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Removal of methyl violet 2B dye from aqueous solution using a magnetic composite as an adsorbent

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Abstract

Despite the important role of the textile industry in the global economy, its effluents generate deep concern with regard to treatment and disposal. Adsorption is a promising technique for the removal of textile color effluent at relatively low cost and with satisfactory efficiency. This study aimed to evaluate the adsorption capacity of a halloysite-magnetite-based composite in the removal of methyl violet 2B cationic dye. After preparation, the obtained composite was characterized by applying several instrumental techniques, including X-ray diffraction, scanning electron microscopy, energy dispersive spectroscopy and determination of pH at the point of zero charge. The influences of stirring rate, adsorbent mass, pH, initial concentration of dye and contact time on the adsorption process were also studied. The adsorption capacity of the composite was then investigated in a temperature-controlled batch system. The experimental results showed that the adsorption kinetics were better described using a pseudo-second-order model. Regarding the adsorption equilibrium, the experimental results suggest that both the Langmuir and Freundlich models were applicable. The thermodynamic data showed that dye adsorption onto the composite was spontaneous and endothermic and occurred by physisorption. The employed composite could also be regenerated at least four times using a 1.0 mol L⁻¹ solution of NaOH as an eluent and was shown to be a promising adsorbent for the removal of cationic dyes.

Keywords: halloysite-magnetite-based composite; methyl violet 2B; adsorption; kinetics; thermodynamics

1 Introduction

The future of Earth and its biodiversity is a common concern for everyone. Rapid technological and industrial development in recent decades has led to a number of environmental problems, particularly with regard to the pollution of water resources [1]. Synthetic dyes are one of the major classes of pollutants responsible for imbalances in aquatic ecosystems; their complex molecular structures keep them relatively stable, making them difficult to remove [2].

Color is usually the first contaminant to be recognized in wastewater because a very small amount of synthetic dye in water ($< 1.0 \text{ mg L}^{-1}$) is typically highly visible, affecting the aesthetic merit, transparency and gas solubility of water bodies. These dyes absorb and reflect sunlight, thereby interfering with the growth of aquatic species and hindering photosynthesis. Additionally, they can have acute and/or chronic effects on organisms, depending on their concentration and exposure time [3].

Methyl violet (MV) is particularly important because of its broad applications in textiles, paints and print inks [4, 5]. MV is often used in the dyeing of cotton, silk, paper, bamboo, straw and leather [6]. In biomedical fields, MV is the active ingredient in Gram's biological stain for bacteria classification [7-10]. It can sometimes also be used as a moderate-class disinfectant but has been found to be poisonous to most animals. The inhalation of MV may cause irritation to the respiratory tract, whereas ingestion typically causes irritation to the gastrointestinal tract [11].

Dyes can be classified according to their chemical structure or method of application. MV belongs to a class of intensely colored organic compounds called triphenylmethane dyes due to the presence of three aryl groups, each of which is bonded to a nitrogen atom that

interacts with one or two methyl groups. Moreover, MV is a basic dye because of the presence of a positive charge on the amino group [12].

MV is a mixture of tetramethyl, pentamethyl and hexamethyl pararosaniline chlorides [13]. This last chemical compound is also known as *crystal violet* or MV 10B and is the primary representative of these three dyes reported in the literature [14-19]. Conversely, in MV 2B, there is a predominance of the pentamethylated compound [13]. Due to this difference, the particular shade of MV differs, depending on the amount of each component present.

Fig. 1 shows the chemical structures of MV 2B and 10B. The small structural difference observed (the presence of an additional methyl group in MV 10B) is responsible for the different physical and chemical properties of the two dyes, which include the absorption maximum in the visible region, solubility, staining intensity and melting temperature [13].

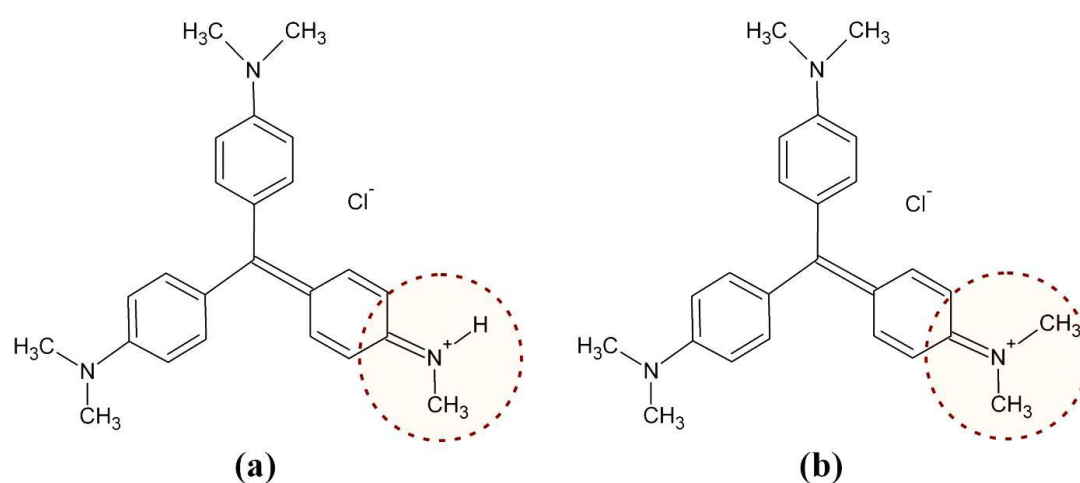


Fig. 1. Chemical structures of MV (a) 2B and (b) 10B.

A wide range of technologies has been developed for the removal of synthetic dyes from waters and wastewaters to decrease their environmental impacts. These include physical methods, such as membrane filtration processes and sorption techniques; chemical methods,

such as coagulation, electroflotation, advanced oxidation processes and irradiation; and biological methods, such as aerobic and anaerobic microbial degradation and the use of enzymes[3]. Although chemical and biological methods are effective at removing dyes, they require specialized equipment and are usually energy intensive; in addition, large amounts of by-products are often generated. Conversely, the physical methods are generally effective at removing dyes without producing unwanted by-products [20, 21].

With regard to the physical methods, sorption of synthetic dyes on inexpensive and efficient solid supports has been considered a simple and economical process for the removal of dyes from water and wastewater, producing high quality water; this process is an attractive alternative for the treatment of contaminated waters, particularly where the sorbent is inexpensive and does not require a pre-treatment step before its application. Sorption is superior to other techniques for water reuse in terms of initial cost, flexibility and simplicity of design, and ease of operation [3].

Activated carbon is the most widely used sorbent, and it has excellent sorption properties for a considerable number of synthetic dyes. However, the preparation of carbon sorbents is generally energy intensive, making commercially available products relatively expensive. Because a large amount of carbon sorbent is needed to remove the dye from a large volume of effluent, high cost can hinder its application [22]. In addition, the technology for manufacturing good-quality activated carbon is not fully available in developing countries. This limitation has prompted increasing research interest in the production of low-cost alternatives to activated carbon from a range of carbonaceous and mineral precursors[3].

According to Bujdák[23], future investigations could be directed towards the optimization of wastewater treatment processes using suitable clay templates and nanomaterials. In this way, adsorbents with magnetic properties have been extensively studied by many researchers. Zhao et al. [24] have reported, for example, a novel magnetic

hydroxamic acid modified polyacrylamide/Fe₃O₄ adsorbent (M-PAM-HA) for the removal of Cd(II), Pb(II), Co(II) and Ni(II) ions from aqueous solutions. Ai et al. [25] and Sun et al. [26] have developed a xylan/poly(acrylic acid) magnetic nanocomposite hydrogel adsorbent and montmorillonite/CoFe₂O₄ magnetic composite, respectively, for removal of methylene blue from wastewater.

The novelty brought by these adsorbents is the improvement in accelerating separation speed, thereby enhancing water treatment efficiency. As a result, solid phase can be easily recovered by the application of an external magnetic field [27-29]. Moreover, adsorbents with magnetic properties produce no contaminants during wastewater treatment. As main disadvantage, most commercially magnetic particles are expensive and cannot be applied to large-scale processes, but magnetic modification of low cost adsorbents could lead to materials suitable for biotechnology and environmental applications [29]. Research has shown that it is possible to produce promising adsorbents in this field, creating new options for textile industry effluent mitigation [30-36].

Therefore, the aim of this work was to prepare, characterize and evaluate the removal of MV 2B from aqueous solution using a halloysite-magnetite-based composite (HNT-Fe₃O₄) as an adsorbent. The adsorption kinetics, equilibrium and thermodynamics of MV 2B onto this composite were also investigated.

2 Experimental

2.1 Materials and cleaning procedure

MV 2B (C₂₄H₂₈N₃Cl, Color Index 42535) was purchased from Vetec Química Fina Ltda (Rio de Janeiro, RJ, Brazil). HNT and iron salts (FeCl₃ · 6 H₂O and FeSO₄ · 7 H₂O) were

acquired from Sigma-Aldrich (São Paulo, Brazil). The chemicals used in this work were of analytical quality and were used without further purification. All aqueous solutions, including solutions of KNO_3 , KOH , HNO_3 , HCl and NaOH (Merck, São Paulo, SP, Brazil), were prepared using deionized water (18.2 $\text{M}\Omega$ cm resistivity) obtained from a Millipore Milli-Q UV Direct-Q 3 UV system (Darmstadt, Germany).

All laboratory glassware used in the preparation of the HNT- Fe_3O_4 composite and in the adsorption experiments was first washed with tap water and then soaked in an alkaline Extran solution (15% v/v) for 24 h. After this period, they were washed thoroughly with tap water and then soaked in a solution of HNO_3 (5% v/v) for 24 h. Finally, the material was rinsed with deionized water and left to dry at room temperature.

2.2 Preparation of HNT- Fe_3O_4 composite

The HNT- Fe_3O_4 composite was prepared using the chemical precipitation method [31]. Initially, 6.25 g of HNT was added into a 500 mL solution of 7.275 g of $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ and 3.75 g of $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$. The suspension was then refluxed for 3 h in a glycerin bath at 120°C under nitrogen gas flow. When the mixed suspension was cooled to 50°C, NaOH solution (4.0 mol L^{-1}) was added dropwise with vigorous magnetic stirring. The pH of the final suspension was controlled to be in the range of 9.0–10.0. The mixture was aged at 50°C for 2.5 h and then filtered and washed with deionized water repeatedly. At the end of this procedure, the obtained composite was dried at 60°C for 24 h.

2.3 Characterization of HNT- Fe_3O_4 composite

The crystalline phases in the HNT and HNT-Fe₃O₄ composite were characterized by X-ray powder diffraction using a Shimadzu XRD-6000 diffractometer (Tokyo, Japan). The samples were scanned at room temperature in reflection mode using incident CuK_α radiation ($\lambda = 1.5405 \text{ \AA}$) at a step width of $0.05^\circ \text{ min}^{-1}$ from $2\theta = 2^\circ$ to 80° .

The morphology of the HNT and HNT-Fe₃O₄ composite was examined by scanning electron microscopy (SEM) using a ShimadzuSSX-550 (Tokyo, Japan) operating at an accelerating voltage of 10 kV. Before analysis, the samples were sputter-coated with a thin gold layer for 2.5 min. The qualitative analysis of iron in the HNT-Fe₃O₄ composite was performed by energy dispersive spectroscopy (EDS) of the same sample used in the SEM analysis and in the same microscope, operating at an accelerating voltage of 15 kV.

Nitrogen adsorption-desorption experiments were performed in order to obtain information on the specific surface area of the HNT-Fe₃O₄ composite. The measurements were carried out at 77 K using a Quantachrome Instruments Nova 2200e Surface Area Analyzer (Boynton Beach, FL, United States of America). About 100 mg of the sample was outgassed at 383 K for 24 h under a residual pressure of 0.01 Pa. Data were recorded for relative vapour pressures from 0.05 to 0.99. The specific surface area was determined using the Brunauer-Emmet-Teller (BET) equation based upon the cross-sectional area of nitrogen (0.163 nm^2) at 77 K.

The point of zero charge (pH_{PZC}) of the HNT-Fe₃O₄ composite was determined by adding 50 mL of $0.01 \text{ mol L}^{-1} \text{ KNO}_3$ with a previously adjusted initial pH (i.e., pH_i values of the solutions were adjusted from 2.0 to 11.0 with 0.10 mol L^{-1} of KOH or HNO₃) to several 150 mL Erlenmeyer flasks. Each Erlenmeyer contained 0.10 g of the magnetic composite and was securely capped immediately with a sheet of aluminum foil. Then, the Erlenmeyers were shaken at a stirring rate of 400 rpm using a thermostated water bath shaker at a constant temperature of 25°C ; the samples were then allowed to equilibrate for 24 h. At the end of this

experimental procedure, the suspensions were filtered, and the final pH (pH_f) values of the solutions were recorded using a Digimed DM-20 pHmeter (São Paulo, SP, Brazil). The value of pH_{PZC} is the point where the curve of ΔpH ($\text{pH}_i - \text{pH}_f$) versus pH_i crosses the line equal to zero[37].

2.4 Adsorption experiments

The adsorption experiments were performed in a Dist multiple spindle stirrer (Florianópolis, SC, Brazil) using 25 mL of dye solution at 25°C for 6 h. Subsequently, the Erlenmeyers were exposed to a magnetic field using a 3000 G magnet for 5 min to separate the magnetic composite from the aqueous solutions.

The initial and final concentrations of the MV 2B remaining in the solutions were determined by visible spectrophotometry using a Thermo Scientific Evolution 60 spectrophotometer (Waltham, MA, United States of America) fitted with a quartz cell with a path length of 1.0 cm. Absorbance measurements were made at 582 nm (i.e., the maximum wavelength of MV 2B dye). A calibration curve was constructed with dye concentrations ranging from 1.0 to 15.0 mg L⁻¹.

The removal percentage ($\%R$, %), the amount of MV 2B adsorbed at time t (q_t , mg g⁻¹), and the adsorption capacity at equilibrium (q_e , mg g⁻¹) were calculated by applying Equations (1), (2) and (3), respectively[31, 33]:

$$\%R = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (1)$$

$$q_t = \frac{(C_0 - C_t)}{m} \times V(2)$$

$$q_e = \frac{(C_0 - C_e)}{m} \times V \quad (3)$$

where C_0 , C_t and C_e are the concentrations of MV 2B initially, at time t and at equilibrium, respectively (mg L^{-1}); m is the weight of the HNT- Fe_3O_4 composite (g); and V is the volume of the MV 2B solution (L).

3 Results and discussion

3.1 Preparation and characterization of HNT- Fe_3O_4 composite

3.1.1 X-ray diffraction (XRD)

The XRD patterns of the HNT and HNT- Fe_3O_4 composite are shown in **Fig. 2**. The new diffraction peaks at 35.45° (3 1 1), 43.20° (4 0 0), 57.15° (5 1 1) and 62.75° (4 4 0) can be identified as Fe_3O_4 , while the other diffraction peaks at 12.29° (0 0 1), 19.78° (0 2 0) and 24.99° (0 0 2) can be indexed to HNT[31, 33, 38]. These results indicated that magnetic particles were successfully anchored onto the surface of the clay.

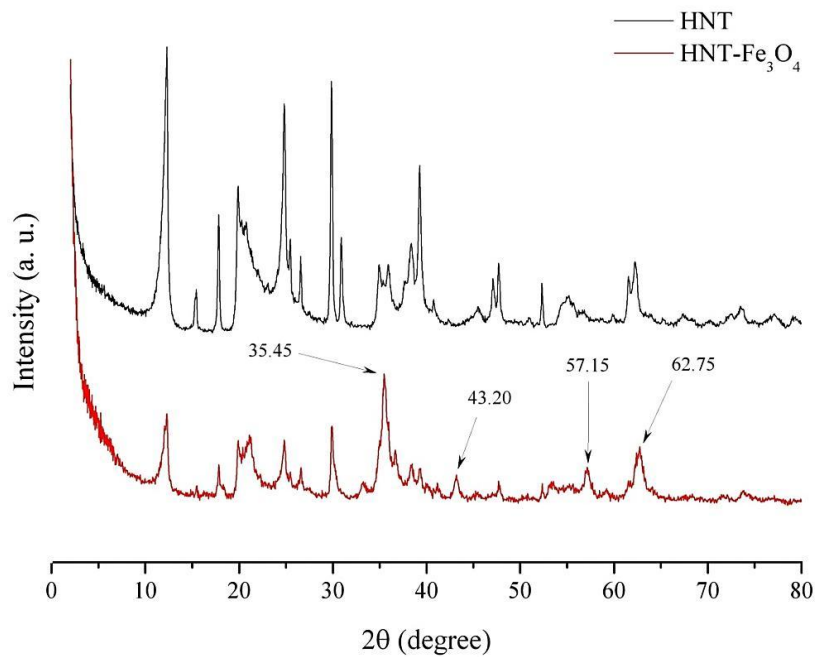


Fig. 2. XRD patterns of the HNT and HNT-Fe₃O₄ composite.

3.1.2 Scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS)

Fig. 3 shows the SEM images and EDS spectra for the HNT and the HNT-Fe₃O₄ composite. As shown in the **Fig. 3(a)**, HNT nanotubes are of different sizes with open ends. Conversely, the SEM image of the HNT-Fe₃O₄ composite (**Fig. 3(b)**) shows that the Fe₃O₄ nanoparticles are adhered to the surface of the HNT nanotubes; this is corroborated by the XRD analysis.

EDS spectra for both materials (**Figs. 3(c)** and **3(d)**) confirmed the presence of aluminum, oxygen, and silicon elements, which are characteristic of aluminosilicates, as well as iron in the composite due to the coating of Fe₃O₄ nanoparticles. In both samples, gold was also detected due to the thin layer deposited to perform these analyses.

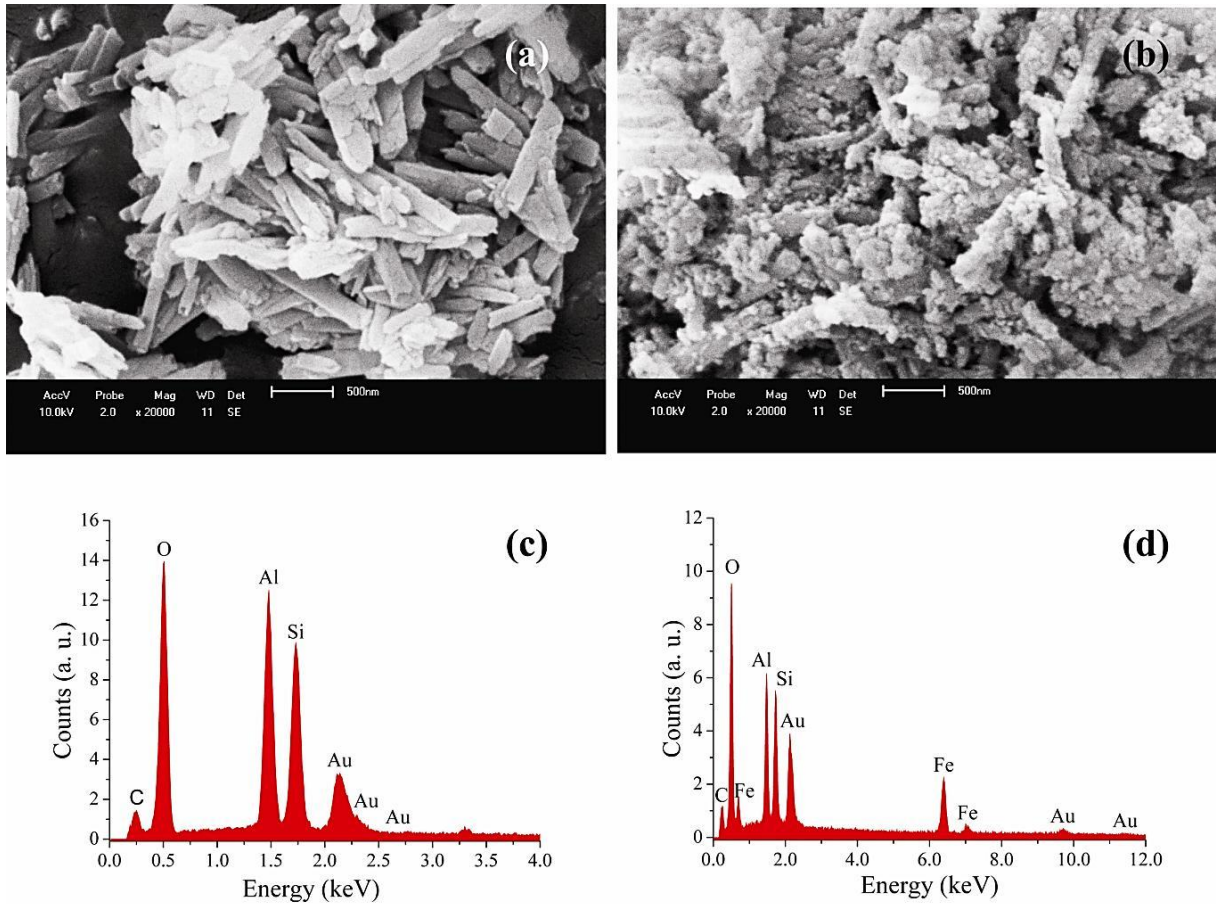


Fig. 3. (a) SEM image of HNT; (b) SEM image of HNT-Fe₃O₄ composite; (c) EDS spectrum of HNT; and (d) EDS spectrum of HNT-Fe₃O₄ composite.

3.1.3 BET analysis

The adsorption and desorption isotherms of nitrogen gas revealed classical features for both non swelling clay mineral and iron oxides. The BET calculation applied to the nitrogen desorption isotherm gave a total specific surface area for the HNT-Fe₃O₄ composite of 46 m² g⁻¹, an intermediate value between the starting materials for which their specific surface area was reported to be in the range of 50-60 and almost 9m² g⁻¹ for kaolinite-halloysite clay minerals [39] and magnetite particles [40], respectively.

3.1.4 pH_{PZC} determination

The pH_{PZC} curve of the HNT- Fe_3O_4 composite is shown in **Fig. 4**. The pH_{PZC} is the pH value where positive and negative charges are equal on the surface of a material, which makes it possible to describe the properties of the resulting electrical double layer interfaces [41].

For pH values lower than pH_{PZC} , the adsorbent presents a positive surface charge that favors the adsorption of negatively charged compounds, such as anionic dyes. In the situation when the pH is greater than pH_{PZC} , the adsorbent presents a negative surface charge that favors the adsorption of positively charged compounds, such as MV 2B [37]. Thus, it can be concluded that the adsorption of this dye by HNT- Fe_3O_4 composite should be favored in media with a pH greater than 5.02.

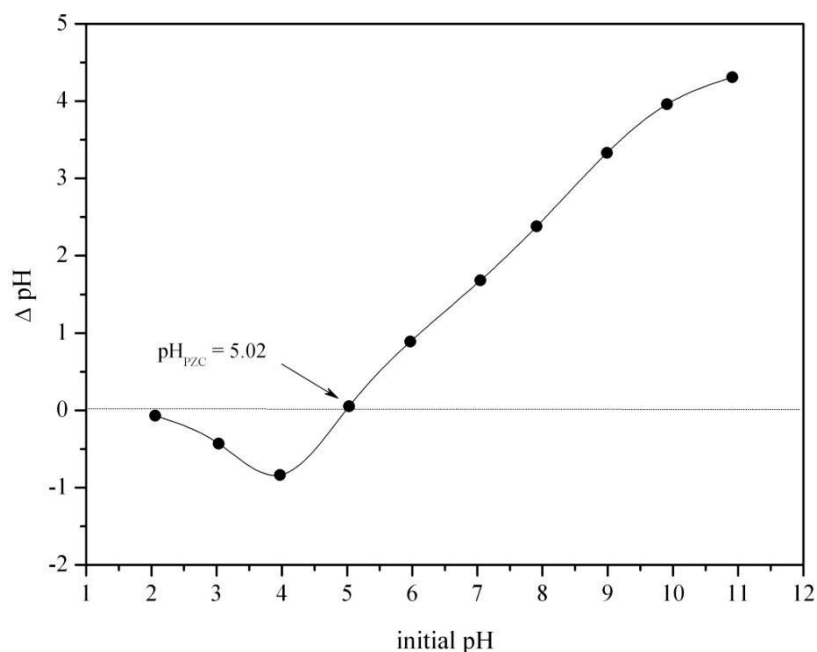


Fig. 4. Curve of the point of zero charge (pH_{PZC}) of the HNT- Fe_3O_4 composite.

Note: the horizontal dotted line shown is used only as a visual guide.

3.2 Effect of experimental conditions on the adsorption process

To evaluate the effect of the experimental conditions on the adsorption process (e.g., stirring rate, adsorbent dosage, initial pH, initial dye concentration and contact time), the results were compared in terms of %R and q_t , which were calculated using Equations (1) and (2), respectively. For this calculation, it was necessary to know the value of the final dye concentration at the end of each experiment as obtained using a calibration curve ($r=0.9997$).

3.2.1 Stirring rate

The experiments used to evaluate the influence of the stirring rate on the adsorption process were conducted in a Dist multiple stirrer spindle at 25°C with an initial weight of 0.15 g of composite in 25 mL of 90 mgL⁻¹ of MV2B (pH~4.2) for 6 h. The effect of the stirring rate on the dye removal percentage is shown in **Fig. 5**.

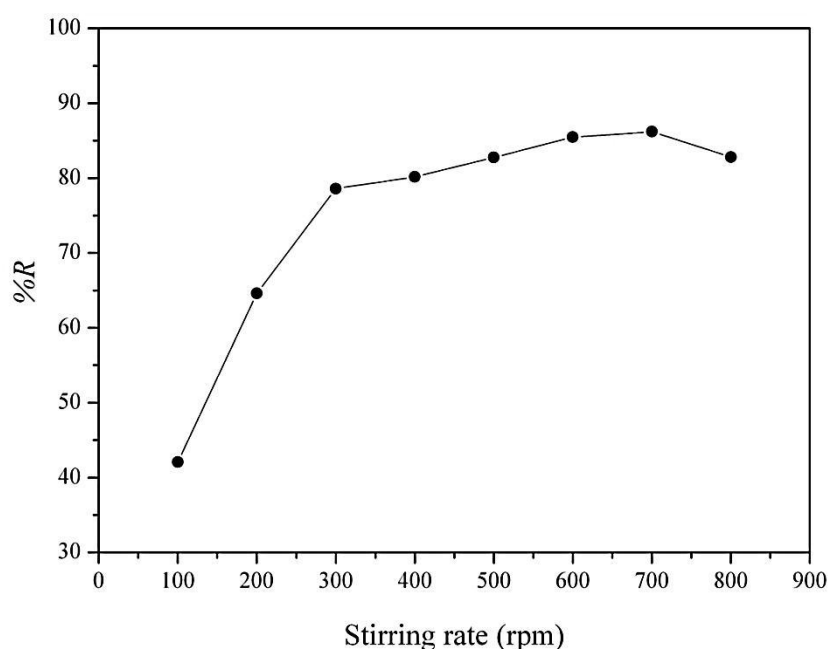


Fig. 5. Effect of the stirring rate on the MV 2B removal percentage.

As shown, %R increases as the stirring rate of the system increases, indicating the occurrence of a stronger interaction between the composite and the dye. Furthermore, a higher removal percentage occurs when the stirring rate of the system is equal to 700 rpm. For higher values, the %R begins to decrease; the associated high rate of turbulence in this case might promote the entrainment of the MV 2B particles before they can interact with the composite. The decrease in percentage removal may also be explained by the fluid dragging HNT-Fe₃O₄ particles due to the high rate of the system, which also affects the interaction of the composite with the dye[42].

3.2.2 Adsorbent dosage

The experiments performed to evaluate the influence of the adsorbent mass on the adsorption process were also conducted in a Dist multiple stirrer spindle at 25°C with 0.025, 0.05, 0.10, 0.15, 0.20 and 0.25 g of composite. A volume of 25 mL of MV2B at a concentration of 90 mgL⁻¹ was used, with the stirring rate previously optimized at a pH value of approximately 4.2 for 6 h. The adsorbent dosage effect on the MV 2B removal percentage is shown in **Fig. 6**.

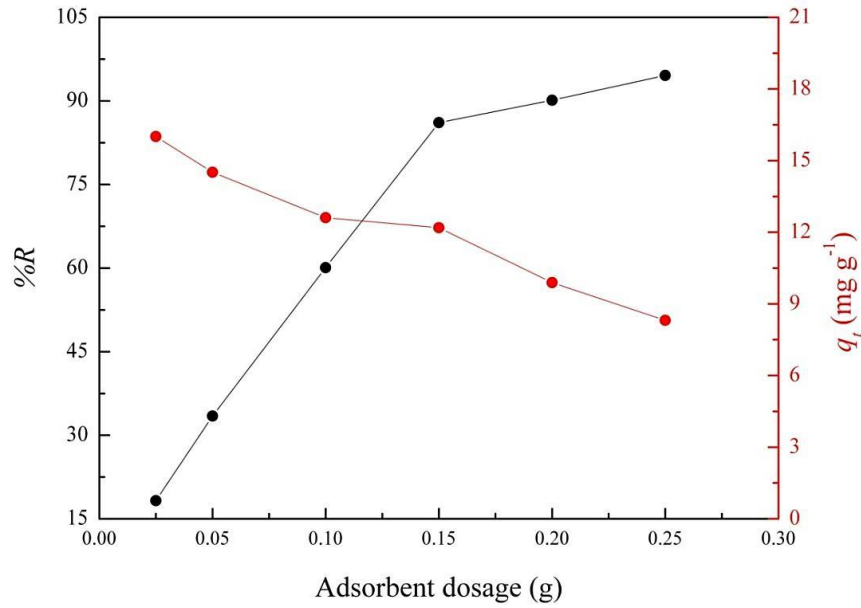


Fig. 6.Effect of the adsorbent dosage on the MV 2B removal percentage.

The results show that %R increases as the adsorbent dosage increases. It was found that the MV 2B removal percentage increased from 18.3% to 94.7% when the adsorbent dosage was increased from 0.025 to 0.25 g. This increase likely occurred due to the increment of the number of adsorption sites available for adsorption [43]. However, q_t shows the opposite behavior of the removal percentage, likely due to the increase in the adsorbent mass at a determined dye concentration; fixed volume also leads to unsaturated adsorption sites during the adsorption process. Additionally, a high adsorbent mass may be favorable to particle aggregation, which would lead a decrease in total surface area of the adsorbent and an increase in diffusional path length [43]. In addition, this reduction of q_t can be mathematically explained by combining Equations (1) and (2), as shown in Equation (4):

$$q_t = \frac{\%R C_0 V}{100 m} \quad (4)$$

where %R is the removal percentage (%), C_0 is initial concentration of MV 2B (mg L^{-1}), m is the weight of HNT- Fe_3O_4 composite (g), V is the volume of MV 2B solution (L), and q_t is the amount of MV 2B adsorbed at time t (mg g^{-1}).

According to Equation (4), the amount of dye adsorbed at a time t (q_t) and the mass of adsorbent (m) are inversely proportional. For fixed values of the dye percentage removal (%R), the treated volume of dye solution (V) and the initial dye concentration (C_0), the increase of adsorbent mass leads to a decrease in q_t values [44].

Based on these results, the value of adsorbent mass should be chosen based on the intersection of the curves %R and q_t with the justification that this location will produce the most cost-effective system [31]. However, for the adsorption experiments, an adsorbent amount of 0.15 g was chosen because this dosage results in a satisfactory removal percentage (i.e., above 85%) and q_t values (e.g., 12.18 mg g^{-1}), particularly when compared to 0.10 g, which typically yields a removal percentage of approximately 60% and a q_t of 12.61 mg g^{-1} . The use of an amount greater than 0.15 g does not show significant advantages in terms of percent removal with an increase of approximately 5%.

3.2.3 Initial pH

To optimize pH, experiments were performed with a range of values between 3.0 and 11.0 in increments of unity, adjusted by adding HCl or NaOH solutions. The concentration of the MV 2B solution was set to 90 mg L^{-1} by applying the stirring rate and adsorbent dosage previously determined to be optimal (i.e., 700 rpm and 0.15 g, respectively) for 6 h at 25°C . The effect of the initial pH on the MV 2B removal percentage is shown in **Fig. 7**.

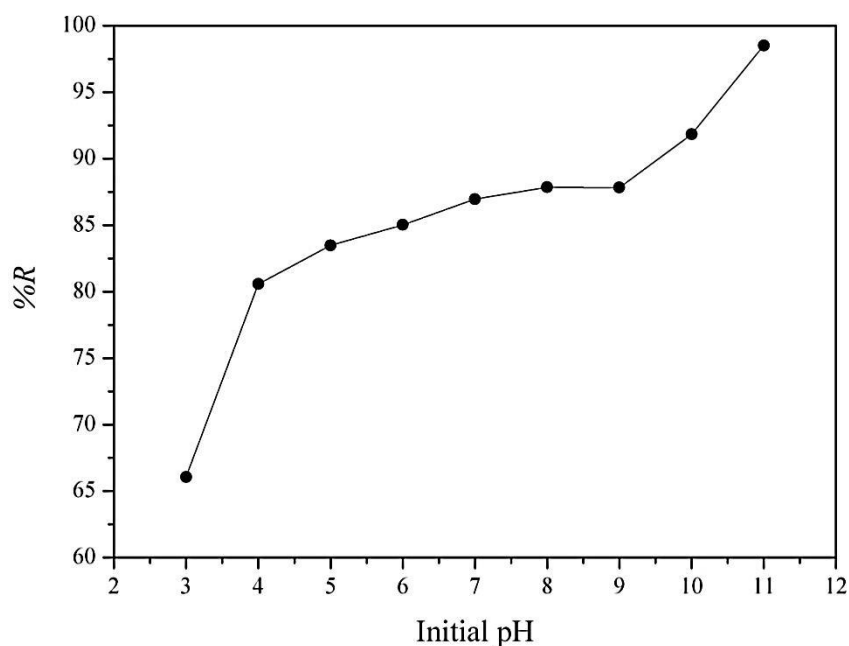


Fig. 7.Effect of initial pH on the MV 2B removal percentage.

As shown, %R increases as pH increases. In an acidic medium, little interaction occurs between the adsorbent and adsorbate. This behavior is expected because the pH_{PZC} value of the adsorbent is lower than 7.0. Under these conditions, the HNT- Fe_3O_4 composite is positively charged (i.e., with the same net charge as the dye), resulting in electrostatic repulsion between the composite and the dye. For pH values lower than 3.2, MV 2B begins to change color towards yellow, which ultimately changes the maximum absorption in the visible region. All of these factors result in a non-optimal scenario for adsorption.

In systems with higher pH (e.g., 9.0 to 11.0), there is a large increase in %R, including values near 100% at pH 11.0. According to Duynstee and Grunwald [45], in the pH range between 9.0 and 13.0, a reaction between the dye and OH^- ions occurs. These ions attack the central carbon atom of the MV 2B molecule, forming a base carbinol with a different molecular geometry. The resulting compound has no color, which explains the high %R values in this pH range.

Despite the nearly complete removal of color, as shown by the high %R value, the dye still remains in solution. When these carbinol bases form, the absorption peak shifts to the UV region, making it difficult to study the adsorption process of the composite because the calibration curve used to quantify the dye was constructed using the maximum absorption of the dye at 582 nm. Finally, the OH⁻ ions compete with the adsorbent in the interaction with MV2B molecules.

Based on these observations, the best conditions for adsorption are in the range of pH values between 5.0 and 9.0; this is the range where removal is improved without a loss of color due to chemical reactions. Because of the differences in percentage removal vary by only 5%, a neutral pH value was adopted for this study. Furthermore, at this pH value (which is higher than the p*H*_{PZC} of the HNT-Fe₃O₄ composite) the adsorbent surface is now completely negatively charged and, as a result, it can better interact with the MV 2B molecules (positively charged) by electrostatic interactions favoring the adsorption process (**Fig. 8**).

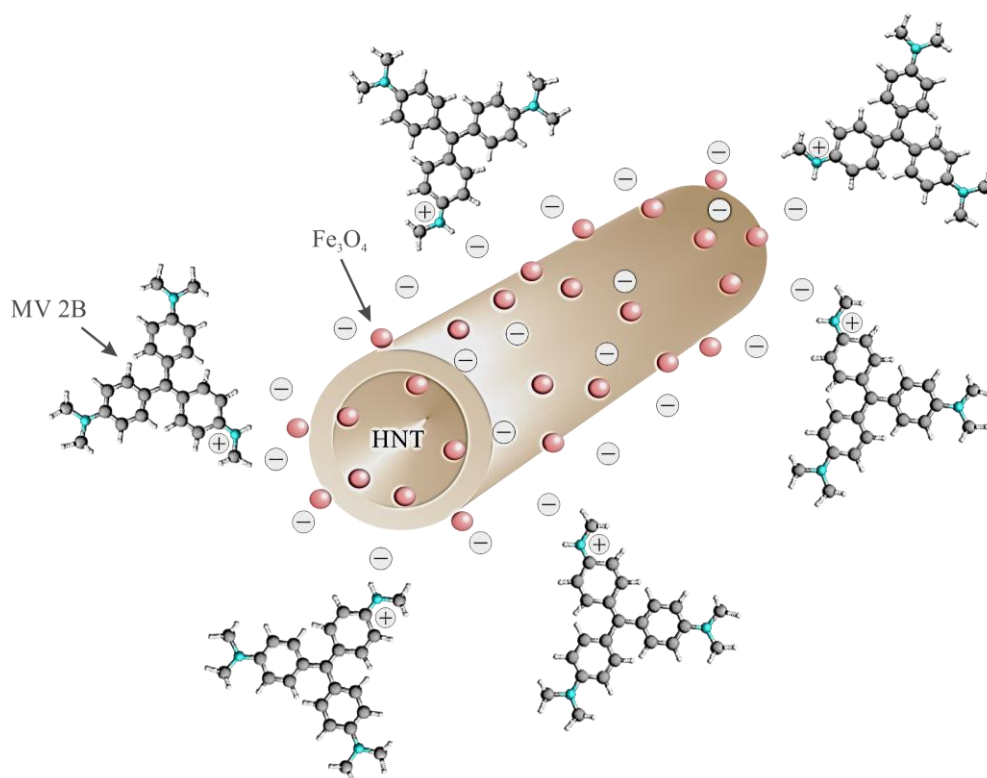


Fig. 8. Electrostatic interactions between MV 2B molecules and HNT-Fe₃O₄ composite at pH values higher than the p*H*_{PZC} of the adsorbent.

3.2.4 Effect of initial dye concentration and contact time

To optimize the initial concentration of dye and contact time on the adsorption process, experiments were conducted with 25 mL of MV2B at concentrations of 60, 90, 120, 150 and 180 mgL⁻¹ over time intervals of 10, 20, 40, 60, 90, 120, 150, 180, 240 and 360 min. The stirring rate, adsorbent dosage and initial pH used were those previously optimized at 25°C.

As shown in **Fig. 9**, q_t increases as the initial concentration of MV 2B in solution increases; however, these values tend to be constant after a certain period of time. The increase in q_t in the experiments that contained higher initial concentrations of dye can be explained by the existence of a higher concentration gradient of MV 2B, which increases the diffusive contribution of the mass transfer process [31, 46]. This increase in the values of q_t at equilibrium does not follow a proportionality, presenting shorter intervals as the initial concentration of MV2B increases, particularly at higher concentrations. According to Gusmão et al. [47], this is an indication that the removal percentage decreases as the initial concentration of MV2B increases due to the greater amount of dye present in the bulk solution. The mass of HNT-Fe₃O₄ composite used (i.e., 0.15 g) is likely not sufficient to promote a high percentage removal for higher concentrations, as discussed in section 3.2.2; this is also in accordance with Hameed [48]. The adsorbed dye molecules likely exert an electrostatic repulsion on those still in solution, increasing resistance to mass transfer.

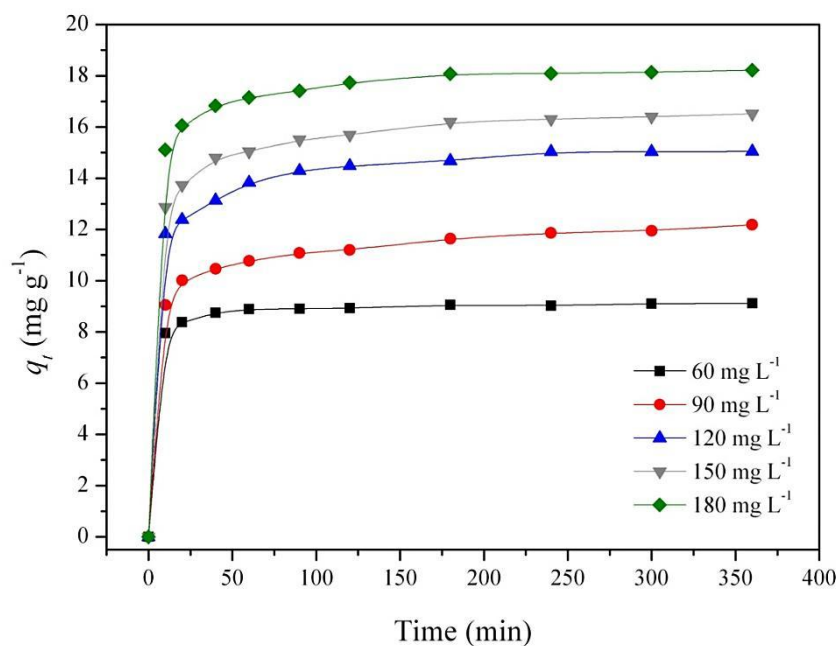


Fig. 9. Effect of the initial dye concentration and contact time on the adsorption process.

Regarding the influence of the contact time, q_t is shown to increase as the process evolves until equilibrium is reached due to the longer period, so that the interaction between the solute and composite occurs, increasing the amount of adsorbed MV2B [31]. However, the curves shown in **Fig. 9** show that the removal is faster in the initial minutes of the process because more adsorption sites are available during this period. As these sites become progressively occupied, adsorption becomes slower and less efficient [37]. Another important aspect to note is that as the initial concentration of MV2B increases, more time is required for equilibrium to be reached. The reason for this phenomenon is that a higher concentration of adsorbate in the solution increases the electrostatic repulsion between molecules present in the medium, increasing the diffusive resistance to mass transfer within the solution but not in the interface as previously discussed; this results in a slower process [48].

3.3 Adsorption kinetics

To identify the mechanism of adsorption, the potential removal rate and the control of the steps involved in the process, two kinetic models (i.e., the pseudo-first- and pseudo-second-order) can be adopted [46]. Kinetics experiments were performed at the same conditions as described in the section 3.2.4. The pseudo-first- and pseudo-second-order kinetic models are shown in **Fig.10**.

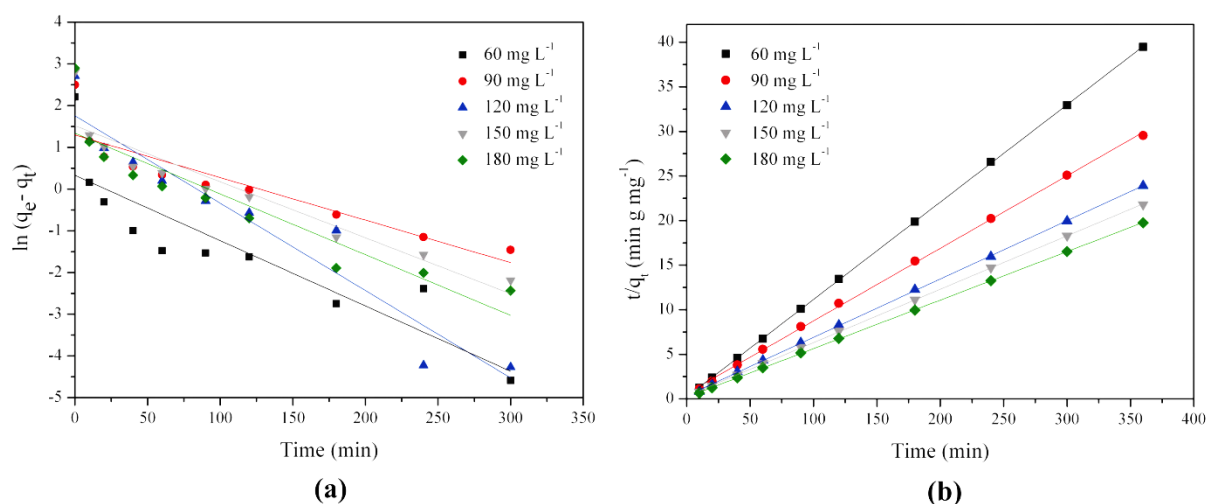


Fig. 10. Kinetics experimental results: (a) pseudo-first- and (b) pseudo-second-order.

The pseudo-first order kinetic model can be expressed by Equation (5) [49]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

where k_1 is the pseudo-first-order rate constant (min^{-1}). The k_1 and q_e parameters can be determined from the slope and intersection of the line of $\log(q_e - q_t)$ versus t . These values are summarized in Table 1.

The coefficient of correlation (r) for the pseudo-first-order model ranged from 0.8734 to 0.9566 for initial concentrations of MV2B of 60, 90, 120, 150 and 180 mg L^{-1} . The experimental values of q_e ($q_{e\text{exp}}$, mg g^{-1}) diverged from the calculated values ($q_{e\text{cal}}$, mg g^{-1}), as shown in Table 1. This result indicates that the adsorption of the MV 2B by the composite does not follow the pseudo-first-order kinetic model (i.e., the process is not a phenomenon controlled by diffusion; other steps are responsible for controlling the kinetics observed). The rate constant k_1 can be interpreted as a temporal scale factor, which is intended to indicate the rate at which the system reaches equilibrium. Higher values of k_1 indicate less time to reach that condition and vice versa. This parameter may or may not be dependent on the experimental conditions of the process [49]. As shown in Table 1, the adsorption process does not reach equilibrium in a short period according to the pseudo-first-order model because the values of k_1 are on the order of 10^{-2} , with the greatest difference occurring in the experiments in which the initial dye concentrations are 90 and 120 mg L^{-1} . This finding also indicates that k_1 does not depend on the initial concentration of MV 2B parameter.

The pseudo-second-order kinetic model can be expressed by Equation (6) [50]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

where k_2 is the pseudo-second-order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$). Analogous to the pseudo-first-order kinetic model, the k_2 and q_e parameters were determined from the linear and angular coefficients of the equations formed by regressing t/q_t versus t , respectively. The r value at

different concentrations of the linear portions is greater than 0.9997, which suggests that the adsorption of the MV 2B follows the pseudo-second-order kinetic model wherein the rate of chemical interactions between the dye and the sites of adsorbent is the step that controls the overall kinetics of the process. Furthermore, the calculated data ($q_{e,cal}$) are consistent with the experimental data ($q_{e,exp}$), as shown in Table 1.

Table 1

Kinetics parameters for MV 2B adsorption by HNT-Fe₃O₄ composite.

	Initial dye concentration (mg L ⁻¹)				
	60	90	120	150	180
$q_{e, exp}$ (mg g⁻¹)	9.12	12.18	15.05	16.72	18.23
Pseudo-first-order					
$q_{e, cal}$ (mg g ⁻¹)	1.39	3.65	5.79	4.56	3.81
$k_1 \times 10^2$ (min ⁻¹)	1.57	1.02	2.09	1.34	1.46
r	0.8734	0.9021	0.9566	0.9315	0.9079
Pseudo-second-order					
$q_{e, cal}$ (mg g ⁻¹)	9.16	12.29	15.29	16.69	18.37
$k_2 \times 10^2$ (g mg ⁻¹ min ⁻¹)	5.24	1.11	1.24	1.10	1.55
r	0.9999	0.9997	0.9999	0.9999	0.9999

The kinetic constant k_2 has the same physical meaning as k_1 and may or may not also depend on the experimental conditions of the adsorption process [49]. In this case, the results shown in Table 1 demonstrate that k_2 does not depend on the initial concentration of MV 2B parameter either. The results of k_2 are also on the order of 10^{-2} , which indicates that adsorption did not reach equilibrium within a short time period, according to the pseudo-second-

order model. Unlike what was previously observed, the value of k_2 differs slightly in experiments with lower MV2B concentrations ($C_0 = 60 \text{ mg L}^{-1}$) than for the other experiments, which show a value approximately 4 times higher, indicating that equilibrium is attained more rapidly under these conditions.

3.4 Adsorption equilibrium

Adsorption isotherm models are fundamental to describing the interactive behavior between the adsorbate and adsorbent and are also important for investigating mechanisms of adsorption. In this study, equilibrium data were analyzed using the Freundlich and Langmuir isotherms. It is important to emphasize that the equilibrium experiments were performed at the same conditions of adsorption kinetics.

To evaluate which model was best suited to describe these processes, r and the error function (F_{error}) were analyzed; a lower result from the error function indicated a smaller difference between adsorption capacity calculated by the model (q_{cal}) and the experimental (q_{exp}). F_{error} can be expressed according to Equation (7) [51]:

$$F_{error} = \sum_i^P \left(\frac{q_{i\text{ cal}} - q_{i\text{ exp}}}{q_{i\text{ exp}}} \right)^2 \quad (7)$$

where $q_{i\text{ cal}}$ is a value of q predicted by the fitted model; $q_{i\text{ exp}}$ is a value of q measured experimentally; i indicates the values of the initial dye concentration of the experiments (60, 90, 120, 150 and 180 mg L^{-1}); and P is the number of experiments performed.

The Freundlich and Langmuir isotherm linearized models are shown in **Fig. 11**.

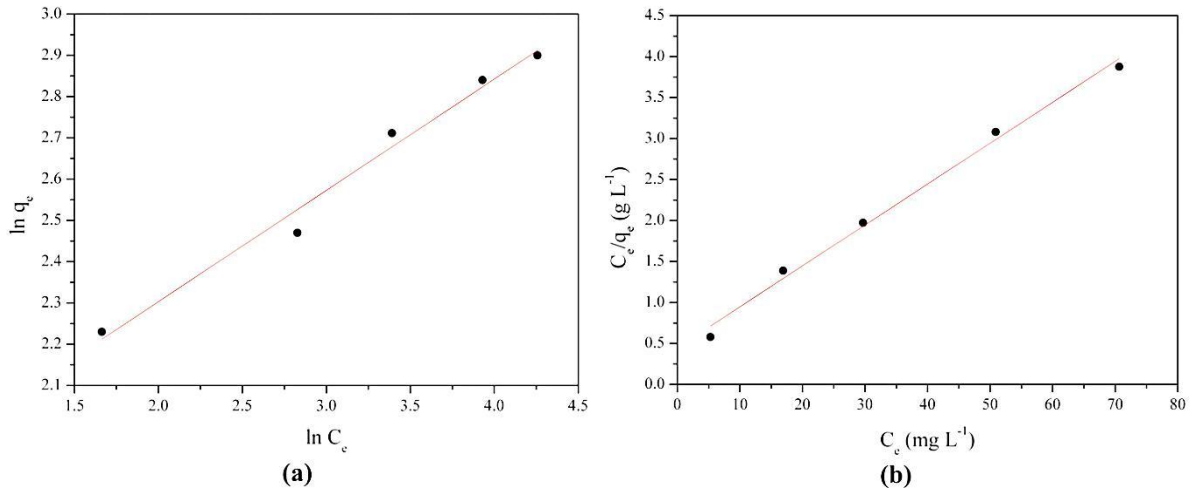


Fig. 11.(a) Freundlich and **(b)** Langmuir isotherm linearized models.

The empirical Freundlich equation is applicable to adsorption on heterogeneous surfaces, where the interaction between the adsorbed molecules is not limited to the formation of a monolayer. The Freundlich constant (k_F) is related to the adsorption capacity of the adsorbent: the higher the value, the greater the affinity for the adsorbate. The empirical parameter $1/n$ is related to the strength of adsorption, which varies with the heterogeneity of the material. When the values of $1/n$ are between 0.1 and 1.0, the adsorption process is considered favorable [46]. The linearized form of the Freundlich equation is expressed according to Equation (8)[52]:

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \quad (8)$$

where k_F is the Freundlich constant (L g⁻¹) and $1/n$ is a dimensionless empirical parameter. The k_F and $1/n$ values were determined from the linear and angular coefficients of the equations formed by regressing $\ln q_e$ as a function of $\ln C_e$, respectively. These values, along with r and F_{error} , are shown in Table 2. In general, the experimental data are shown to be well

adjusted to the Freundlich model because the r value is greater than 0.98, and F_{error} is near 0.0022. The value of 0.2696 for the parameter $1/n$ is lower than 1.0, suggesting that the adsorption is favorable under the conditions proposed by the Freundlich model.

The Langmuir model is based on the assumption of monolayer adsorption on a structurally homogeneous adsorbent, where all sorption sites are identical and energetically equivalent [42]. The linear form of the Langmuir equation can be expressed according to Equation (9)[52]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m k_L} \quad (9)$$

where q_m is the theoretical maximum adsorption capacity corresponding to monolayer coverage (mg g^{-1}), and k_L is the Langmuir constant (L mg^{-1}). The k_L and q_m were determined from the linear and angular coefficients of the equations formed by regressing C_e/q_e as a function of C_e , respectively.

To determine whether the adsorption process is favorable, a dimensionless constant separation factor R_L is defined. The adsorption process is irreversible when R_L is 0.0, favorable when R_L is between 0.0 and 1.0, linear when R_L is equal to 1.0, and unfavorable when R_L is greater than 1.0. The R_L parameter can be defined based on Equation (10)[52]:

$$R_L = \frac{1}{1 + k_L C_0} \quad (10)$$

where C_0 is the initial dye concentration (mg L^{-1}).

The isotherm parameters for MV 2B adsorption by the HNT-Fe₃O₄ composite are shown in Table 2. As shown, the experimental data are well adjusted to the Langmuir model as well. The R_L values are between 0.130–0.048, confirming that the adsorption process is also favorable. Although the r value is greater than 0.99, its F_{error} is higher than 0.04 and, thus, higher than the one obtained for the Freundlich model. It can be inferred that analyzing the correlation coefficient of the fitting is not the only parameter that should be accounted for to verify the best fitting isotherm model. Thus, these data suggest that both models were suitably fitted [53]. Similar results were also observed by Lima et al. [51], Namasivayam and Sureshkumar [54], and Kalavathy and Miranda [55]. According to these authors, the adsorption mechanism by both monolayer adsorption and heterogeneous energetic distribution of active sites on the adsorbent surface is possible [54].

Table 2

Isotherm parameters for MV 2B adsorption by HNT-Fe₃O₄ composite.

Isotherm	Temperature (25°C)	
Freundlich	k_F (L g ⁻¹)	5.835
	$1/n$	0.2696
	r	0.9892
	F_{error}	0.0022
Langmuir	q_m (mg g ⁻¹)	20.04
	k_L (L mg ⁻¹)	0.112
	R_L	0.130–0.048
	r	0.9955
	F_{error}	0.0417

A comparison of the q_m of a few adsorbents available in the literature for removal of MV 2B in aqueous solution is given in Table 3. It is clear shown that HNT-Fe₃O₄ composite used in this work had a moderate adsorption capacity, despite of its relatively small surface area.

Table 3

Comparison of maximum adsorption capacity(q_m) of other adsorbents for removal of MV 2B.

Adsorbent	q_m (mg g ⁻¹)	Reference
Modified cation exchange membrane	10.1	[56]
Cellulose-based wastes	10.5	[57]
Mansonia wood sawdust	16.11	[58]
HNT-Fe ₃ O ₄ composite	20.04	This study
Sunflower seed hull	92.59	[48]

3.5 Thermodynamics studies

Thermodynamics experiments were performed at 283, 293 and 303 K at an initial dye concentration of 90 mg L⁻¹. This initial concentration was chosen because it provided the best opportunity to monitor the adsorption process. The other conditions used were the same as those used in the kinetics and equilibrium studies.

The values of the standard Gibbs free energy change (ΔG°) for each temperature were calculated from the Equation(11)[59]:

$$\Delta G^\circ = -RT \ln k_c \quad (11)$$

where R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is temperature (K) and k_c is the equilibrium stability constant, which was calculated at each temperature by the Equation (12)[59]:

$$k_c = \frac{C_s}{C_e} \quad (12)$$

where C_s and C_e are the equilibrium concentrations on the adsorbent and on the aqueous phase, respectively.

The enthalpy change (ΔH°) and entropy change (ΔS°) are calculated from the slope and intercept of the plot of $\ln k_c$ versus $1/T$, based on the Van't Hoff equation (Equation 13)[59]:

$$\ln k_c = \left(\frac{\Delta S^\circ}{R} \right) - \left(\frac{\Delta H^\circ}{R} \right) \frac{1}{T} \quad (13)$$

The results of the thermodynamics experiments are shown in Table 4. The negative values of ΔG° describe the spontaneous nature of the adsorption process. As the temperature increases, ΔG° increase as well, indicating less driving force and hence slower adsorption capacity at higher temperatures[60].

The negative value of ΔH° indicates that the adsorption process is exothermic. This magnitude is related to adsorbate interactions with the adsorbent and rearrangement of the surface during the adsorption process. It is also observed experimentally as the fraction of the surface that is covered by adsorbate. Enthalpy change data is useful for distinguishing physisorption and chemisorption. The typical value for physisorption usually lies below 84 kJ

mol⁻¹, which agrees with the value obtained for MV 2B adsorption onto HNT-Fe₃O₄; for chemisorption, bond strengths lie between 84 and 420 kJ mol⁻¹. Finally, the results of ΔS° indicate decreased randomness at the solid/solute interface during the adsorption of MV 2B onto the HNT-Fe₃O₄ composite [60]. This behavior (negative values of ΔG° , ΔH° and ΔS° ; slower adsorption capacity at higher temperatures and physisorption) was also observed by others researchers that employed magnetic composites for removal of dyes [61-63].

Table 4

Thermodynamics parameters for the adsorption of MV 2B onto HNT-Fe₃O₄ composite.

Temperature (K)	Thermodynamics			
	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	<i>r</i>
283	- 4.09			
293	- 3.75	- 13.23	- 32.32	0.9744
303	- 3.44			

3.6 Reusability of HNT-Fe₃O₄ composite

It is crucial to investigate the reusability of adsorbents for practical applications to address ecological and economic demands for sustainability [64]. Adsorption experiments were performed at a 700 rpm stirring rate and a pH equal to 7.0 with 0.15 g of composite in 25 mL of a 90 mg L⁻¹ solution of MV2B at 25°C for 6 h. After each adsorption experiment, the adsorbent was collected by external magnet force (3000 G) and recovered by a 1.0 mol L⁻¹ solution of NaOH at 250 rpm for 3 h. Then, the HNT-Fe₃O₄ composite was removed from the alkaline solution and placed in a 0.5% v/v acetic acid solution at the same stirring rate and

contact time. Finally, it was washed several times with distilled water, dried and reused again. The effect of recycling times of HNT-Fe₃O₄ composite on MV 2B adsorption performance was repeated four times.

Fig. 12 showed that the removal percentage of MV 2B was still near 80% after four cycles, indicating that HNT-Fe₃O₄ can be reused. The decrease in %R might be due to irreversible adsorption of the adsorbent during the regeneration process [64].

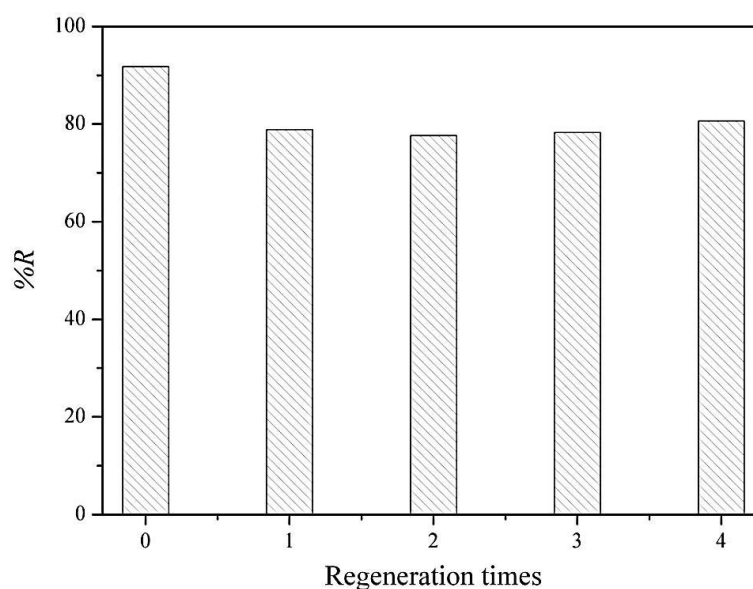


Fig. 12. Reusability cycles of HNT-Fe₃O₄ composite.

4 Conclusion

In general, the method used to prepare the HNT-Fe₃O₄ composite was efficient, as shown by the characterization analysis, which verified that the magnetite nanoparticles are anchored onto the surface of the HNT.

The kinetics of the adsorption process was shown to be better described by a pseudo-second-order model. The experimental results also suggest that both the Langmuir and

Freundlich models were suitable to predict adsorption equilibrium. The experimental data concerning the Langmuir constant (k_L), maximum adsorption capacity (q_m), Freundlich constant (k_F), and $1/n$ were 0.112 mg L^{-1} , 20.04 mg g^{-1} , 5.835 L g^{-1} and 0.2696 , respectively. Moreover, the thermodynamic data have shown that the adsorption of MV 2B onto HNT- Fe_3O_4 composite is a spontaneous and exothermic process by physisorption.

Finally, the employed composite could also be regenerated at least four times using a 1.0 mol L^{-1} solution of NaOH as an eluent and was shown to be a promising adsorbent for the removal of MV 2B cationic dye.

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