_t values. It was noted that the fast adsorption process of MB occurred during the first 30 minutes, contributing to 87.4%, 84.4% and 71.8% of the ultimate adsorption amount for 10, 20, and 30 mg/L MB, respectively, and then slowed considerably. Experimental results suggested that the amount of MB adsorbed (mg/g) increased with increasing contact time and reached equilibrium at 240 min. The two-stage adsorption mechanism with the first rapid and quantitatively predominant and the second slower and quantitatively insignificant, has been extensively reported in literature [71]. The results were ascribed to the higher concentration gradient and more available adsorption sites in the beginning of the adsorption processes, and then they reduced with the progress of the adsorption, leading to decrease in the adsorption rate [70,72].



Fig. 7. Effect of contact time and initial MB concentration on adsorption capacity of MB on iron-TA. (Adsorption conditions: adsorbent dosage = 1.0 g/L, initial pH = 8.0, and temperature = 298 K).

Furthermore. the experimental data were tested with pseudo-first-order, pseudo-second-order, and Elovich kinetic models in order to understand the kinetics of MB removal using iron-TA nanocomplexes as adsorbents. Kinetic parameters including the pseudo-first-order rate constant k_1 , pseudo-second-order rate constant k_2 , adsorption rate (α) for the Elovich model, calculated equilibrium adsorption capacity $(q_{e,cal})$, experimental equilibrium adsorption capacity $(q_{e,exp})$ for MB, and regression coefficients (R^2) , were all presented in Table 1. The non-linear fitting of the experimental kinetic results to the three models is shown in Figure 7. The validity of the models was checked by R^2 and similarity of $q_{e,exp}$ with those values predicted by the models. The values of R^2 obtained from pseudo-second-order kinetics were higher (> 0.93) than those from pseudo-first-order and Elovich kinetic models, and the values of $q_{e,cal}$ were closer to $q_{e,exp}$, hence, it was ascertained from a comparison of the predicted (best fitted) time dependencies with the experimental data that the pseudo-second-order kinetic model described the MB adsorption more accurately. It is generally considered that if MB adsorption is controlled by diffusion through a boundary layer as a reversible reaction, the kinetics of the adsorption process should fit to the pseudo-first order model [73]. However, adsorption always involves various mechanisms such as electrostatic and chemical interactions between functional groups and dyes. Therefore, the pseudo-second order model usually provides the best fit for dyes and other pollutants adsorption processes [74]. Moreover, the value of k_2 of the pseudo-second order model was found to decrease with increased initial MB concentration implying a higher diffusion rate of adsorption at lower concentration, which might be attributed to the greater degree of distribution of MB over the surface of adsorbent for the adsorption process [75]. Also, similar results were reported by Anirudhan et al. [17] and Wang et al. [62] for the adsorption of MB.

	Parameter	Initial MB concentration (mg/L)		
Fitting model		10	20	50
Pseudo-first-order model	<i>k</i> ₁ (1/min)	0.1760	0.1311	0.0625
	$q_{ m e,cal}$	9.542	18.032	26.138
	R^2	0.9022	0.82148	0.8396
Pseudo-second-order model	$k_2(g/(\text{mg}\cdot\text{min}))$	0.0283	0.0115	0.0034
	$q_{ m e,cal}$	10.042	18.957	27.968
	R^2	0.9819	0.9393	0.9387
Elovich model	α	0.879	0.429	0.232
	eta	49.41	43.58	11.23
	R^2	0.8904	0.9128	0.9039
$q_{\mathrm{e,exp}}~(\mathrm{mg/g})$		9.95	18.98	26.91

 Table 1. Parameters of three kinetic models for MB adsorption on iron-TA nanocomplexes
 at different initial MB concentrations.

3.5 Effect of ionic strength on MB adsorption

The wastewater containing dye has commonly higher salt concentration and leads to high ionic strength, which may significantly affect the performance of the adsorption process. In order to investigate the effect of inorganic salts on MB adsorption process, the experiments were carried out using 10-50 mg/L MB solution containing various NaCl, MgCl₂, or CaCl₂ concentrations ranging from 0.01 to 0.1 mol/L. As shown in Figure 8, the increasing ionic strength in the solution caused a decrease in the adsorption of MB dye on iron-TA nanocomplexes. Theoretically, when the electrostatic forces between the adsorbent surface and adsorbate ions are attractive, an increase in ionic strength will decrease the adsorption capacity. Conversely, when the electrostatic force is

repulsive, an increase in ionic strength will increase adsorption [76]. In other words, it is anticipated that for ionic molecules that adsorb primarily by an electrostatic mechanism, adsorption decreases when the ionic strength of the background solution increases [77]. Therefore, electrostatic interaction played an important role in the adsorption of MB by iron-TA nanocomplexes. The effect of ionic strength on MB adsorption could be attributed to several mechanisms. On one hand, since NaCl, MgCl₂ and CaCl₂ in MB solution can release Na⁺, Mg²⁺ and Ca²⁺, which could screen the electrostatic interaction of opposite charges of the adsorbent surface active sites and MB molecules, and accordingly, the adsorption amount of MB decreased [78,79]. On the other hand, ionic strength is one of the key factors affecting the electrical double layer structure of a hydrated particulate. An increase in ionic strength can lead to a decrease in electrical double layer thickness and an increase in the amount of indifferent ions approaching the adsorbent surface. Thus, results in Figure 8 could be attributable to the competitive effect between the cationic MB ions and the salt cations (Na⁺, Mg²⁺ and Ca²⁺) for the sites available for the adsorption process. Furthermore, it was also found that divalent cations had significantly more adverse effects than NaCl on MB adsorption. This result was consistent with that of Han et al. [78] and Maurya et al. [80], who reported that the effect of divalent ions was more prominent than that of monovalent ions for MB adsorption. This phenomenon was probably due to the fact that Ca^{2+} and Mg²⁺ contributed more to the ionic strength and had a greater positive charge than Na⁺; therefore, the effect of Ca^{2+} and Mg^{2+} on adsorption is greater than that of Na^{+} [81].



Fig. 8. Effect of ionic strength on MB adsorption on iron-TA. (Adsorption conditions: adsorbent dosage = 1.0 g/L, initial pH = 8.0, contact time = 4 h, and temperature = 298 K).

3.6. Adsorption isotherms and thermodynamic analyses

The adsorption equilibrium isotherm is important for describing how the adsorbate molecules distribute between the liquid and the solid phases when the adsorption process reaches an equilibrium state. The adsorption isotherms of MB on iron-TA nanocomplexes at temperatures of 283, 298 and 313 K were shown in Figure 9. It indicated that the equilibrium adsorption capacity increased with the increasing of equilibrium MB concentrations at the range of experimental concentrations, which was due to the increase in the driving force from the concentration gradient. Furthermore, the increase of the adsorption capacity with increased temperature indicated that the adsorption of MB on iron-TA nanocomplexes was endothermic in nature.



Fig. 9. Nonlinear Langmuir (a), Freundlich (b) and Sips (c) isotherm models at different temperatures for the adsorption of MB on iron-TA; (d) Plots of $\ln q_e/C_e$ vs q_e for the MB adsorption on iron-TA at different temperatures (q_e : mg/g, C_e : mg/mL). (Adsorption conditions: adsorbent dosage = 1.0 g/L, initial pH = 8.0, contact time = 4 h).

The different isotherm models are used to analyze adsorption equilibrium data in order to find a suitable model to depict the adsorption data, since an accurate mathematical depiction for the equilibrium adsorption process is essential for reliable prediction of adsorption parameters and quantitative comparison of adsorption behaviors for different adsorption systems [70]. In the present work, adsorption equilibrium data have been tested by using Langmuir (Figure 9a), Freundlich (Figure 9b) and Sips (also known as Langmuir-Freundlich, Figure 9c) isotherms at various temperatures. The Langmuir model assumes the monolayer coverage of adsorbate over a homogeneous adsorbent surface. A basic assumption is that adsorption takes place at specific homogeneous sites within the adsorbent. Once a dye molecule occupies a site, no further adsorption occurs on the surface of an adsorbent, suggesting non-ideal adsorption on the heterogeneous surface [45]. The Sips isotherm model [46] is a combination of the Langmuir and Freundlich isotherm type models and expected to describe heterogeneous surface much better. At low adsorbate concentrations, the Sips isotherm approaches the Freundlich isotherm, whereas it approaches the Langmuir isotherm at high concentrations.

The non-linear forms of the Langmuir, Freundlich and Sips isotherm models have been used to interpret the experimental isotherm data and the results are showen in Figure 9 (a,b,c). The parameters and correlation coefficients of Langmuir, Freundlichm and Sips adsorption isotherms are presented in Table 2. From correlation coefficients, it is evident that the Freundlich and Sips models with high correlation coefficient ($R^2 > 0.9685$) at all the temperatures fitted the adsorption data better than the Langmuir model, which indicated that the distribution of adsorption sites on the surface of iron-TA was heterogeneous, in violation of the assumption of Langmuir model. In this work, the Langmuir model proved to be incapable of describing the adsorption process for MB. In addition, the results in Table 2 also showed that the Sips model gave the best description of the adsorption with $R^2 > 0.9968$. While Figure 9d also showed that the experimental points were in good agreement with the nonlinear model generated by Sips isotherm. K_S values of Sips model were between 0.0539 and 0.1565, which were very small. In this case, the Sips isotherm equation was reduced to the Freundlich isotherm model, indicating a heterogeneous multilayer adsorption process. The values of K_F of Freundlich model were 7.2155, 12.8103 and 20.6238 [mg/g(L/mg)^{1/n}] at 283, 298 and 313 K, respectively. K_F increased with the increase in the temperatures, revealing

that the adsorption capacity of MB on iron-TA increased with the increase in the temperatures. The constant n of Freundlich model is the empirical parameter related to the intensity of adsorption, which varies with the heterogeneity of the material. When 1/n values are in the range 0.1 < 1/n < 1, the adsorption process is favorable. On the other hand, the Freundlich exponent of 1/n gives information about surface heterogeneity and surface affinity for the solute. The Freundlich exponent 1/n between 0.2292 and 0.3602 indicated favorable adsorption and a high affinity of iron-TA for MB. In summary, the results showed that the adsorption of MB onto the iron-TA nanocomplexes was correlated well with the Sips and Freundlich model as compared with Langmuir equation under the concentration range studied, according to the R^2 values shown in Table 2. Based on the Sips isotherm model, the predicted maximum adsorption capacity (q_m) for MB was found to be 43.15, 62.63 and 67.41 mg/g at 283, 298 and 313 K, respectively. In order to assess the performance of iron-TA nanocomplexes as an adsorbent for MB, a comparison with other adsorbents is given in Table 3. It could be seen that the adsorption capacity of MB on iron-TA was higher than that of many other previously reported adsorbents [82-95], suggesting that the as-synthesized iron-TA nanocomplexes had great potential application in MB removal from aqueous solution.

Fitting model	Deremator	Temperature (K)		
ritting model	Farameter	283	298	313
Langmuir	$q_{\rm m}$ (mg/g)	31.03	34.48	44.84
	$K_{\rm L}$ (L/mg)	0.1743	0.7913	0.9478
	R^2	0.9411	0.9064	0.9214
Freundlich	$K_{\rm F} ({\rm mg/g} ({\rm L/mg})^{1/{\rm n}})$	7.2155	12.8103	20.6238
	1/n	0.3602	0.2917	0.2292
	R^2	0.9685	0.9819	0.9741
Sips	$q_{\rm m}$ (mg/g)	43.15	62.63	67.41
	$K_{\rm S}$ (L/mg)	0.0561	0.0539	0.1565
	1/n	0.7434	0.5225	0.4501
	R^2	0.9968	0.9989	0.9985

Table 2. Parameters of adsorption isotherms of MB on iron-TA nanocomplexes at different temperatures.

Adsorbent	a (mg/g)	References
	$q_{\rm m}$ (mg/g)	
Hydroxyapatite	0	[82]
Bone charcoal	5	[83]
Clay	6.3	[84]
Natural phosphate	7.232	[85]
Kaolinite	7.59-20.49	[11]
Biochar	9.5	[86]
Goethite nanoadsorbents	9.6	[87]
Activated carbon	9.813	[88]
Iron humate	10.5*	[32]
Poorly crystalline hydroxyapatite	14.27	[89]
HA Based biopolymeric membrane	20.83	[90]
Fe(III)/Cr(III) hydroxide	22.8	[91]
Magnetic biochar	31.25	[92]
Carbon nanotubes	35.4-64.7	[93]
Halloysite nanotubes	40.82	[94]
graphene nanosheet/magnetite composite	43.82	[95]
Sepiolite	59.81*	[12]
TA modified Fe ₃ O ₄ nanoparticles	90.9	[18]
HA-coated Fe ₃ O ₄ nanoparticles	93.1*	[69]
Iron-TA complexes	67.41	This study

Table 3 The comparison of maximum MB adsorption capacities of various adsorbents.

*values were converted from mol/g.

Furthermore, the thermodynamic parameters were applied to evaluate the orientation and feasibility of MB adsorption by iron-TA nanocomplexes. The thermodynamic parameters (ΔG , ΔH and ΔS) of the adsorption of MB were calculated using equations as below:

$$\Delta G = -RT\ln K_0 \tag{7}$$

$$\ln K_0 = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$
(8)

where ΔG is the standard free energy of adsorption (kJ/mol); *R* is the universal gas constant (8.314 J/(mol·K)); *T* is the temperature in Kelvin; K_0 is the thermodynamic equilibrium constant, which was determined by plotting $\ln q_e/C_e$ vs q_e and extrapolating to zero q_e using a graphic method described by Khan and Singh [96]. Regression straight lines were fitted through the data points by the least-squares method, and their intersections with the vertical axis gave the value of K_0 (Figure 8d). ΔS is the standard entropy change (J/(mol·K)) and ΔH is the standard enthalpy change (kJ/mol). The values of ΔH and ΔS could be obtained from the slope and intercept of a plot of $\ln K_0$ against 1/T.

The obtained results are listed in Table 4. The free energy changes (ΔG) obtained were -0.6564, -0.6912 and -0.7260 kJ/mol at 283, 298 and 313 *K*, respectively. The negative values of ΔG indicated the spontaneous nature of MB adsorption by the synthesized iron-TA. The enthalpy (ΔH) was 2.09 kJ/mol, which illustrated the endothermic nature of adsorption. This confirmed the

previous results in the section regarding adsorption isotherm studies. The positive value of entropy $(\Delta S = 3.03 \text{ J/(mol} \cdot \text{K}))$ showed an irregular increase in the randomness in the system solid/solution interface during the adsorption process and also reflected the affinity of iron-TA nanocomplexes towards MB.

Table 4. Thermodynamic parameters of the MB adsorption on iron-TA nanocomplexes at different temperatures.

Temperature (K)	$\ln K_0$	ΔG (kJ/mol)	ΔH (kJ/mol)	$\Delta S (J/(mol \cdot K))$
283	1.8932	-0.6564	2.09	3.03
298	3.4435	-0.6912		
313	5.3062	-0.7260		

4. Conclusions

In this study, we have successfully synthesized iron-TA nanocomplexes by a facile method using TA and iron(III) nitrate under the conditions of room temperature and neutral pH. Structure and phase composition of iron-TA were characterized and confirmed by XRD and FTIR analyses. Iron-TA could be effectively used to remove MB from aqueous solution. The solution pH, ionic strength and temperature greatly affected the adsorption of MB on iron-TA. Adsorption of MB reached equilibrium within 4 h and more than 70% of MB was being adsorbed at 30 min. The kinetics of MB adsorption obeyed the pseudo-second-order model. The equilibrium data were fitted well by the Sips model. The maximum adsorption capacity of iron-TA, determined to be 67.41 mg/g, was considerably higher than that of some other reported adsorbents. FTIR analyses clearly indicated that the hydroxyl groups on iron-TA were the main binding sites for MB. Results of this work suggest that the iron-TA nanocomplexes may be promising adsorbents for the removal of MB from aqueous solution.

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