

RESEARCH PAPER

Using of Polyacrylonitrile/Fe₂O₃ Nanocomposite in Adsorption of Methyl Green Dye

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ABSTRACT

Alkaline precipitation process was used to prepare iron oxide nanoparticles (Fe₂O₃NPs) to be employed in the polyacrylonitrile matrix and produce the polymer nanocomposite, which used as an adsorbent surface in this study. Polyacrylonitrile - Fe₂O₃ composite was characterized using FT-IR, FE-SEM, EDS and XRD. The ability to adsorb methyl green dye from the aqueous solution was investigated. The following variables have been investigated: adsorbent mass, contact time, initial concentration, and ionic strength, as factors impacting adsorption. Maximum adsorption quantity was (117.803) mg/g that achieved by (0.01) g of adsorbent mass at (308) K and (75) min. To analyze the adsorption data and estimate the maximum adsorption capacity, Freundlich and Langmuir isotherm models were utilized. The results confirmed that the experimental data is more consistent with the Freundlich model. The endothermic nature of the reaction is indicated by the rising adsorption capacity with increasing temperature.

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INTRODUCTION

Environmental contamination is caused by a variety of different components, such as phenols, heavy metals, dyes, pesticides, radionuclides, etc. [1]. However, the production of textiles, leather, plastics, paper, cosmetics, and paint all consume a significant number of dyes, making them a significant contributor to environmental degradation [2, 3]. In general, dyes are impair photosynthesis by limiting the amount of light that reaches plant leaves [4]. They can pose a risk to human health as well as aquatic life due to their toxicity and carcinogenic properties [5]. Because of its low cost and strong surface adhesion strength, methyl green is a common cationic dye used in a variety of fields [6]. It has also strong surface adhesion due to its potential to be converted to

benzidine, which has been classified as a carcinogen [7]. Water purification techniques include chemical oxidation, coagulation, electrochemical oxidation and adsorption [8-12]. In addition to being a practical method, adsorption is also a reasonable, useful and low-cost strategy. [13-15]. The ability to remove cationic dyes from water is enhanced when the surfaces of adsorbent materials are activated with nanoparticles. In addition to providing a high surface area compared to the total volume, these particles form additional active adsorption sites [16]. Many technological uses of iron oxide nanoparticles (IONPs) advance nanotechnology due to its industrial importance. Several methods have been studied to manufacture iron oxide nanoparticles (IONPs) with attractive properties. The most widely utilized iron oxide nanoparticles in

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scientific research are magnetic Fe₃O₄ and γ-Fe₂O₃, which have outstanding optical, magnetic and electrical properties. The industrial importance of Fe₂O₃ nanoparticles is increasing due to their high catalytic properties and their high-temperature calcining makes them ideal for separations and biological applications. These materials are ideal for photocatalysis due to their semiconducting properties and chemically reactive surface for ions, so they have enjoyed numerous uses in the electronics, healthcare, energy, agriculture and animal biotechnology scopes [17].

Polymeric nanocomposites have a variety of applications in nanotechnology as a result of combining the processability and adaptability of an organic polymer matrix with inorganic particles with different properties. Therefore, these composites are nanoparticles embedded in a polymer matrix. Electrical, mechanical, catalytic and magnetic properties have been seen in inorganic nanoparticles and by combining polymers with these particles we produce a new material that has multiple applications [18].

By conducting a review of previous studies on the polyacrylonitrile-Fe₂O₃ composite and its use as an adsorbent surface for some pollutants; Kai Pan *et al.* demonstrated that a polyacrylonitrile (PAN) nanofibre mat infused with α-Fe₂O₃ can successfully remove Pb²⁺ from water that has been polluted. Control experiments were performed to evaluate the adsorption capabilities. The adsorption results corresponded to Langmuir model. The adsorption mechanism's conclusions revealed that the adsorption is caused by ion exchange between the proton of the surface hydroxyl groups and Pb²⁺[19]. Furthermore, Seyed Mohammadreza Miraboutalebi *et al* investigated the use of a composite adsorbent of α-Fe₂O₃/polyacrylonitrile (PAN) to remove

methylene blue (MB) from aqueous solution. Because of the existence of Fe₂O₃ as nanoparticles photocatalyst on the surface of PAN produced an excellent composite adsorbent for the MB photocatalytic decomposition. PAN was selected as an essential component, they investigated the effects of α-Fe₂O₃ nanopowder loading, contact time, initial concentration, temperature, pH and solar light. The adsorption behaviour has been examined further using isotherms of Langmuir, Freundlich and Temkin. Freundlich equation has the best agreement with experimental results. At a practical range of temperature, thermodynamic analyses revealed the presence of a spontaneous thermal adsorption mechanism [20].

This work aims to prepare iron oxide nanoparticles (Fe₂O₃NPs), then impregnate polyacrylonitrile matrix with them to produce the polymer nanocomposite and diagnose with FTIR, FE-SEM, EDS and XRD techniques to verify the chemical composition and determine the surface morphology of the prepared materials. The composite was then used as an adsorbent surface for methyl green dye from aqueous solutions at various temperatures, including research into the optimal adsorption parameters, which included adsorbent mass, initial concentration, contact time, temperature, and ionic strength. In addition, the experimental adsorption data are apply to Freundlich and Langmuir isothermal models and thus the thermodynamic functions are calculating to know the adsorption behavior.

MATERIALS AND METHODS

Chemicals

In this research, the chemicals utilized were obtained from Sigma-Aldrich, including Polyacrylonitrile, Dimethylformamide, Ferric Chloride, Sodium Hydroxide, Ethanol and Methyl

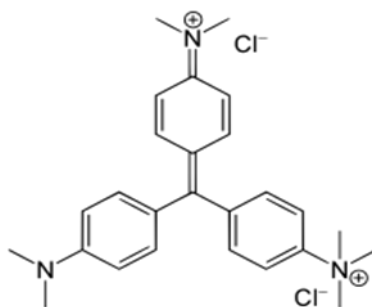


Fig. 1. Chemical structure of methyl green dye.

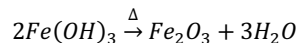
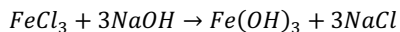
Green Dyes (Fig. 1).

Instruments

LabTech LMS-1003 Hotplate Stirrer, Sartorius CPA-22 Digital Balance, and an HS-30D Mechanical Stirrer Honest iv, Using the SWB-25 HYSC Water Bath Shaker, pH paper, Filter paper, we used a 600-micron sieve, a Shimadzu S8400 spectrophotometer, and a Shimadzu X-ray diffraction spectrophotometer. In addition to the AA-3000 Phywe atomic force microscope and the S8000 TESCAN scanning electron microscope.

Prepared of Iron oxide nanoparticles Fe₂O₃NPs

Iron oxide nanoparticles (Fe₂O₃NPs) were prepared using a precipitation method [21]. The following equation illustrates the reaction between ferric chloride and sodium hydroxide, which results in iron oxide.



(8.125) g of ferric chloride were dissolved

in (500) mL of distilled water and heated to 30 °C continuously stirring. Another aqueous solution were prepared by dissolving (6) g of sodium hydroxide in (400) mL of water. The last solution is added to the first while maintaining the temperature (30 °C) using a water bath with continuous stirring. After the addition, the temperature of reaction mixture was kept below (30°C) for (60) min. The resulting precipitate was washed with water and ethanol several times until (pH=7) was reached, then it was transferred to a drying oven at 90 °C for 120 min. Finally, the product was calcined in a furnace oven at 400 °C for 180 min.

Preparation of polyacrylonitrile - Fe₂O₃ nanocomposite

(5) g of polyacrylonitrile was weighed and dissolved in (40) mL of DMF. It was shaken until a homogeneous polymer solution was obtained. To produce the polymer nanocomposite, (0.5) g of prepared iron oxide nanoparticles was added to previous solution with continuous shaking. Polyacrylonitrile - Fe₂O₃ nanocomposite was

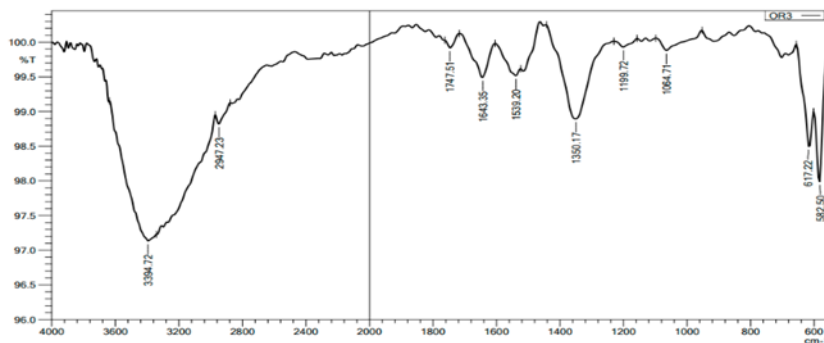


Fig. 2. FT-IR spectrum of the prepared Fe₂O₃NPs.

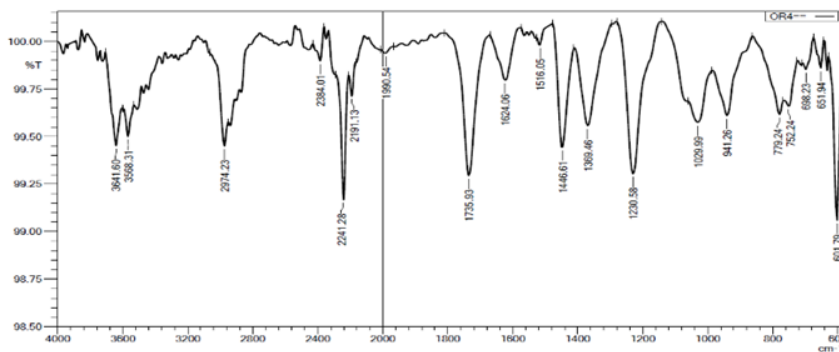


Fig. 3. FT-IR spectrum of the prepared polyacrylonitrile – Fe₂O₃ nanocomposite.



dried in an oven for (120 min) at (90 °C), then the product was ground to use as a surface adsorbent later.

Adsorption Experiments

Methyl green dye adsorption from aqueous solutions was investigated using polyacrylonitrile – Fe₂O₃ nanocomposite as adsorbent surface. Adsorption capacity was calculated by measuring the absorbance of a methyl green dye at a wavelength of (λ = 632 nm) using a Uv-Vis spectrophotometer.

RESULTS AND DISCUSSION

Characterization techniques

Fourier-transform infrared spectroscopy (FTIR)

Spectroscopy of fourier transform infrared was performed for the prepared Fe₂O₃NPs and polyacrylonitrile – Fe₂O₃ nanocomposite, Figs. 2 and 3, respectively. The vibration of stretching O-H bond in hydroxyl group is responsible for the significant broad band at 3394 cm⁻¹. The absorption is caused by the asymmetric and symmetric bending vibration of C=O peaks at 1643 cm⁻¹, 1539 cm⁻¹, and 1350 cm⁻¹ can be attributed

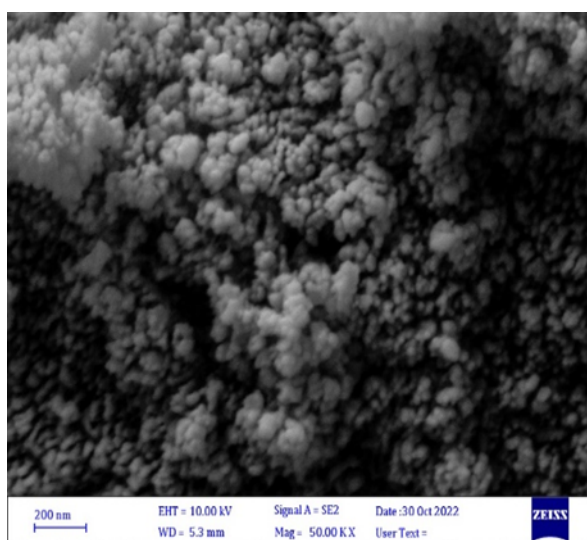


Fig. 4. FE-SEM micrograph of the prepared Fe₂O₃NPs.

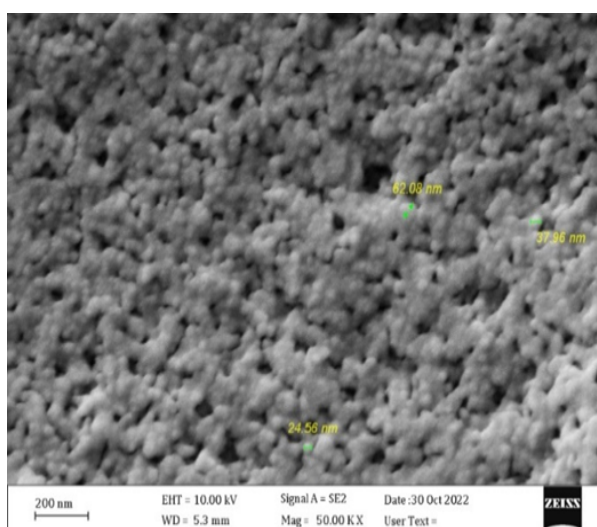


Fig. 5. FE-SEM micrograph of the prepared polyacrylonitrile – Fe₂O₃ nanocomposite.

to these vibrations. The Fe-O stretching band of Fe₂O₃ was seen 582 cm⁻¹, Fig. 2. It is noted from Fig. 3 that the diagnostic peaks of polyacrylonitrile were appeared. Peaks at 3568 cm⁻¹ and 3641 cm⁻¹ as a result of the presence of absorbed water. There is also a peak at 2241.28 cm⁻¹ was assigned to -C≡N group vibration. The peak at 2974.23 cm⁻¹ is also attributed to the asymmetry of C-H methyl stretching. In addition, a peak at 1369.46 cm⁻¹ was observed due to the C-H bent methyl group vibration [22]. It is also observed that the peak of Fe-O was shifted to a frequency slightly higher than it appeared in the spectrum of nanoparticles, where it appeared at 601cm⁻¹.

Scanning electron microscope (SEM)

Scanning electron microscopy was conducted for the prepared Fe₂O₃NPs and polyacrylonitrile – Fe₂O₃ nanocomposite, Figs. 4 and 5, respectively. It is noted in Fig. 4 that the particles have high adhesion forces and dimensions within the range (40–50) nm. In comparison, the nanoparticles were observed to be completely encapsulated by polyacrylonitrile and appeared to be slightly

larger, Fig. 5[23].

Energy dispersive X-ray spectroscopy (EDS)

Energy dispersive X-ray spectra was done for the prepared Fe₂O₃NPs and polyacrylonitrile – Fe₂O₃ nanocomposite, as shown in Figs. 6 and 7, respectively. Fig. 6 confirms the purity of the prepared iron oxide nanoparticles, as both iron and oxygen were found at a percentage (71.4%) and (28.6%), accordingly. On the other hand, it is noted from Fig. 6 that carbon and nitrogen, the main components of polyacrylonitrile are present in higher percentages than the iron and oxygen which present in the chemical composition of nanoparticles, which supports success of the composite preparation. As the proportions for each of carbon constitutes 81%, nitrogen 9.2%, oxygen 5.4% and iron 4.5%, respectively.

X-ray diffraction spectroscopy (XRD)

The technique of X-ray diffraction spectroscopy was used for the prepared Fe₂O₃NPs and polyacrylonitrile – Fe₂O₃ nanocomposite, Figs. 8 and 9, respectively. Fig. 8 shows the XRD spectrum

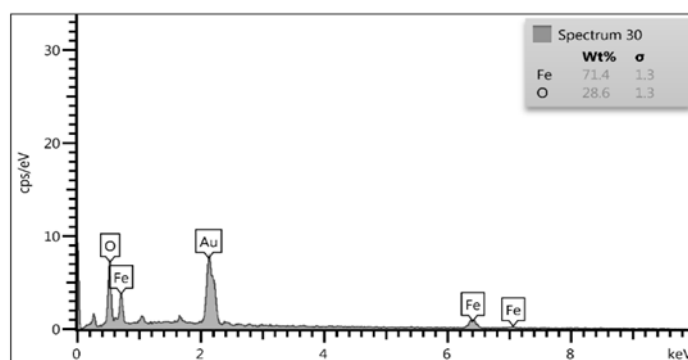


Fig. 6. EDS spectra of the prepared Fe₂O₃NPs.

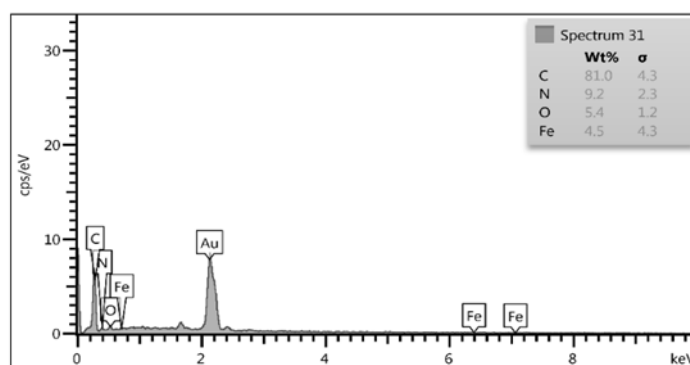


Fig. 7. EDS spectra of the prepared polyacrylonitrile – Fe₂O₃ nanocomposite.

of nanoparticles with nine different peaks at (2 theta) = 24.24144, 31.77991, 33.22697, 35.70110, 45.51337, 54.10791, 57.3153, 62.5168, 64.07628, and 75.4018. They could all be correctly indexed to the peak location of rhombohedral Fe₂O₃ (JCPDS No. 24-0072) [24]. Hence, the crystalline size of nanoparticles was determined using Deby Scherrer's formula [25,26]. Typically, it was (30) nm, according the full width at half maximum (FWHM).

$$D = \frac{0.94\lambda}{\beta \cos\theta} \quad (1)$$

where D is the size of particle in nanometers, λ is the wavelength of x-ray, β is the broadening of line at the half maximum intensity (FWHM) in

radians and θ is the angle of Bragg. Fig. 9 shows that the nanopolyacrylonitrile retained its semi-crystalline character. The diffraction patterns of Fe₂O₃NPs were not clearly seen in the spectrum due to the low doping percentage.

The Adsorption Effect Factors

Adsorbed amounts for methyl green dye (mg/g) were calculated using the equation [27].

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

In this equation, C₀ is the initial concentration of adsorbate (mg/L), C_e is the equilibrium concentration of adsorbate (mg/L), V is the volume of solution (L) and w is the mass of adsorbent (g).

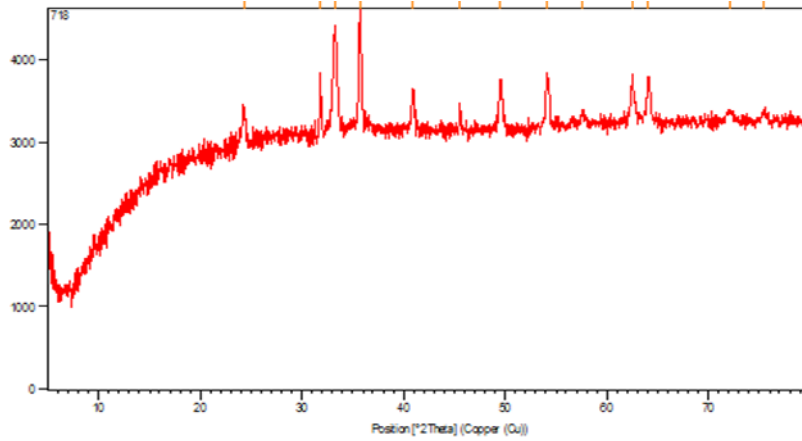


Fig. 8. X-ray diffraction pattern of the prepared Fe₂O₃NPs.

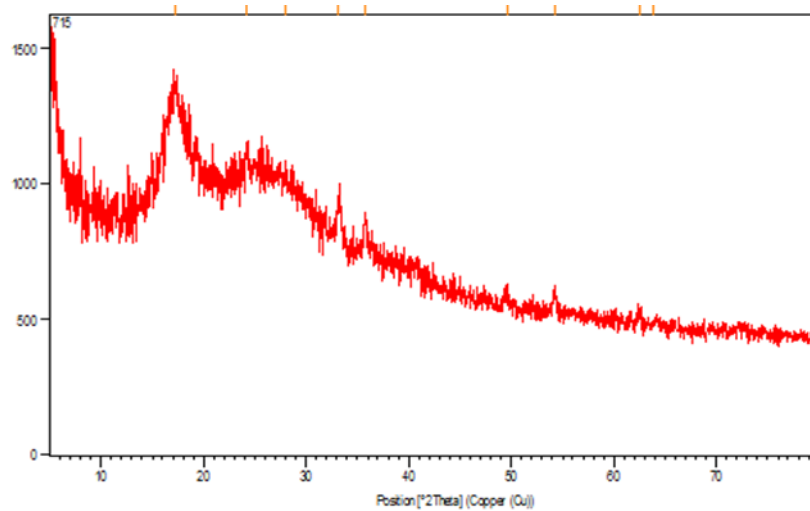


Fig. 9. X-ray diffraction pattern of the prepared polyacrylonitrile – Fe₂O₃ nanocomposite.

The effect of adsorbent mass

Using an initial dye concentration of 30 mg/L, the adsorption of methyl green dye on polyacrylonitrile modified by Fe₂O₃NPs at 298 K was investigated. Increases in both surface area and the number of adsorption sites cause increases in the quantity of dye absorbed with increasing adsorbent mass [28]. Fig. 10 and Table 1 show that the largest amount of dye that could be absorbed by the adsorbent mass was 0.01 g, which meant that saturation had been reached.

The effect of initial concentration

Fig. 11 and Table 2 illustrate the adsorption of methyl green dye onto polyacrylonitrile modified with Fe₂O₃NP at concentrations of (5, 10, 15, 20, and 25) mg/L on a 0.01 g of adsorbent material at 298 K. More dye may be absorbed when there is a larger concentration of it accessible. It's because more mass transfer occurs on the adsorbent surface when the diffusion rate is higher [29]. To

get the greatest outcomes, we choose the 30 mg dose with the greatest concentration.

Effect of contact time

At a temperature 298 K, an initial concentration 30 mg/L and an adsorbent mass 0.01g, the impact of contact time on the adsorption of methyl green dye on polyacrylonitrile functionalized with Fe₂O₃NPs was studied (Fig. 12 and Table 3). When the adsorbed amount levels off after increasing for 75 minutes, equilibrium has been reached in the adsorption system. Caused by the saturation of the adsorbent with methyl green dye molecules [30].

Effect of ionic strength

When the initial concentration is 30 mg/L, the adsorbent mass is 0.01 g and the temperature is 298 K, the impact of ionic strength on the adsorption of methyl green dye on polyacrylonitrile modified by Fe₂O₃NPs was examined (Fig. 13). Increases in salt

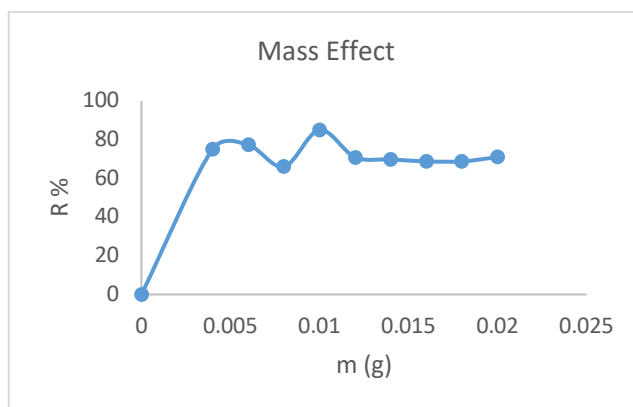


Fig. 10. The adsorbed amount of methyl green dye onto polyacrylonitrile – Fe₂O₃ nanocomposite.

Table 1. The adsorbent mass effect.

Adsorption	m	R%
polyacrylonitrile -Fe ₂ O ₃ NPs	0.0000	0.0000
	0.0040	75.1592
	0.0060	77.2823
	0.0080	66.0297
	0.0100	85.0318
	0.0120	70.9129
	0.0140	69.8513
	0.0160	68.7898
	0.0180	68.7898
	0.0200	71.0191

concentration reduce the amount of methyl green dye adsorbent on the polyacrylonitrile modified by Fe₂O₃ NPs surface for several reasons, including the salt's greater solubility and the surface charge, which decreases the dye's attraction to the surface and thus the adsorbent amount. When the solubility of the dye decreases in the solvent,

the overlap between solvent molecules and ions (NaCl or KCl) decreases or increases, causing the solubility of the dyes to decrease in the aqueous solution [31].

Adsorption Isotherms

Adsorption isotherms represent the equilibrium

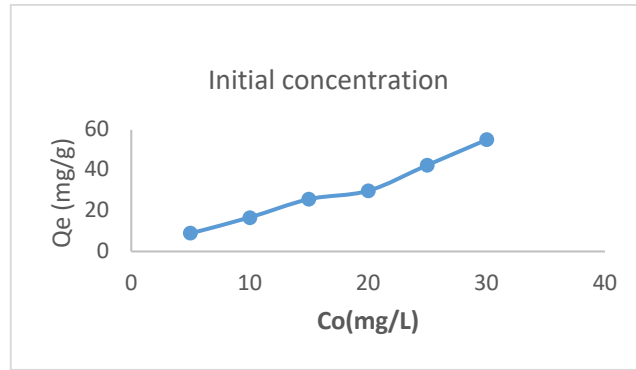


Fig. 11. The initial concentration of methyl green dye adsorption onto polyacrylonitrile – Fe₂O₃ nanocomposite.

Table 2. The effect of initial concentration.

Adsorbent	Ce(mg/L)	Qe(mg/g)
polyacrylonitrile - Fe ₂ O ₃ NPs	0.0000	0.0000
	1.4331	8.9172
	3.2803	16.7994
	4.6815	25.7961
	8.0255	29.9363
	7.9618	42.5956
	7.9618	55.0956

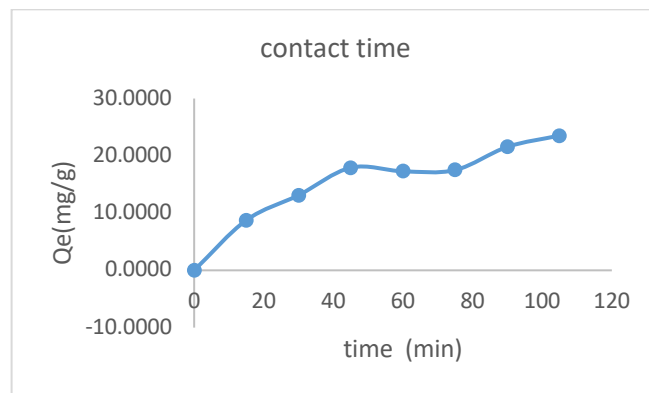


Fig. 12. The contact time of methyl green dye adsorption onto polyacrylonitrile – Fe₂O₃ nanocomposite.



relationship between the concentration of the solution and the amount adsorbed on the adsorbent surface at a particular temperature. Hence, the best adsorption process parameters can be established by examining the adsorption isotherms, which determine the nature of adsorbent-adsorbate association. [32].

$$\frac{C_e}{q_e} = \frac{1}{q_{max}k_L} + \frac{C_e}{q_{max}} \quad (3)$$

where q_e is the equilibrium dye concentration in mg/g, C_e is in mg/L, q_{max} is its maximum adsorption capacity, and k_L has the experimental

value of Langmuir constant. C_e/q_e versus C_e is the plot that yields the values of the Langmuir constants q_{max} and k_L . In this case, q_{max} is shown by the line's slope and k_L the intercept (Fig. 14 and Table 4).

The values of k_L and q_{max} in Table 1 demonstrate some variability over a range of temperatures. Moreover, the average R^2 value of 0.5371 for the investigated adsorption system disproves the validity of the Langmuir model. To solve the challenge of calculating the energy distribution across a heterogeneous adsorbent surface, the Freundlich isotherm model is expected to be used.

Table 3. The Contact Time Effect.

Adsorbent	t (min)	Qe(mg/g)
polyacrylonitrile - Fe ₂ O ₃ NPs	0	0.0000
	15	8.7580
	30	13.1210
	45	17.9299
	60	17.2930
	75	17.5159
	90	21.5605
	105	23.5350

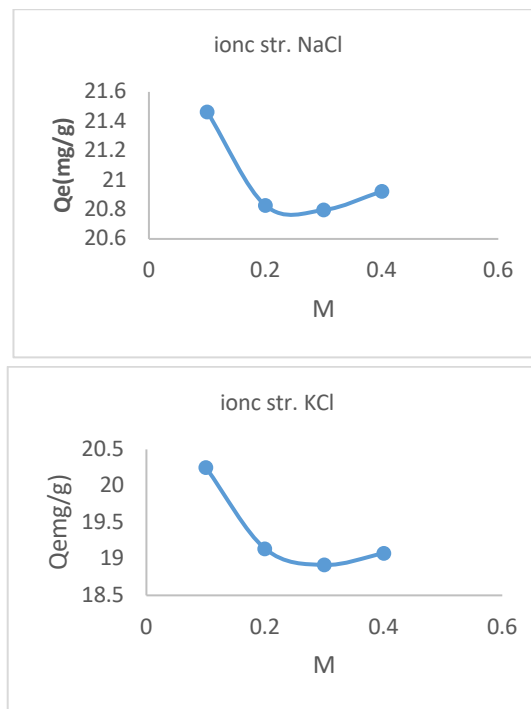


Fig. 13. The ionic strength of methyl green dye adsorbed onto polyacrylonitrile – Fe₂O₃ nanocomposite.

Only if the [33] is present is adsorption considered.

This is an expression for the linear Freundlich equation:

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (4)$$

where q_e is the adsorbed dye amount at equilibrium (mg/g), C_e is the adsorbed dye concentration at equilibrium (mg/L) and k_f or n are the experimental Freundlich parameters. The

intercept and slope of a plot of $\ln q_e$ vs $\ln C_e$ have been used to compute k_f and n (Fig. 15 and Table 5).

The values of the Freundlich constant k_f shown in the table decrease with increasing temperature, indicating that the capacity for adsorption decreases at high temperatures. The examined adsorption system is endothermic because the intensity of adsorption rises with increasing temperature. The Freundlich model is appropriate

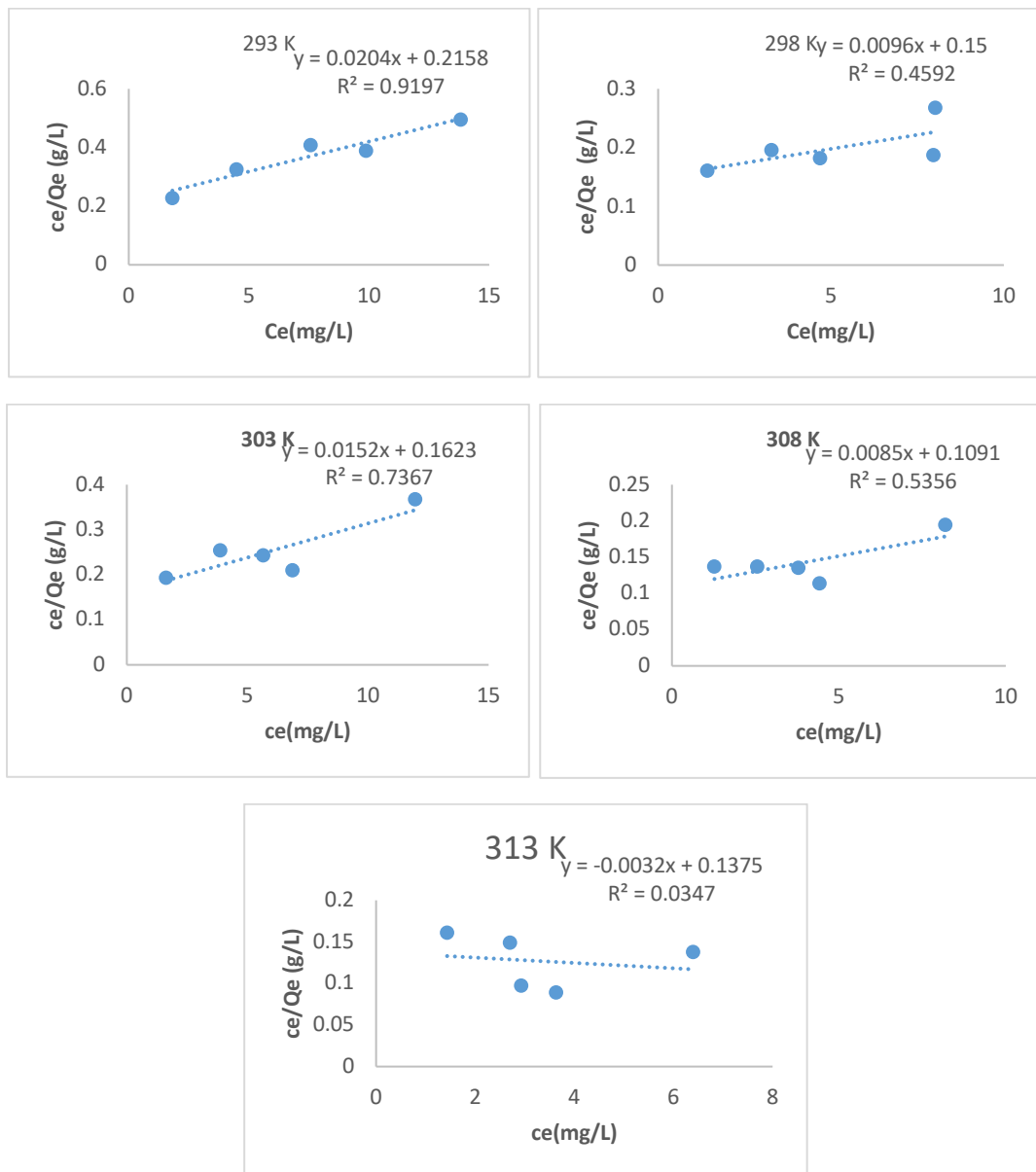


Fig. 14. Langmuir isotherm plots of methyl green dye adsorbed onto polyacrylonitrile – Fe₂O₃ nanocomposite at the temperatures investigated.

Table 4. Langmuir parameters of methyl green dye polyacrylonitrile – Fe₂O₃ nanocomposite at the studied temperatures

T (K)	R ²	Q _{max}	K _L
293	0.91971	48.9253	0.0947
298	0.4592	104.5936	0.0637
303	0.7367	65.9213	0.0934
308	0.5356	117.8031	0.0778
313	0.0347	310.5291	0.0234

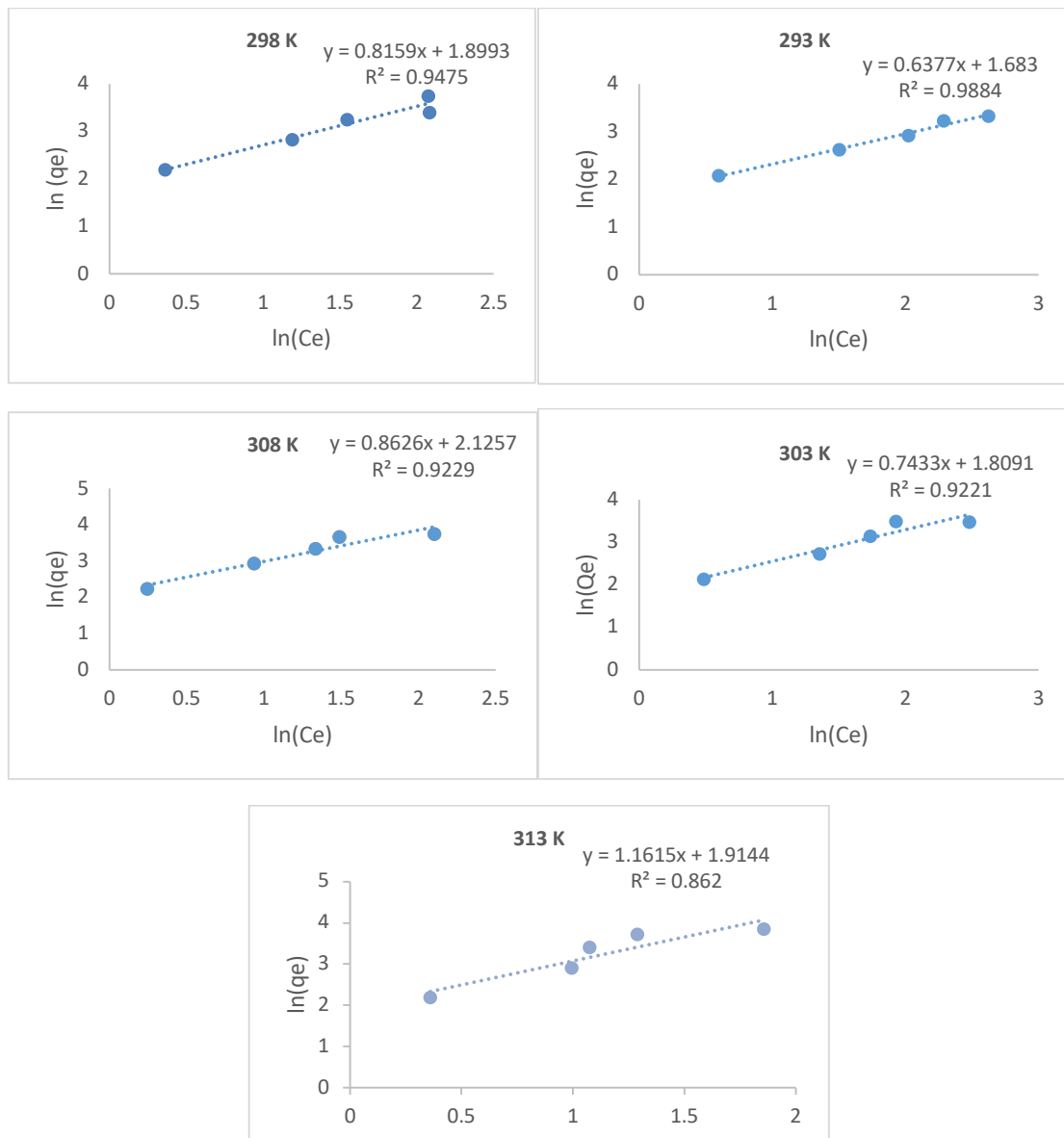


Figure 15. Freundlich isotherm plots of methyl green dye adsorbed onto polyacrylonitrile – Fe₂O₃ nanocomposite at the temperatures investigated.

since the correlation coefficient R² is consistently high, at 0.9285.

$$\ln K = \frac{-\Delta H}{RT} + \text{constant} \quad (5)$$

In this equation, T is the Kelvin temperature unit, R is the universal gas constant, k is the thermodynamic equilibrium constant and DH is the adsorption enthalpy change.

The enthalpy change was determined by the straight line's slope of van't Hoff equation, as showed in Fig. 16, which is the result of plotting

lnK against 1/T. The following equation was used to get an approximation of the free Gibbs energy, Go:

$$\Delta G^0 = -RT \ln K \quad (6)$$

An equilibrium Gibbs formula was used to calculate the value of entropy changes (ΔS°):

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (7)$$

Table 6 provides a summary of the thermodynamic parameters that were determined.

Table 5. Freundlich parameters of methyl green dye adsorbed onto polyacrylonitrile – Fe₂O₃ nanocomposite at the studied temperatures.

T (K)	R ²	n	K _f
293	0.9884	1.5682	5.3819
298	0.9475	1.2435	6.8255
303	0.9221	1.5013	7.1215
308	0.9229	1.1593	8.3786
313	0.8623	0.8609	6.7830

Table 6. The calculated thermodynamic functions of methyl green dye adsorbed onto polyacrylonitrile – Fe₂O₃ nanocomposite.

T(K)	ΔG°	ΔH°	ΔS°
293	-62.067	+58192.22	+198.8201
298	-991.425		+198.6028
303	-1626.720		+197.4222
308	-3221.090		+199.3938
313	-3919.100		+198.4387

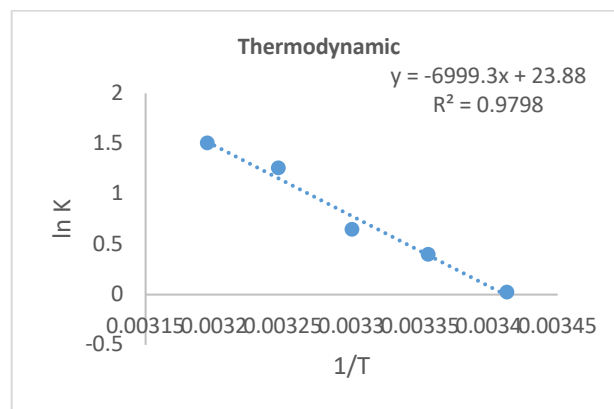


Fig. 16. Van't Hoff plot of methyl green dye adsorbed onto polyacrylonitrile – Fe₂O₃ nanocomposite.

The findings reveal that endothermic adsorption occurs when the enthalpy change is positive, and that adsorbent (MG) spreads out on the adsorbent surface at the start of the adsorption, eventually penetrating the pores of the surface as the temperature rises. Moreover, the adsorption process is spontaneous, as shown by the negative value of the Gibbs free energy change. Moreover, all ΔG° values dropped with increasing temperature, providing further evidence that the methyl green dye adsorption enhanced with rising temperature. This might be because the molecules are more stable in solution than they are on the surface of the Fe₂O₃NP-functionalized polyacrylonitrile. Positive values of the entropy change indicate that the adsorbate-adsorbent interface is becoming more ordered [34].

CONCLUSION

Polyacrylonitrile matrix was successfully modified with Fe₂O₃NPs, so that it could be used to remove methyl green dye from aqueous solution. Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (FE-SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction spectroscopy (XRD) techniques were used to characterize polyacrylonitrile – Fe₂O₃ nanocomposite. All of which confirmed the success of the preparation process and the purity and correctness of the composition of the product. Adsorption process parameters such as adsorbent mass, starting concentration, contact time, and ionic strength were examined. The results confirmed that the studied system is effective in removing methyl green dye from aqueous solutions. So, from application of adsorption isotherms to experimental data, it was observed that the adsorption system conforms to Freundlich model more than to Langmuir model. The calculations of thermodynamic functions indicated that the adsorption process is spontaneous from the negative Gibbs energy values. Hence, the positive value of the enthalpy change confirmed the endothermic nature of the system, while the positive entropy change values referred that the arrangement of the dye molecules on the adsorbent surface was more regular than they were in the solution.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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