

Removal Phenol from Aqueous Solutions Using Environmental friendly and Effective Adsorbent onto Mn-Fe₂O₄-NPs-AC

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ABSTRACT

The applicability of Mn-Fe₂O₄-NPs-AC for removing Phenol from aqueous solutions has been reported. This novel material was characterized by different techniques such as FT-IR, XRD and SEM. The influence of nanoparticle dosage, pH of the sample solution, individual Phenol concentration, contact time between the sample and the adsorbent, temperature, and ionic strength of the sample solution were studied by performing a batch adsorption technique. The maximum removal of 5-25 mg L⁻¹ of individual Phenol from an aqueous sample solution at pH 6.0 for Phenol was achieved within 30 min when an adsorbent amount of 0.1 g was used. Regarding the Kinetic models both pseudo-first-order and pseudo-second-order diffusion models of Phenol revealed that the kinetic of adsorption process followed second-order equation model. After using various Isotherm models to fit the experimental equilibrium data with, the adequacy and applicability of Langmuir model has been proven. The adsorption data fitted well with the Langmuir isotherm model with correlation coefficient ($R^2 > 0.995$), The maximum adsorption capacity of the Phenol removal onto Mn-Fe₂O₄-NPs-AC was roughly 4.27 mg/g, respectively. Thermodynamic parameters of free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) of adsorption were determined using isotherms. $\Delta H^0 = -4.947$ kJ/mol, $\Delta G^0 = -3.937$ kJ/mol and $\Delta S^0 = -1.521$ kJ/mol.K. The fact that the sorption process was endothermic was well reflected by the negative value of (ΔG^0 , ΔH^0 and ΔS^0) which on its own expressed the affinity of Mn-Fe₂O₄-NPs-AC to wards Phenol. These results indicate that the pretreatment of Mn-Fe₂O₄-NPs-AC can optimize the removal of Phenol from aqueous solution.

Keywords: Adsorption; Phenol; Isotherm Study; Kinetic; Thermodynamic

1. INTRODUCTION

The contamination of water sources with organic and inorganic pollutants has been being the most important concern in

water treatment plants [1,2]. Of all organic matter, phenol derivative compounds are among the most common contaminants

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that make water non-drinkable, even in very low levels [3-6]. Phenol intruding water bodies as a result of natural processes and human activities is a considerable concern due to its persistency, unpleasant taste and odor, solubility, carcinogenic, toxicity, mutagenic and malformation effects, poor biodegradability and accumulation potential in plants and tissues (i.e., fish living in lakes and rivers contaminated with phenolic compounds have a queer taste and bad odor) [7,8]. The US Environmental Protection Agency listed phenolic compounds as priority pollutants with a discharge limit to water bodies of < 1 mg/L in the treated effluent to protect human health from the potential toxic effects caused by exposure to phenol [9]. Furthermore, according to the World Health Organization regulation recommended 0.001 mg/L as the permissible limit for phenol concentration in potable water. In Iran, a maximum phenol level of 1.0 mg/L is permitted in wastewater for discharge to surface water resources by the Institute of Standard and Industrial Research of Iran [10]. There are various methods for removing phenol from aquatic solutions such as adsorption, aerobic and anaerobic biological processes [11]. Oxidization by ozone, and ion exchange through resins [12,13]. are some adsorbents used in previous studies for Phenol removal.

Adsorption is one of the best and simple techniques for the removal of toxic and noxious impurities in comparison to other conventional protocols like chemical coagulation, ion exchange, electrolysis, biological treatments is related to advantages viz. lower waste, higher efficiency and simple and mild operational conditions. Adsorption techniques also have more efficiency in the removal of pollutants which are highly stable in biological degradation process through

economically feasible mild pathways [14,15]. The best figures of merit in multi component dyes systems removal are based on development of novel method that permits their accurate simultaneous determination in mixtures. The encounter difficulties are serious peaks overlapping that subsequently impossible their direct determination in mixture using general equation like Beer–Lambert. Derivative spectroscopy efficiently is applicable to resolve absorption peaks overlap through their separation and correction of background interferences. This method is based on searching the wavelengths that possible the accurate and repeatable monitoring of each species in complex matrices without any interference from other target compounds [16,17]. Hence, it has been extensively used for removal of different chemicals from aqueous solutions [18,19]. Of these methods, nanomaterial's based adsorbents is highly recommended for dyes pollutants removal [20]. The efficient applicability of an adsorption process mainly depends on the physical and chemical characteristics of the adsorbent, which is expected to have high adsorption capacity and to be recoverable and available at economical cost. Currently, various potential adsorbents have been implemented for removal of specific organics from water samples. In this regard, magnetic nanoparticles (MNPs) have been studied extensively as novel adsorbents with large surface area, high adsorption capacity and small diffusion resistance. For instance, they have been used for separation of chemical species such as environmental pollutants, metals, dyes, and gases [21]. It should be considered that adsorption as an adored technique has a lot of advantages over other conventional techniques [22].

In this work, Mn–Fe₂O₄ nanoparticles loaded on activated carbon (Mn–Fe₂O₄–NPs–AC) as a novel adsorbent followed by

the characterization using different techniques such as Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM). This adsorbent was used for the removal of Phenol from aqueous solutions [23]. Therefore, we were motivated to prepare Mn-Fe₂O₄-NPs-AC as an alternative to expensive or toxic adsorbents for the removal of Phenol from wastewater. The experimental conditions, such as pH of solution, contact time, initial Phenol concentration, and adsorbent dosage as well as the Phenol removal percentage as response, were studied and optimized. Various isotherm models, such as Langmuir and Freundlich were used to fit the experimental equilibrium data. The results showed the suitability and applicability of the Langmuir model. Kinetic models, such as pseudo-first-order, pseudo-second-order diffusion models indicated that the pseudo-second-order model controls the kinetic of adsorption process. The maximum capacity (Q_{max}) of adsorbent was comparable to other adsorbents. It was shown that the Mn-Fe₂O₄-NPs-AC can be effectively used to remove the Phenol from wastewater.

2. EXPERIMENTAL

2.1. Reagents and instruments

UV-vis spectrophotometer (Jasco, Model UV-vis V-530, Japan). Fourier transform infrared (FT-IR) spectra were recorded on a PerkinElmer (FT-IR spectrum BX, Germany). The morphology of samples was studied by scanning electron microscopy (SEM: KYKY-EM 3200, Hitachi Company, China) under an acceleration voltage of 26kV). The pH/Ion meter (model-728, Metrohm Company, Switzerland, Swiss) was used for the pH measurements. Laboratory glassware was kept overnight in 10% nitric acid solution.

2.2. Preparation of Stock Solution

In this regard, aqueous solution of Phenol was used and its concentration was adjusted according to the real wastewater from the past study. sodium hydroxide, hydrochloric acid, FeCl₃.6H₂O, active carbon, and MnCl₂.4H₂O. They were supplied from Merck (Darmstadt, Germany). All used chemicals were of reagent grade and utilized without further purification. For the pH adjustment, HCl (hydrochloric acid) and NaOH (sodium hydroxide) were applied.

2.3. Preparation of Mn-Fe₂O₄-NPs-AC

The reaction solution for synthesis of Mn doped Fe₂O₄ nanoparticles was prepared as follows: first 10 g of ammonium iron (III) sulfate, 5.0 g iron (II) sulfate solution and 5.0 g manganese sulfate were dissolved (by 6mL of concentrated sulfuric acid at pH=2.4) and mixed thoroughly in 20 mL deionized water. Then, 130 mL distilled water and 20 g activated carbon (AC) were added to above solution and 140 mL of 1.5 mol L⁻¹ sodium hydroxide was added drop-by-drop during 70 minutes along with strong stirring at room temperature in an Erlenmeyer flask. After 70 minutes, again 100 mL of 3 mol L⁻¹ sodium hydroxide solution was added to the mixed reaction solution drop-by-drop during 40 minutes at room temperature. The prepared reaction solution was stirred strongly for 27 hours at room temperature. The Mn-Fe₂O₄-NPs-AC were filtered and washed several times by distilled water and dried at 35°C for 15 hours and finally characterized and used as an adsorbent for adsorptions experiments [24].

2.4. Batch adsorption Boron Ions adsorption process

Batch adsorption experiments were carried out to determine the Phenol adsorption isotherm onto Mn-Fe₂O₄-NPs-AC composite and its thermodynamic

properties: 250 mL solution having 15 mg/L concentration of Phenol was prepared and Initial pH of the solution was adjusted with the help of 0.01N HCl / 0.01N NaOH aqueous solution without any further adjustments during the experiments. 10 samples of 50 mL solution were taken in ten 250 mL flasks containing fixed adsorbent dose of 250 mg/L. These flasks were agitated at a constant rate of 190 rpm in a temperature controlled orbital shaker maintained at 25°C temperatures. One of the sample after fixed time intervals (5, 10, 20, 30 at 40 min) and analyzed for remaining Phenol present in the adsorbate solution. Mn-Fe₂O₄-NPs-AC was separated from aqueous solution by filtration through Whatman No. 42 filter paper. The Phenol concentration in the solution was measured using a double beam UV-vis spectrophotometer (jasco, Model UV-vis V-530, Japan) set at wavelengths 460 nm for Phenol. The amount of adsorbed ions at equilibrium (q_e (mg/g)) was calculated using equation:

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

Where C_0 (mgL⁻¹) and C_e (mgL⁻¹) is the concentration of target at initial and after time t respectively.

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

In the above equation Q refers to the

quantity of phenol adsorbed onto unit quantity of sorbent (mg g⁻¹); C_0 demonstrates the concentrations (mg mL⁻¹) of phenol in the primary solution and the concentrations of phenol in the aqueous phase after adsorption is demonstrated by C_e . The volume of the aqueous phase (mL) is shown by V; and w shows the weight of the sorbent (g). The evaluation of the thermodynamic properties of the adsorption process was performed by adding 50 mg of Mn-Fe₂O₄ NPs – AC into 50 mL initial Phenol concentration ranging from 15 mg/L in each experiment. For 30 min and at 25°C, each solution was shaken uninterruptedly. The Phenol concentration were estimated after the solution equilibrium and desorption outcomes were obtained in the present work.

2.5. Adsorption of Phenol onto Mn-Fe₂O₄-NPs-AC

A batch process using Mn-Fe₂O₄-NPs-AC in presence of applied for binary adsorption of Phenol, while all experiments were under taken in a cylindrical glass vessel by adding 0.1 g of adsorbent to 100 ml of PH 6.0 for Phenol as optimum value. The vessel was immersed in an ultrasonic bath for 30 min at room temperature and subsequently the solutions were centrifuged. Then non-adsorbed Phenol contents were determined by using UV-Vis spectrophotometer set at wavelengths 460 nm for Phenol, respectively [25].

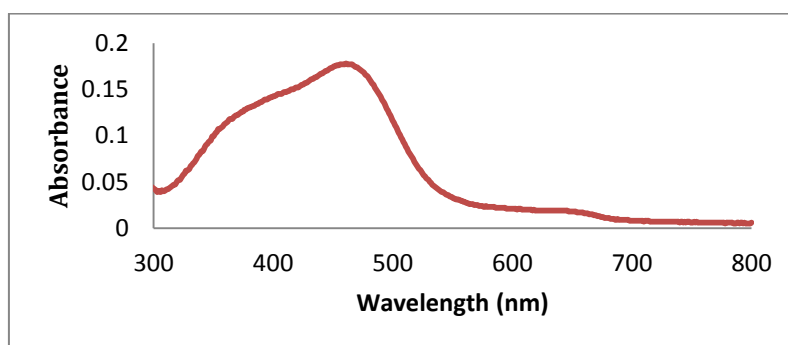


Fig. 1. Physisorption isotherm of Mn-Fe₂O₄-NPs-AC

3. RESULTS AND DISCUSSION

3.1. Characterization of adsorbent

The FTIR spectrum of Mn- Fe₂O₄ NPs – AC (Fig2.), The broad peaks at ≤ 900 in Mn – O and Fe – O, $996-1127\text{cm}^{-1}$ could be assigned to C–H stretching from Mn-Fe₂O₄ NPs, and $1389-1637\text{cm}^{-1}$ to C=O bonds. The new peak appearing at $2366 - 2928 \text{ cm}^{-1}$ corresponds to C–H stretching new peak appearing at 3423 cm^{-1} corresponds to – OH stretching [26]. The XRD pattern of the Mn- Fe₂O₄ NPs – AC (Fig.3b) represents a peak at $64.6(440)$, $44.15(400)$, $31.0(220)$ and $58.25(511)$ correspond to diffractions and reflections from the carbon atoms. As seen, the highly

crystalline nature of the after functionalizing with Mn- Fe₂O₄ NPs is confirmed, while the high intensity of peak at $36.5 (311)$ shows that there has been a small amount of material in amorphous state. The observed XRD pattern indicates that the prepared Mn- Fe₂O₄ NPs – AC is well-synthesized are shown in Fig.3). The morphological features of the samples studied by SEM are shown in Fig.4). Mn–Fe₂O₄–NPs–AC are observed to be smooth, homogeneous, tidy and approximately uniform in size distribution, After the surface modification with Mn-Fe₂O₄ NPs – AC became rough, larger and bundled (Fig. 4) [27].

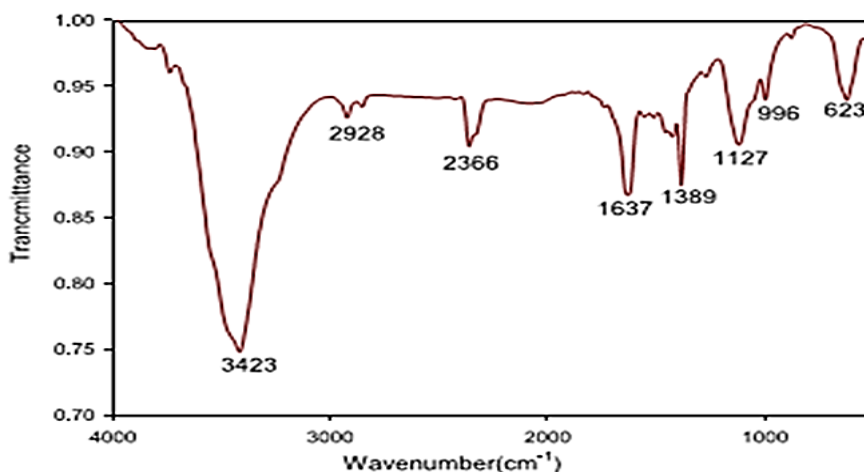


Fig. 2. FT-IR transmittance spectrum of the prepared Mn- Fe₂O₄ NPs – AC.

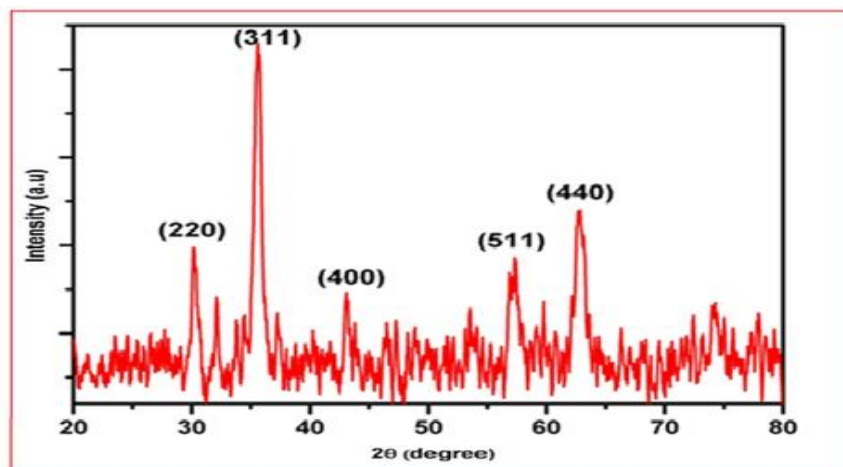


Fig. 3. The XRD of the prepared Mn- Fe₂O₄ NPs – AC

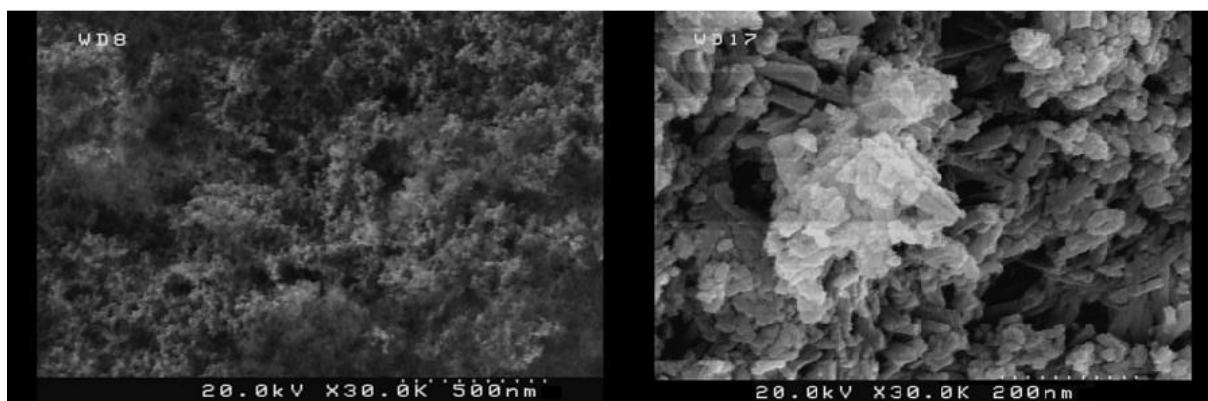


Fig. 4. The SEM image of the prepared Mn- Fe₂O₄ NPs – AC

3.2. Effect of pH on Phenol adsorbent

The pH has been identified as one of the most important parameter that is effective on ions sorption. The effect of pH on the Phenol onto Mn- Fe₂O₄ NPs – AC was studied at pH 4.0–10.0, Fig.5. The maximum adsorbent was observed at pH 6.0 for Phenol. The remaining all adsorbent experiments were carried out at this pH value. The adsorbent mechanisms on the Mn- Fe₂O₄ NPs – AC surface reflect the nature of the physic chemical interaction of the solution [28, 29]. The adsorbent mechanisms on the Mn- Fe₂O₄ NPs – AC surface reflect the nature of the physic chemical interaction of the solution. At highly acidic pH, the overall surface charge on the active sites became. Positive and Phenol and protons compete for binding sites on Mn- Fe₂O₄ NPs – AC, which results in lower uptake of boron ions. The adsorbent surface was more negatively charged as the pH solution increased from 6.0. The functional groups of the Mn- Fe₂O₄ NPs – AC was more deprotonated and thus available for the Phenol. Decrease in Mn- Fe₂O₄ NPs – AC yield at higher pH=6 is not only related to the formation of soluble hydroxylated complexes of the Phenol, but also to the ionized nature of the Mn- Fe₂O₄ NPs – AC of the Mn- Fe₂O₄ NPs – AC under the

studied pH. Previous studies also reported that the maximum Mn- Fe₂O₄ NPs – AC efficiency of Phenol on biomass was observed at pH 6.0.

3.3. Effect of adsorbent dosage

The adsorbent dosage is an important parameter because this determines the capacity of a adsorbent for a given initial concentration. The adsorbent efficiency for Phenol as a function of adsorbent dosage was investigated. The percentage of the Phenol adsorbent steeply increases with the adsorbent loading up to 0.1 g Fig.6. This result can be explained by the fact that the s adsorbent ites remain unsaturated during the adsorbent reaction, whereas the number of sites available for adsorbent site increases by increasing the adsorbent dose [30]. The maximum adsorbent was attained at adsorbent dosage, 0.1 g. Therefore, the optimum adsorbent dosage was taken as 0.1 g for further experiments. This can be explained by when the adsorbent ratio is small, the active sites for binding Phenol on the surface of Mn- Fe₂O₄ NPs – AC is less, so the adsorbent efficiency is low. As the adsorbent dose increased, more active sites to bind Phenol, thus it results an increase in the adsorbent efficiency until saturation.

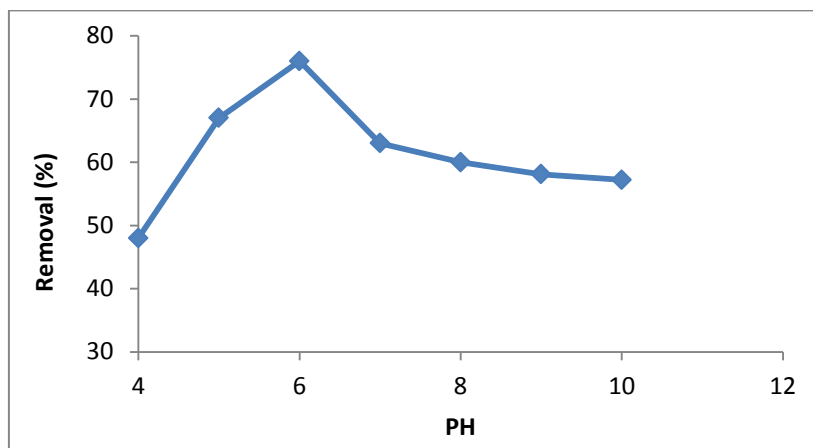


Fig. 5. Impact of initial solution pH on the sorption quantity of Phenol onto Mn- Fe₂O₄ NPs – AC [Phenol conc = 15 mgL⁻¹; adsorbent dose = 0.1g; contact time =30 min; stirring speed = 190 rpm; temp = 25°C].

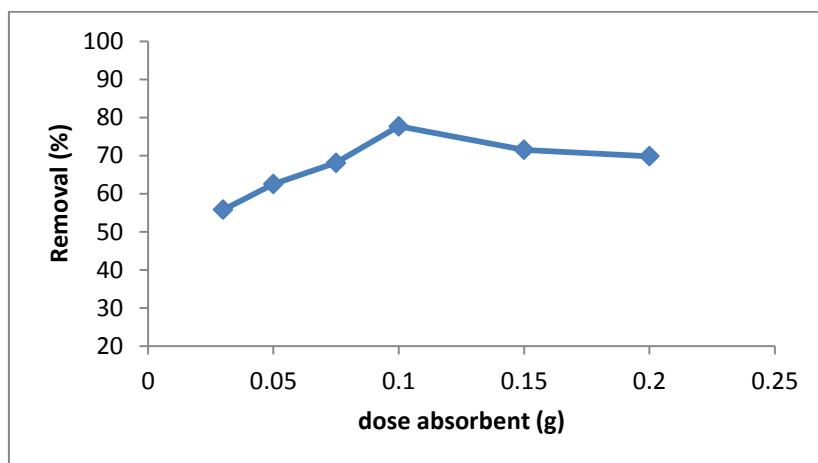


Fig. 6. Impact of dosage Mn- Fe₂O₄ NPs – AC on the adsorption quantity [Phenol conc = 15 mgL⁻¹; pH= 6.0; contact time =30 min; stirring speed = 190 rpm; temp = 25°C].

3.4. Effect of temperature

To study the effects of temperature on the adsorption of ions by Mn- Fe₂O₄ NPs – AC, the experiments were performed at temperatures from 298.15 to 323.15 K. Fig.7. shows the influence of temperature on the adsorption of Phenol on Mn- Fe₂O₄ NPs – AC. As it was observed, the equilibrium adsorption capacity of Phenol onto Mn- Fe₂O₄ NPs – AC was found to increase with increasing temperature. This fact indicates that the mobility of Phenol molecules increased with the temperature, additionally the viscosity of Phenol solution reduces with rise in temperature and as a result, it increases the rate of

diffusion of Phenol molecules. The results were in agreement with the effect of the solution pH, and temperature on adsorption behavior of reactive Phenol on activated carbon [31,32].

3.5. Effect of contact time

The effect of contact time on the adsorption capacity of Phenol onto Mn- Fe₂O₄ NPs – AC is shown in fig.8, When the initial Phenol concentration is increased 15 mg/L the amount of Phenol adsorbed onto Mn- Fe₂O₄ NPs – AC, 5 at 40 min contact time, pH value 6 for Phenol, 0.1 g adsorbent dose and the constant temperature 298.15 K. The

increase of loading capacity of Mn- Fe₂O₄ NPs – AC with increasing initial Phenol concentration may be due to higher interaction between Phenol and adsorbent [33,34]. These results show that rapid increase in adsorbed amount of Phenol is achieved during the first 30 minutes. Similar results were reported before for removal of hazardous contaminants from wastewater.

3.6. Adsorption isotherms

An adsorption isotherm expresses the fraction of adsorbate molecules which are

divided up between liquid and solid phases at equilibrium. With a help of four adsorption isotherms: 1-Langmuir, 2-Freundlich, 3-Temkin, and 4-Dubinin - Radushkevich isotherms, adsorption of Phenol onto Mn- Fe₂O₄ NPs – AC was displayed.

3.6.1. Langmuir isotherm

The Langmuir isotherm assumes monolayer adsorption on a homogeneous surface with restricted number of adsorption sites [35]. Therefore, when a site is occupied, no further sorption can

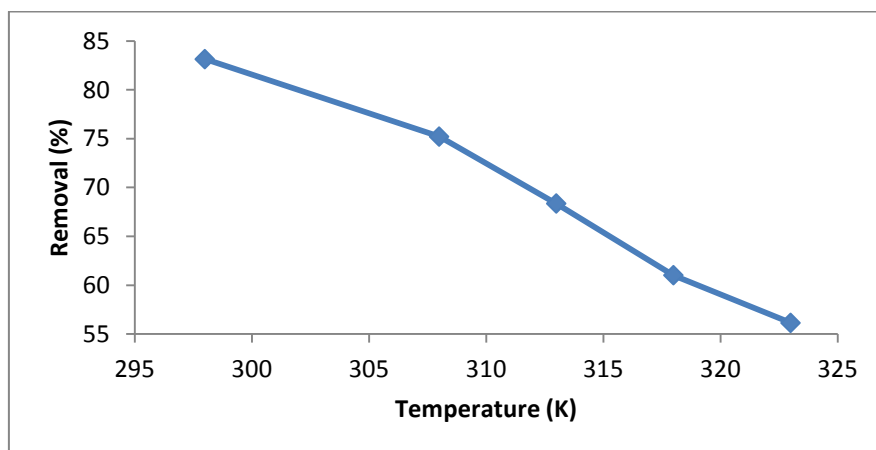


Fig. 7. Impact of temperature on the sorption quantity of Phenol onto Mn- Fe₂O₄ NPs – AC [Phenol conc = 15 mgL⁻¹; pH= 6.0; adsorbent dose = 0.1g; contact time =30 min; stirring speed = 190 rpm].

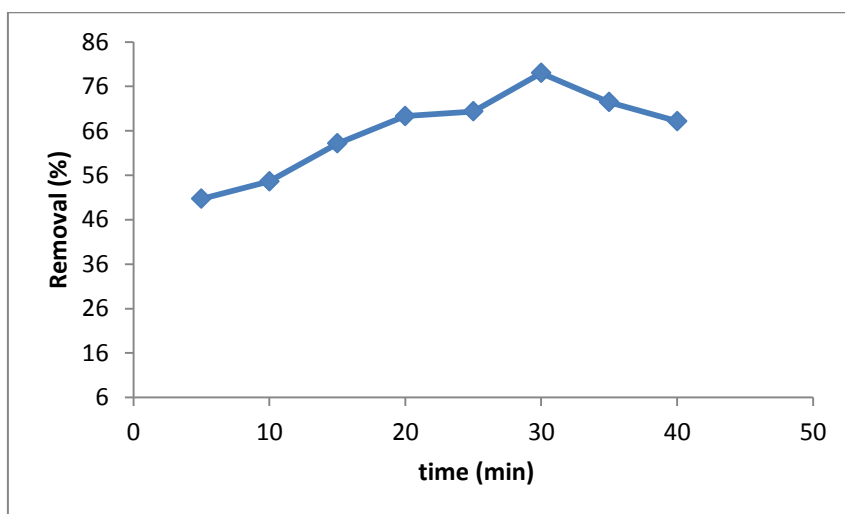


Fig. 8. Impact of contact time on the sorption of Phenol onto Mn- Fe₂O₄ NPs – AC [Phenol conc = 15 mgL⁻¹; pH= 6.0; adsorbent dose = 0.1g; stirring speed = 190 rpm; temp = 25°C].

occur at that site. Consequently, saturation point is equal to the maximum adsorption of the surface. The linearized form of the Langmuir isotherm model is as follow [36]:

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

Where K_L stands for the Langmuir constant associated with the energy of adsorption and q_{\max} shows the highest adsorption capacity (mg/g). As it is demonstrated in Fig.9, the calculation of the values of Langmuir parameters (q_{\max} and K_L) was done from the slope and discontinuity of the linear plot of C_e/q_e versus C_e . The list of values of q_{\max} , K_L and regression coefficient R^2 is exhibited in Table1. Based on Langmuir model, these values for Mn-Fe₂O₄ NPs-AC prove the suitability of the absorption.

3.6.2. Freundlich isotherm

Freundlich isotherm model is a useful and famous model for defining the adsorption process. This model is based on the assumptions that sorption occurs onto a non-uniform surface with interactions between adsorbed molecules. Also the application of the Freundlich equation

expresses that sorption energy exponentially lessens with completion of the sorption sites of an adsorbent. This isotherm is presented as an empirical equation and is applied to explain the non-uniform systems. The linearized form of the equation is as follow [37]:

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

In the above formula, K_F stands for the Freundlich constant connected to the bonding energy. $1/n$ shows the heterogeneity factor and n (g/L) shows a measure of the deviation from linearity of adsorption, From the plot of $\ln q_e$ versus $\ln C_e$, Freundlich equilibrium constants were found out as shown in Fig.9. The degree of non-linearity between solution concentration and adsorption is shown by the n value as follow: if $n = 1$, then adsorption is linear; if $n < 1$, then adsorption is a physical process; if $n > 1$, then adsorption is a chemical process. As shown in Table 1, the n value in Freundlich equation was proved to be 0.56 for Phenol. Therefore, the physical adsorption of metal ion onto Mn-Fe₂O₄-NPs-AC is confirmed because n lies between 1 and 10.

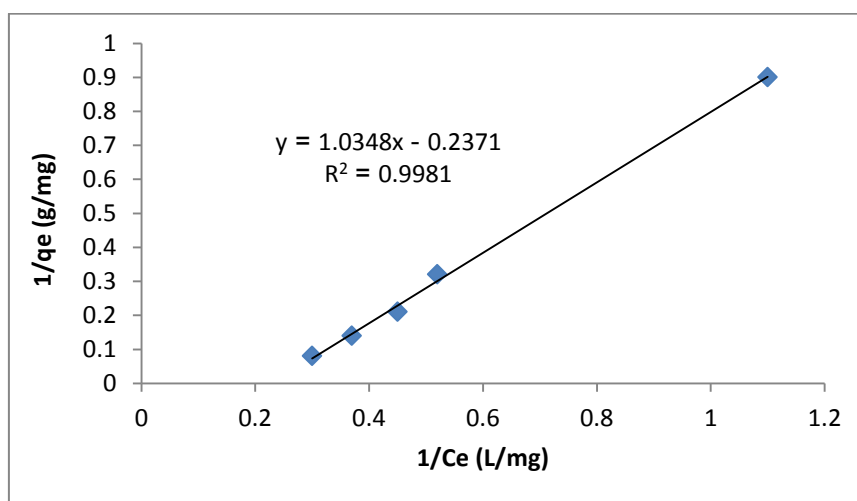


Fig. 9. (a) Impact of Langmuir Isotherm on the sorption quantity of Phenol onto Mn- Fe₂O₄ NPs – AC [Phenol conc = 15 mgL⁻¹; pH= 6.0; adsorbent dose = 0.1g; contact time =30 min; stirring speed = 190 rpm; temp = 25°C].

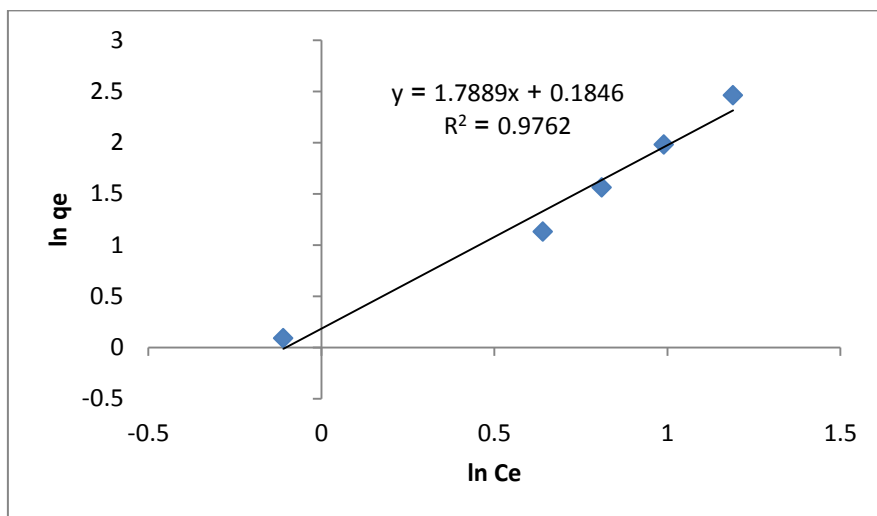


Fig. 9. (b) Impact of Freundlich Isotherm on the sorption quantity of Phenol onto Mn-Fe₂O₄-NPs-AC [Phenol conc = 15 mgL⁻¹; pH= 6.0; adsorbent dose = 0.1g; contact time =30 min; stirring speed = 190 rpm; temp = 25°C].

3.6.3. Temkin isotherm

Temkin isotherm equation. it is presumed that the heat of biosorption of all the molecules in the layer reduces linearly with coverage owing to adsorbent-adsorbate interactions and that the adsorption is characterized by a homogeneous distribution of the binding energies up to some topmost binding energy [38]. The linear form of the Temkin isotherm is expressed as follows:

$$\log\left(\frac{1}{q_e}\right) = \log\left(\frac{k_L + 1}{k_L q_m}\right) + \frac{1}{n} \log \frac{1}{C_e} \quad (5)$$

In Fig. 9, the plots of ln (C_e) versus q_e for Phenol are exhibited and in Table. 1, the linear isotherm parameters b_T, K_T and the correlation coefficient are summarized. The b_T constant relative to heat of sorption for Phenol onto Mn-Fe₂O₄-NPs-AC adsorbent equals 1.007 J/mol.

3.6.4. Dubinin-Radushkevich (D-R) isotherm

Dubinin-Radushkevich (D-R) isotherms: For investigated the nature of adsorption, this model is used. The linear form of this model expressed by the following equation:

$$\text{Ln}q_e = \text{Ln}q_m - \beta \varepsilon^{\gamma} \quad (6)$$

Where β is the activity coefficient related to mean sorption energy. (mol² / kJ²), and ε is the Polanyi potential, that can be calculated from bellow equation:

$$\varepsilon = RT \ln(1+1/C_e) \quad (7)$$

where R and T are the ideal gas constant (8.3145 J/mol K) and absolute temperature (K), respectively (Fig. 9). E_a is the free energy change of adsorption (kJ/mol), which required transferring 1 mol of ions from solution to the adsorbent surface, that it can be calculated from bellow equation [39]:

$$E_a = 1/(-2\beta)^{1/2} \quad (8)$$

In this model, if E_a < 8 kJ/mol, the mechanism of adsorption is Physical adsorption, if 8 > E_a < 20 kJ/mol adsorption is dominated by chemical ion exchange and if E_a > 20 kJ/mol, mechanism of Phenol adsorption is chemical adsorption [40]. The E values - 264.58 for Phenol onto Mn-Fe₂O₄-NPs-AC respectively.

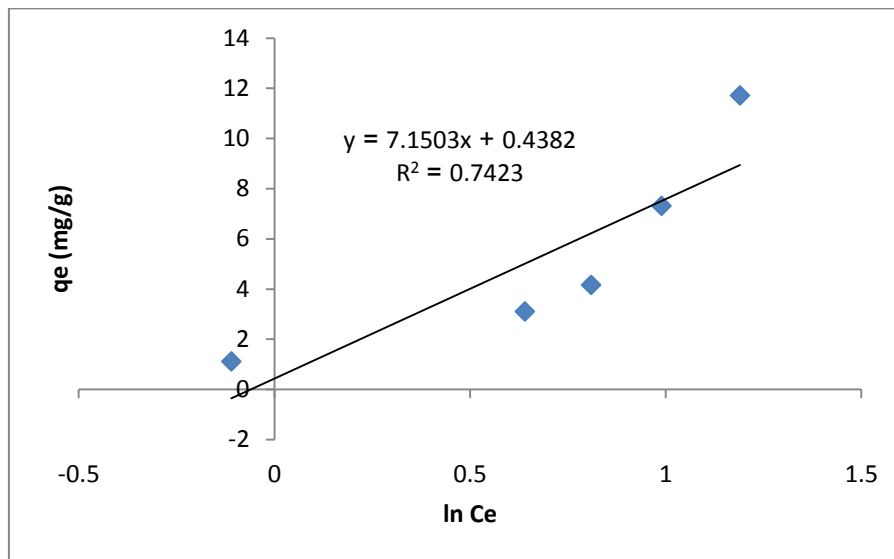


Fig. 9. (c) Impact of Temkin Isotherm on the sorption quantity of Phenol onto Mn-Fe₂O₄-NPs-AC [Phenol conc = 15 mgL⁻¹; pH= 6.0; adsorbent dose = 0.1g; contact time =30 min; stirring speed = 190 rpm; temp = 25°C].

Table 1: diverse isotherm constants and correlation coefficients computed for the sorption of Phenol onto Mn-Fe₂O₄-NPs-AC [Phenol conc = 15 mgL⁻¹; pH= 6.0; adsorbent dose = 0.1g; contact time =30 min; stirring speed = 190 rpm; temp = 25°C].

Isotherm	Equation	parameters	Value of parameters For Phenol
Langmuir	$q_e = q_m b C_e / (1 + b C_e)$	Q_m (mg g ⁻¹)	4.27
		K_L (L mg ⁻¹)	0.23
		R^2	0.9981
Freundlich	$\ln q_e = \ln K_F + (1/n) \ln C_e$	n	0.56
		K_F (mg) ¹⁻ⁿ L ⁿ g ⁻¹	1.2
		R^2	0.9762
Tempkin	$q_e = B_T \ln K_T + B_T \ln C_e$	B_T	1.07
		A_T (L mg ⁻¹)	7.2
		R^2	0.7423
Dubinin-Radushkevich (DR)	$\ln q_e = \ln Q_d - B \epsilon^2$	Q_d (mg g ⁻¹)	4.18
		$K_D \times 10^{-6}$ (mol/J) ²	0.7
		E (kj mol ⁻¹)	-264.58
		R^2	0.8662

3.7. Kinetic study

Different parameters like the state of the solid (mostly with nonuniform reactive surface) and physico- chemical conditions under which the adsorption took place can strongly influence the adsorption of a solute by a solid in aqueous solution via complicate stages [41]. The rate of Phenol

adsorption onto adsorbent was conformed to conventional models including pseudo-first and pseudo- second-order models The adsorption kinetic data were perfectly described by the Lagergren pseudo-first order model. The ensuing equation represents the Lagergren:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (9)$$

Where q_e stands for the adsorption capacities at equilibrium and q_t (mg/g) refers to the adsorption capacities at time t . the rate constant of the pseudo-first-order adsorption (L/min) is represented with k_1 . The plot of the $\log(q_e - q_t)$ versus t was provided and k_1 and q_e values were ascertained utilizing the slope and intercept of the line respectively.

$$\log(q_e - q_t) = \log q_t - \left(\frac{k_1}{2.303}\right)t \quad (10)$$

The improbability of this issue that the action could follow the first-order was proven from the fact that the intercept was not equal to q_e . When pore diffusion restricted the adsorption process, the linearity relationship between initial solute concentration and rate of adsorption was detected. Thus, the necessity to fit experimental data to another model (Table.2), became apparent. Consequently, Pseudo-second order model [42] was introduced based on the ensuing equation:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (11)$$

Over the interval 0 to t for t and 0 to q_t for q_t , Eq.(11) was integrated to provide

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (12)$$

Based on what has been said, perfect outcomes for entire sorption period were not provided by the plot of $\log(q_e - q_t)$ versus t , while the plot of t/q_t versus t demonstrated a straight line. The calculation of the values of k_2 and equilibrium adsorption capacity (q_e) was conducted from the intercept and slope of the plot of t/q versus t (Table.2). The similarity of the estimated q_e values at different conditions like different initial ions concentrations and/or adsorbent masses to the experimental data was observed. Also, the appropriateness of this model for the explanation of experimental data was confirmed from higher R^2 values. Accordingly, pseudo-second-order kinetic model was chosen for the adsorption of Phenol for the whole sorption period [43].

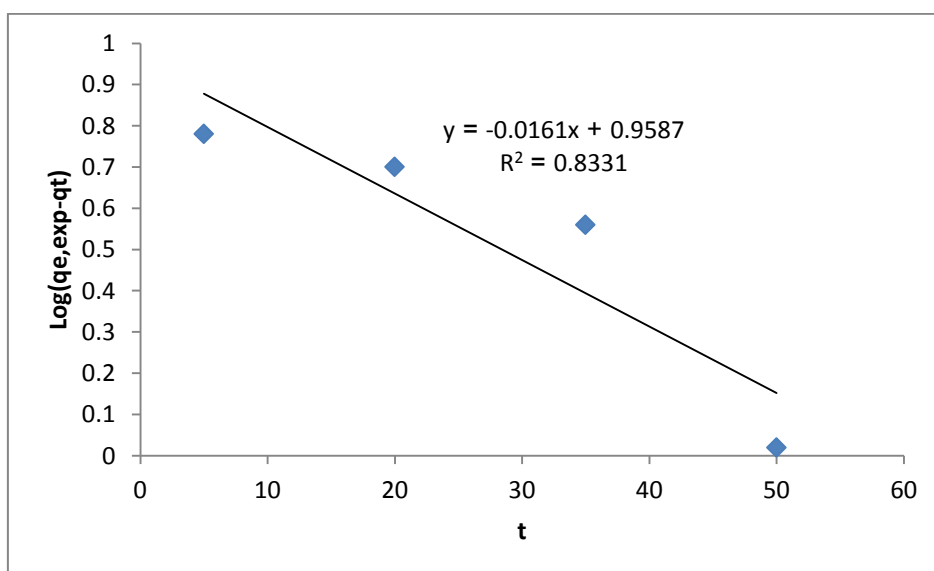


Fig. 10. Pseudo-first order model for the sorption of Phenol onto Mn-Fe₂O₄-NPs-AC [Phenol conc = 15 mgL⁻¹; pH= 6.0; adsorbent dose = 0.1g; contact time =30 min; stirring speed = 190 rpm; temp = 25°C].

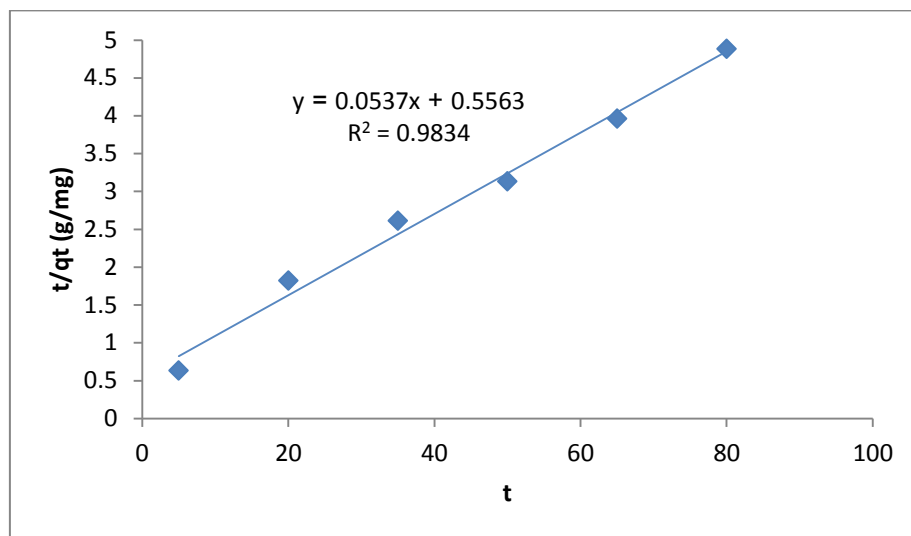


Fig. 11. Pseudo-second order model for the sorption of Phenol onto Mn-Fe₂O₄-NPs-AC [Phenol conc = 15 mgL⁻¹; pH= 6.0; adsorbent dose = 0.1g; contact time =30 min; stirring speed = 190 rpm; temp = 25°C].

Table. 2: Kinetic parameters for the sorption of Phenol onto Mn-Fe₂O₄-NPs-AC [Phenol conc = 15 mgL⁻¹; pH= 6.0; adsorbent dose = 0.1g; contact time =30 min; stirring speed = 190 rpm; temp = 25°C].

Model	parameters	Value of parameters for Co (II) ions
pseudo-First-order kinetic	k ₁ (min ⁻¹)	0.0921
	q _e (mg g ⁻¹)	8.39
	R ²	0.8331
pseudo-Second-order kinetic	k ₂ (min ⁻¹)	0.21
	q _e (mg g ⁻¹)	12.8
	R ²	0.9834
q _e (mg g ⁻¹)		12.8

A favorable concurrence between the experimental and estimated q_e values for diverse initial Phenol concentrations was shown by the linear plots of t/q_t versus t. Moreover, greater correlation coefficients of the pseudo-second-order kinetic model (R²= 0.8331) for Phenol respectively in comparison with those of the pseudo-first-order model (R²= 0.9834) for them proved that the sorption fitted to the pseudo-second-order better than the pseudo-first-order kinetic model.

3.8. Adsorption thermodynamics

The thermodynamic parameters, namely Gibbs free energy change (ΔG°), enthalpy

change (ΔH°) and entropy change ΔS°, for the adsorption processes were determined using the following equations [44]:

$$\Delta G^\circ = -RT \ln K_{ad} \quad (13)$$

$$\ln K_{ad} = \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (14)$$

A graph (Fig. 12) is developed from a plot of lnK_e against 1/T, from the slope of which ΔG can be procured. In Table.3, the summary of the thermodynamic parameter outcomes for the adsorption of Phenol onto derived Mn-Fe₂O₄-NPs-AC at different temperatures is shown.

Via applying the equation adsorption of Phenol, the ΔG° values were computed. As shown in Fig. 12, upon the increase in the temperature from 298 to 348 K, Mn-Fe₂O₄-NPs-AC adsorbent diminished and therefore the exothermicity nature of the process was confirmed. The values of the thermodynamic parameters (Table 3) [45]. were computed using the plots. The feasibility and spontaneity nature of the process was revealed by the negative value of ΔG° . On the other hand, the exothermicity nature of adsorption was proven by the negative value of ΔH° and the value of ΔS° was a good indication of change in the randomness at the derived Mn-Fe₂O₄-NPs-AC solution interface during the sorption. The fact that ΔG° values up to -3.939 kJ/mol boron ions are

accordant with electrostatic interaction between sorption sites and the Phenol (physical adsorption) has been reported. The obtained ΔG° values in this article for Phenol are <-5 kJ/mol suggesting the predominancy of the physical adsorption mechanism in the sorption process [46].

3.9. Recycling of the Adsorbent

The ability of recovering and reusing of the adsorbent was tested in several steps of adsorption and desorption. The result is shown in Fig.13. As shown in Figure 95/0 of Phenol was desorbed from the adsorbent after first cycle and after 4 cycles, there were slight changes in Phenol desorption. So, it was concluded that the desired removal of 95% can be achieved after 4 cycles.

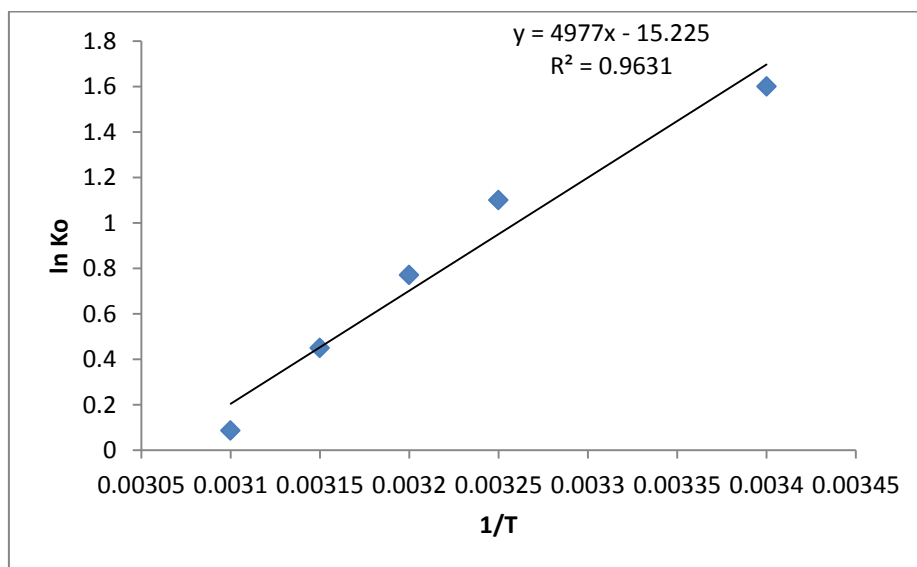


Fig. 12. Plot of $\ln K_c$ vs. $1/T$ for the estimation of thermodynamic parameters. Phenol onto Mn-Fe₂O₄-NPs-AC [Phenol conc = 15 mgL⁻¹; pH= 6.0; adsorbent dose = 0.1g; contact time =30 min; stirring speed = 190 rpm; temp = 25°C].

Table. 3: The thermodynamic parameters for the adsorption of Phenol onto Mn-Fe₂O₄-NPs-AC [Phenol conc = 15 mgL⁻¹; pH= 6.0; adsorbent dose = 0.1g; contact time =30 min; stirring speed = 190 rpm; temp = 25°C].

Ions concn. (mg/L)	ΔH° (kJ/mol)	ΔS° (kJ/mol K)	ΔG° (kJ/mol)				
			298K	308K	313K	318K	323K
Phenol 15 (mg/L)	-4.947	-1.521	-3.939	-2.816	-2.004	-1.16	-0.21

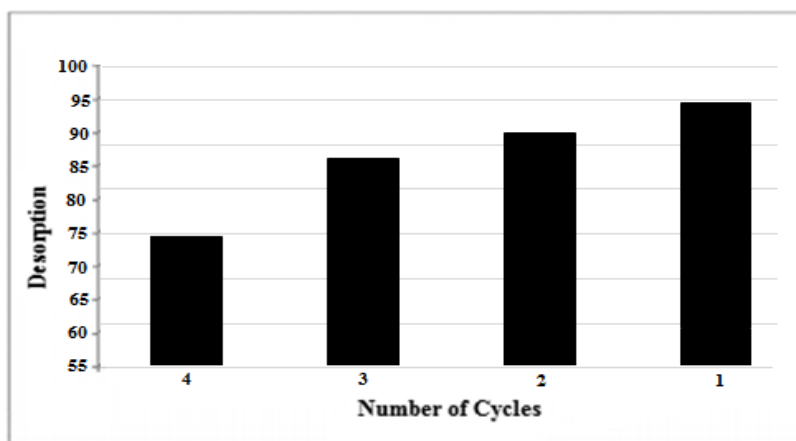


Fig. 13. Desorption of Phenol onto Mn-Fe₂O₄-NPs-AC [Phenol conc = 15 mgL⁻¹; pH= 6.0; adsorbent dose = 0.1g; contact time =30 min; stirring speed = 190 rpm; temp = 25°C].

4. CONCLUSION

The Mn-doped Fe₂O₄ nanoparticles loaded on activated carbon has been synthesized and used as an effective adsorbent for the removal of Phenol from aqueous solutions. the optimum values of the pH, adsorbent dosage, Phenol concentration, and contact time were found to be 6, 0.1 g, 15 mg/L, and 30 min for Phenol respectively. The effect of various process parameters showed that percent adsorption decreased with increase in initial Phenol concentration while it increased with increase in adsorbent dose. Maximum Phenol removal by adsorbent was at pH 6.0. Regarding the Kinetic models both pseudo-first-order and pseudo-second-order diffusion models of Phenol revealed that the kinetic of adsorption process followed second-order equation model. After using various Isotherm models to fit the experimental equilibrium data with, the adequacy and applicability of Langmuir model has been proven. The adsorption data fitted well with the Langmuir isotherm model with correlation coefficient ($R^2 > 0.995$), The maximum adsorption capacity of the Phenol removal onto Mn-Fe₂O₄-NPs-AC was roughly 4.27 mg/g, respectively. Thermodynamic parameters of free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0)

of adsorption were determined using isotherms. $\Delta H^0 = -4.947$ kJ/mol, $\Delta G^0 = -3.937$ kJ/mol and $\Delta S^0 = -1.521$ kJ/mol.K. The fact that the sorption process was endothermic was well reflected by the negative value of (ΔG^0 , ΔH^0 and ΔS^0) which on its own expressed the affinity of Mn-Fe₂O₄-NPs-AC to wards Phenol. The goal for this work is to develop inexpensive, highly available, effective Phenol adsorbents from natural waste as alternative to existing commercial adsorbents. Mn-doped Fe₂O₄ nanoparticles loaded on activated carbon has a high adsorption capacity when compared to other adsorbents for Phenol removal from an aqueous medium.

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