Maryam Heydari[1], Mehrnaz Gharagozlou[1], Mehdi Ghahari[1], and Omid Akbarzadeh Pivehzhani[2]

[1]Department of Nanomaterials and Nanocoatings, Institute for Color Science and Technology
[2]Nanotechnology & Catalysis Research Centre, University of Malaya

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## 1. Introduction

The drug curcumin scientifically known as diphtheria methane and is one of the main elements of the turmeric plant which belongs to the ginger family. In addition to curcumin, turmeric contains other compounds such as curcuminoid, cyclochurcumin, dimethoxy curcumin and bisdemethoxycurcumin. Curcumin was first extracted in impure from the Curcuma Longa plant in 1815 and called curcumin [1-4]. Curcumin is a multifaceted molecule and has many therapeutic effects. Careful research over the past decade has proven the effectiveness of curcumin as an antioxidant, anti-inflammatory, anti-diabetic and anti-arthritic [5, 6]. Its hydroxy groups are for antioxidant activity and methoxy groups are for anti-inflammatory and anti-proliferative activities. Curcumin has been used in traditional medicine for thousands of years, as well as in food coloring. Although there are different reports and opinions about the therapeutic benefits of curcumin, researchers should be careful because it is an unstable chemical [7]. It is insoluble in water but dissolves easily in solvents such as ethanol, acetone and methanol [8]. The only limiting factor in the use of this substance is its low solubility and low stability in the body. Curcumin is difficult to dissolve in water and is highly sensitive to changes in body pH. In addition, its absorption through the gastrointestinal tract and in acidic environments is very low and after consuming it, the liver destroys a high amount of it [9]. Therefore, drug delivery systems based on nanotechnology, due to their potential characteristics and other unique properties, nanoparticles change the pharmacokinetics of the drug and also greatly improve the life of the drug in the bloodstream and the therapeutic properties of the drug. A group of nanoparticles is porous metal-organic framework (MOF) materials that synthesized in various types and considered by researchers due to various applications such as gas storage and separation, catalyst, sensor and drug storage and release [10-18]. Therefore, the metal-organic framework can be used in applications such as drug absorption due to their high specific surface area and porosity. Among the porous nanoparticles of the metal-organic framework, magnetic metal-organic framework have received great attention in recent decades. Magnetic metal-organic framework are crystalline and porous materials and structure consist of metal clusters, organic ligands, and magnetic nanoparticles [19-21]. The metal ions of the co-ordination centers and ligands are also the link between the metal centers and the magnetic particles. Different metal-organic frameworks have been used to absorb and interact with drugs. For example, Dong et al. synthesized and characterized the metal-organic framework (UiO-66) based on Zn and Hf by the macro method. They used the synthesized metal-organic framework as an adsorbent for the drug curcumin and achieved an absorption capacity of more than 450 mg $g^{-1}$ for each [14]. Prince et. al. synthesized the metal-organic framework (Ga-BDC) to absorb the drug curcumin. They first synthesized and identified the desired metal-organic framework by microwave method and finally, to investigate the application of this metal-organic framework, it was used as an adsorbent for the drug curcumin [22]. Naseh et al. used a magnetic nanocomposite ($FeNi_3/SiO_2/CuS$) to absorb and interact with the drug Metronidazole, which is an antibiotic and after examining the effective parameters of cysteine and isotherms, adsorption is studied. They found that the optimal conditions for absorbing metronidazole is at pH = 7, room temperature and 180 minutes [23]. Maggie et.al. used magnetic

metal-organic framework absorbers ($Fe_3O_4$/HKUST-1) to absorb the fluoroquinolone antibiotics. They first synthesized and identified the magnetic metal-organic framework ($Fe_3O_4$/HKUST-1) by co-precipitation. Finally, to investigate the application of this synthesized magnetic metal-organic framework, they used it as an adsorbent of fluoroquinolones and studied isothermal and kinetic studies [24]. However, no report has been published on the synthesis and use of the magnetic metal-organic nanocomposite ($NiFe_2O_4$@$SiO_2$@HKUST-1) to absorb the drug curcumin. Therefore, the aim of this project is to synthesize and identify the magnetic metal-organic framework nanocomposite ($NiFe_2O_4$@$SiO_2$@HKUST-1) with different weight ratios of nickel ferrite to silica substrate and study their application in the process of uptake and drug interaction of curcumin (Table 1). The next step is to investigate the type of nanocomposite and suitable magnetic metal-organic framework as a better adsorbent and also to find effective parameters for optimal adsorption and study conditions of isothermal and kinetic adsorption.

Table 1: Specifications of the drug curcumin.

| Chemical Structure | |
|---|---|
| Molecular formula | $C_{21}H_{20}O_6$ |
| Molecular weight | gr/mol 38/368 |

## 2. Experimental:

### 2.1. Chemicals

In this study, salts of iron nitrate (Fe (NO3)3.9 H2O), nickel nitrate (Ni(NO3)2.6H2O) and copper nitrate (Cu(NO3)2.3H2O) as metal precursors and the organic matter trichloroacetic acid (BTC) as the organic binding agent in the metal-organic framework were used. Also, tetraethyl ortho silica (TEOS) were used as a substrate for magnetic particles, 3-aminopropyl triotoxycylan were used as an amine agent, ethanol and water as solvents were used in synthesis. The water used were distilled water, and the curcumin aqueous solution were used as a drug as well as an oral dye to investigate its interaction and adsorption on the synthesized adsorbent. It should be noted that all the raw materials used, made by the German company Merck. By keeping the percentage of the metal-organic framework (HKUST-1) constant, the silica substrate was prepared by the weight ratio of 10, 30 and 50 percent on the nickel ferrite magnetic composite.

### 2.2 Synthesis of nickel ferrite on silica substrate ($NiFe_2O_4$@$SiO_2$)

The synthesis method of magnetic nickel ferrite nanocomposite on a silica substrate is in accordance with the Gharagozlou M. et.al. method reported in the sources [25]. Nickel ferrite has weight ratios of 10, 30, and 50 percent to the 90, 70 and 50 weight percent of silica substrate respectively.

In this method, the nickel nitrate and iron nitrate were weighed in the amount of 6 and 9 grams respectively, and dissolved in 10 ml of deionized water under reflux conditions and stir well with a mechanical mixer for 30 minutes to mix thoroughly. Next step, pour 60 ml of tetraethyl ortho silica (TEOS) into 50 ml of ethanol and 10 ml of water and acidify its pH using hydrochloric acid, and then pour it into the decanter and add it drop by drop to the solution inside the balloon and allow to stir for 2 hours for further mixing. In the third step, the contents of the balloon are poured into the crystallizer and placed slightly in the exposure of air for 7 days, and the alcogel is obtained. After 7 days, place the resulting alkogel in an oven at 110 oC for 24 hours to allow it to dry and xerogel obtain. The xerogel were calcined for 2 hours in an oven at 800 oC with a heating rate of 10 oC/min and the product were milled by a satellite mill.

### 2.3. Synthesis of Nanocomposite magnetic metal-organic framework $NiFe_2O_4$@$SiO_2$@HKUST-1

Dispense 1 g of nickel ferrite prepared in the previous section (2.2) with 50 ml of ethanol then add 2 ml (3-aminopropyl triotoxycylan) and under reflux conditions at 80 oC for 6 hours, allow to mix thoroughly and resulting sediment was separated using a magnet.

Pour 1 gram of the resulting powder with 25 mmol of copper nitrate, 22.5 mmol of lycopene tritactic acid (BTC) and 60 ml of distilled water in the balloon and re-mixed under reflux conditions at 100 oC for 8 hours. After washing, the resulting deposit was placed in a vacuum oven at 120 oC for 10 hours to allow the precipitate to dry and the magnetic metal-organic framework nanocomposite ($NiFe_2O_4$@$SiO_2$@HKUST-1) formed.

### 2.4 Preparation of curcumin solution

The tested curcumin powder was first dissolved in 10 ml of pure ethanol and then solution diluted using deionized water. The amount of curcumin was calculated according to its mass and purity, and accordingly, the available solution for the study was made with different concentrations in a volume of 500 ml, and finally, 100 ml of it was considered as a statistical population.

### 2.5 Investigation and study of the curcumin absorption process

To investigate the process of absorption of curcumin solution on the synthesized adsorbents, 100 ml of the curcumin solution was taken as a sample and the adsorbent was added to it and placed on the shaker at room temperature for 2 hours. After a while, the sample was taken and centrifuged for better separation. The concentration of curcumin solution in the samples taken at different times and were measured using a UV light spectrometer.

Finally, using equation (1), the absorption percentage of curcumin solution and using equation (2), the adsorption capacity of the synthesized magnetic metal-organic framework nanocomposite was calculated and determined.

$$\%\text{Adsorption} = (C_0 - C_t / C_0)*100 \quad (1)$$

$$q_t = (C_0 - C_t)\ V/m \quad (2)$$

Where $C_0$ and $C_t$ are the initial concentration of curcumin solution and the concentration of curcumin solution at time t respectively, V is the volumes of curcumin solution per liter, m the amount of adsorbent (gr) and $q_t$ are the adsorption capacity of the magnetic metal-organic framework nanocomposite in terms of ($mg.g^{-1}$) [26-29]. Finally, the effect of parameters such as adsorbent dose, adsorbent type and concentration of curcumin solution on the adsorption of curcumin solution by synthesized magnetic metal-organic framework nanocomposites was studied.

To investigate the behavior of the synthesized adsorbent, the relationship between the absorbing sample and the adsorbent surface and sample interaction with the adsorbent requires the equations that are used to investigate this adsorption behavior. There are several ways to look at absorption isotherms. These isotherms include the Langmuir, Freundlich and the Temkin. In this study, two isotherms of Langmuir and Freundlich with the following equations have been used to investigate the ruling isotherm to the absorption process [29-31].

The Langmuir adsorption isotherm model is examined and calculated with Equation 3 and its variables are presented in Table 6. The Langmuir adsorption isotherm is based on the single-layer adsorption of the adsorbent, which here is the curcumin solution, on the adsorbent surface, indicating that no reaction occurs between the absorbed sample and adsorbent molecules.

$$C_e/q_e = 1/K_L.\ q_L + C_e/q_L \quad (3)$$

In this equation, $C_e$ is the concentration of curcumin solution at equilibrium ($mg.l^{-1}$), $q_e$is the amount of material absorbed per unit mass of the adsorbent, $q_L$ the maximum absorption capacity is synthesized on the nanocomposites of the magnetic metal-organic framework, and $K_L$ is the Langmuir constant which refers to the energy of absorption.

The Freundlich isotherm model is examined and calculated with Equation 4 and its variables are presented in Table 6. Frondelich adsorption isotherm is synthesized on the adsorbent based on multi-layered and

heterogeneous adsorption of the adsorbent. The closer value of 1/n to zero showing more heterogeneous absorption and if the value is 0.1>1/ n> 1, the absorption process is optimal [32].

$$\text{Ln } q_e = \text{Ln } K_F + (1/n_F) \text{ Ln } C_e \quad (4)$$

In the above relation $C_e$ the concentration of curcumin solution at equilibrium ($mg.l^{-1}$), qe the amount of material absorbed per unit mass of the adsorbent, 1/n the heterogeneous factor that indicates the type and severity of absorption and $K_F$ is the constant isotherm of the Frondelich.

The third isothermal model studied is Temkin isotherm with linear equation 5, this calculation model and its variables are presented in Table 6.

$$q_e = B_1 \text{ Ln } K_T + B_1 \text{ Ln } C_e \quad (5)$$

In the above relation $C_e$ the concentration of curcumin solution at equilibrium ($mg.L^{-1}$), $q_e$the amount of substance absorbed per unit mass of the adsorbent, $K_T$ isotonic absorption coefficient of Temkin and $B_1$ is the slope of the diagram of this isotherm [32-36].

Absorption kinetics is used to determine the mechanism and rate of the kinetic of the synthesized magnetic metal-organic framework nanoparticle and to control the absorption processes [37]. There are several different kinetic models used in this study to better understand the experimental data of the process of absorption of curcumin solution by magnetic metal-organic framework nanocomposite synthesized from quasi-first and second-order kinetics and intramolecular penetration to quantify the quantitative absorption kinetics. The quasi-first-order model occurs with an equation of 6 expressing penetration into the single layer, and the changes in adsorption value over time are proportional to the number of unoccupied adsorbent sites [38-40].

$$\text{Ln } (q_e - q_t) = \text{Ln } q_e - k_1 t \quad (6)$$

In equation 6, $K_1$ equilibrium constant quasi-first order velocity ($min^{-1}$), $q_e$ the amount of curcumin absorbed in equilibrium (mg/g) and $q_t$ is the amount of curcumin absorbed at time t (mg/g). The quasi-second order model with Equation 7 represents the chemical adsorption rate with a slowing speed which controls surface absorption where the square of the number of unoccupied sites in the adsorbent is proportional to the occupancy rate of the absorbed sites [41].

$$t / q_t = 1 / K_2 q_e^2 + t / q_e \quad (7)$$

In this regard, $K_2$ is the equilibrium constant of the second-order kinetic and in terms of (g/mg .min). The parameters $q_e$ and $q_t$, indicate the amount of curcumin absorbed in equilibrium and the amount of curcumin absorbed at time t and in terms of (mg/g) respectively. Finally, by comparing these three kinetic models, it can be estimated which synthesized metal-organic framework nanocomposite follows which kinetics model and its adsorption rate are calculated [42-45].

### 2.6 Instrumental method

The formed phases and crystal structure of the synthesized metal-organic framework nanoparticles examined using X-ray diffraction (XRD, Philips) device equipped with copper lamp (Cu-Ka) and to detect the phases and sizes of nanoparticles crystals of magnetic metal-organic framework nanocomposite composites from X 'Pert software and standard scatter plot (JCPDS) was used to compare and match the peaks obtained. External structure and geometric shape of magnetic metal-organic framework nanocomposite, phase differences and changes in nanocomposite it were studied by type MIRA3 field emission scanning electron microscopy (SEM) device made by TE-SCAN company. The magnetic properties of the synthesized metal-organic framework nanocomposites were performed using the vibrational magnetometer analysis (VSM) by the LBKFB device. Special surface area (SBET) measurement was performed according to the BET method and by analyzing the measurement of porosity and effective surface area (BET) using a device (Belsorp mini II from Microtrac Bel Corp company of Japan).

## 3. Results and Discussion

### 3.1 Characterization of synthesized magnetic metal-organic framework nanocomposite

The synthesized magnetic metal-organic framework nanocomposite with different weight ratios from ferrite nickel and silica substrate was characterized by analyzes SEM, TEM, XRD, VSM and BET.

Fig (1): TEM analysis image of magnetic metal-organic framework nanocomposite ($NiFe_2O_4$@$SiO_2$@HKUST-1)

Fig 1 shows the image of the electron microscopy associated with the magnetic metal-organic framework nanocomposite ($NiFe_2O_4$@$SiO_2$@HKUST-1) synthesized in this study with magnification KX200. According to the image, the metal-organic framework nanocomposite were almost rod-shaped, and the nickel ferrite were dispersed inside and outside the silica substrate. In this study, to analyze the morphology and size of the magnetic metal-organic framework nanocomposite ($NiFe_2O_4$@$SiO_2$@HKUST-1), the analysis of scanning electron microscopy were used.

Fig. (2): Image analysis of SEM analysis of magnetic metal-organic framework nanocomposite $NiFe_2O_4$@$SiO_2$@HKUST-1

SEM of the synthesized magnetic metal-organic framework shows that these nanocomposites have rod morphology (Fig.2). The nickel ferrite nanoparticles in the silica matrix are placed side by side in such a way that they form a rod structure and the HKUST-1 metal-organic framework is placed on them. It has also been shown that the synthesized nanocomposite is hollow and has a crystalline and dense structure [46].

The X-ray diffraction analysis was used to investigate the formed phases and the structure of the synthesized magnetic metal-organic framework nanocomposites and to calculate the size of the crystals. Fig (3) shows the XRD diagram of the synthesized samples.

Fig (3): XRD diagram of magnetic metal-organic framework nanocomposite synthesized with different nickel ferrite percentages

The crystal structure of metal-organic framework (HKUST-1) at $2\vartheta$ has index peaks at 20.66°, 15.92° and 13.65°, as well as the presence of index peaks at 20-35° related to nickel ferrite and the presence of silica in the nanocomposite. Peaks at the 52- 40 degree range are due to the presence of nickel ferrite in the silica substrate, indicating that the xerogel amorphous nickel ferrite is located in the silica matrix. Finally, the Sherler equation was used to calculate the crystal size of the synthesized magnetic metal-organic framework. Crystal sizes obtained from Equation (8) showed that the higher ratio of nickel ferrite to the silica matrix led to the larger nanocomposite. In Table 2, the crystal sizes for synthesized magnetic metal-organic framework nanocomposites are calculated and presented.

$D = 0.99\lambda \ / \ \beta \cos \vartheta$ (8) Eq.

In this regard, D diameters of nanocomposites, $\lambda$ is the X-ray wavelength irradiated, $\beta$ is the peak width at half height or FWHM, which should be placed in the formula according to radians and $\vartheta$ is the peak location on the horizontal axis of the scatter pattern.

Table (2): Crystal parameters of synthesized magnetic metal-organic framework nanocomposites

| Sample | Peak pos. [°2$\vartheta$] | Crystallite size [nm] | d-spacing [nm] |
|---|---|---|---|
| ($NiFe_2O_4$@$SiO_2$@HKUST-1) 10% | 19.909 | 20.5 | 4.45 |
| ($NiFe_2O_4$@$SiO_2$@HKUST-1) 30% | 20.627 | 32.8 | 4.30 |
| ($NiFe_2O_4$@$SiO_2$@HKUST-1) 50% | 20.467 | 41.0 | 4.33 |

The synthesized metal-organic framework nanocomposites were examined using VSM analysis at ambient temperature to investigate the magnetic properties. Fig 4 shows the VSM magnetic analysis diagram for the synthesized magnetic metal-organic framework nanocomposites.

Fig (4): VSM analysis charts of synthesized magnetic metal-organic framework nanocomposites.

The magnetized curves of the synthesized samples show that the synthesized magnetic metal-organic framework nanocomposites having a good superparamagnetic property with different magnetic saturation. In magnetic metal-organic framework nanocomposites, as the weight ratio of ferrite nickel to the silica substrate increases, the magnetic saturation increasing. The parameters obtained from this analysis are presented in Table (3). Therefore, it can be concluded that, studied metal-organic framework nanocomposites are easily dispersed in water and can be collected by an external magnetic field [26, 27, 47-49].

Table (3): VSM analysis parameters for synthesized metal-organic framework nanocomposites.

| Sample | $M_r$ [emu/g] | Ms [emu/g] | Hc [$O_e$] |
|---|---|---|---|
| ($NiFe_2O_4$@$SiO_2$@HKUST-1) 10% | 0.0039 | 0.34 | 0.003 |
| ($NiFe_2O_4$@$SiO_2$@HKUST-1) 30% | 0.016 | 0.87 | 0.04 |
| ($NiFe_2O_4$@$SiO_2$@HKUST-1) 50% | 0.11 | 2.09 | 0.1 |

Accurate measurement of surface area and material porosity is important in many applications, such as nano sorbent for the metal-organic framework and metal nanoparticles. Therefore, using BET analysis, the type of porosity, surface area and diameter of puros in synthesized magnetic metal-organic framework nanocomposites can be measured. Table (4) presents the BET analysis parameters for the synthesized magnetic metal-organic framework nanocomposites with different percentages of ferrite nickel to the silica matrix.

Table 4: BET analysis parameters for the synthesized magnetic metal-organic framework nanocomposites with different percentages of ferrite nickel to the silica matrix.

| Pore type | Pore volume (nm) | BET ($m^2$/gr) | Sample |
|---|---|---|---|
| Mesoporous | 7.28 | 37.87 | ($NiFe_2O_4$@$SiO_2$@HKUST-1) 10% |
| Mesoporous | 6.99 | 43.38 | ($NiFe_2O_4$@$SiO_2$@HKUST-1) 30% |
| Mesoporous | 5.14 | 89.84 | ($NiFe_2O_4$@$SiO_2$@HKUST-1) 50% |

Based on table 4 results, by increasing the percentages of nickel ferrite from 10 to 50%, the BET surface area increases and pore volume decreases. These pores, which are only due to the presence of the HKUST-1 metal-organic framework, are not uniform in pores diameter because the ferro-nickel nanocomposites are non-dispersed. Also, as the percentage of nickel ferrite, which is the same as the heavy nuclei in the silica bed, increases, these pores fill and the pore volume decreases [28]. According to SEM images and BET analysis, the synthesized magnetic metal-organic framework nanocomposite is a porous material and since the pore diameter of these nanocomposites is bigger than 4 nm, they are in the category of mesoporous materials. These pores, which are only due to the presence of the HKUST-1 metal-organic framework, are not uniform in diameter because nickel ferrite nanocomposites are non-dispersed in them. Therefore, as the percentage of nickel ferrite, which is the heavy nuclei in the silica bed, increases, these pores fill and the pore volume decreases [28].

### 3.2 Adsorption optimization tests

### 3.2.1 Investigating effect of magnetic metal-organic framework nanocomposite dose on curcumin uptake

To investigate the effect of the interaction of curcumin molecules with magnetic metal-organic framework nanocomposite, prepared the aqueous solution of curcumin with a concentration (100 mg /L) and then 100 ml of solution were sampled. Calculate the amount of curcumin in solution and added to various ratios of (1:2), (2:1) and (1:1) magnetic metal-organic framework nanocomposites ($NiFe_2O_4$@$SiO_2$@HKUST-1) with weight percentage (30% wt.). Placed the solution on the shaker for better mixing. Sampling and centrifugation performed every 2 hours and spectrophotometer used to measure the wavelength and the absorption value was calculated.

Fig(5). Investigation of the effect of nanocomposite concentration on curcumin

Fig (5) showed, as the nanocomposite ratio of the magnetic metal-organic framework to curcumin increases, the adsorption efficiency increases. It was also obtained that the maximum efficiency (90%) were riched after 8 hours when the nanocomposite of the magnetic metal-organic framework of the magnet was double of the amount of curcumin used in the solution. This increase in efficiency is due to the increase in sites and free puros due to the increase in the concentration of metal-organic framework nanocomposite compared to the concentration of curcumin in the solution.

### 3.2.2 Investigation effect of type of magnetic metal-organic framework nanocomposite on curcumin uptake

First made a 10 mg/lit solution of curcumin and sampled 100 cc of it. Synthesized magnetic metal-organic frameworks HKUST-1 with different weight percentages and $NiFe_2O_4$@$SiO_2$nanocomposites as adsorbents in a ratio of (2:1) and the drug added to 100 cc curcumin solution sample. Then it was placed on the shaker at room temperature. As in the previous step, sampling and absorption amounts were calculated.

Fig (6): Effect of different percentages of containing metal-organic framework nanocomposite and Nickel ferrite nanocomposite on the silica substrate on adsorption.

The results showed in Fig (6), the magnetic nanocomposite ($NiFe_2O_4$@$SiO_2$) adsorbed 73% after 8 hours. This value was less than the adsorption of curcumin by metal-organic framework nanocomposite ($NiFe_2O_4$@$SiO_2$@HKUST-1) and under the same conditions, metal-organic framework nanocomposite ($NiFe_2O_4$@$SiO_2$@HKUST-1) absorbed 78.45% after 8 hours. After 8 hours, these particles were homogeneous in curcumin solution and could not be separated. Over a period of 8 hours, magnetic nanocomposite containing a metal-organic framework with a 30 %wt weight higher percentage showed the highest absorption value (94%). According to the obtained results, for further investigation, magnetic metal-organic framework nanocomposite with a weight percentage of 30% wt. were used as an optimum percentage.

As shown in Table 5, based on the obtained results and comparison with other metal-organic frameworks, it can be concluded that magnetic metal-organic framework nanocomposite ($NiFe_2O_4$@$SiO_2$@HKUST-1), like other metallic organic frameworks, is a viable option for uptake and drug interaction of curcumin.

Table (5): Evaluation of curcumin adsorption capacity on various metal-organic framework nanocomposites

| **Ref** | **Absorption Capacity** | **Adsorbed** | **MOF** |
|---|---|---|---|
| [50] | 3.45 | Curcumin | UiO-66 |
| [14] | 463.02 | | Hf- UiO- 66 |
| [14] | 466.39 | | Zr- UiO- 66 |
| [51] | 393.22 | | Zr- UiO- 66ST |
| [22] | 39.21 | | Ca-BDC |
| This study | 358 | | $NiFe_2O_4$@$SiO_2$@HKUST-1 |

### 3.2.3 Investigating the effect of curcumin solution concentration on adsorption

To investigate the effect of curcumin concentration, first curcumin solutions with concentrations of 10, 30 and 50 ppm were prepared. As in the previous steps, the optimal amount of adsorbent was added to it and placed on the shaker at room temperature. Every 2 hours, it was sampled, centrifuged and sample wavelength was measured using a spectrophotometer.

Fig (7): Investigation of the effect of curcumin drug concentration on absorption.

The results in Fig (7) indicated, higher concentration of curcumin drug solution led to lower adsorption efficiency. It was also obtained curcumin solution at the highest concentration (ppm10) showed the highest absorption efficiency because at this concentration the amount of curcumin in the solution is less than the concentration of 30 and 50 and resulted, special surfaces, empty puros and many active sites still exist in the nanocomposite surface of the metal-organic framework that is not saturated and increases the efficiency of the metal-organic framework nanocomposite absorption.

### 3.2.4 Curcumin absorption kinetics study

To check the absorption rate, kinetic adsorption and interaction behavior between curcumin and synthesized metal-organic nanocomposites with weight percentages 30, 10, and 50, three kinetic models of first-order, second-order and intra-molecular adsorption were used (Fig.8). The kinetic variables of the surface adsorption process of curcumin by the magnetic metal-organic framework nanocomposites studied and presented in Table 5.

Fig (8): Investigation of kinetic absorption models

The quasi-second order were found to be better than the other two models for synthesized magnetic metal-organic frameworks nanocomposites because of the above equation, the $R^2$ correlation coefficient for the quasi-second order is calculated. All coefficients are very close to one, while the two models of the quasi-first order and the intra-molecular diffusion, are more distant from the quasi-second order model, respectively.

So we can conclude curcumin absorption kinetics using a variety of synthesized nanocomposites follows the quasi-second order. On the other hand, the amount of $(q_e)$Cal absorption obtained from the above equations in the kinetic model absorption is quasi-secondary order it is much closer to the experimental absorption of $(q_e)$ exp.

Table 6: Data obtained from the calculation of different synthetic adsorption models for different types of synthesized nanocomposites

Adsorbent

| F-S-MOF50% | F-S-MOF30% | F-S-MOF10% | Parameter | Model |
|---|---|---|---|---|
| 446.5 | 454.95 | 453.78 | $(q)_{ex}$ | Pseudo First-Order |
| 190.1078 | 272.897 | 139.63 | $(q)_{cel}$ | |
| 1.864 | 2.097 | 1.077 | $K_1$ | |
| 0.7029 | 0.838 | 0.942 | $R^2$ | |
| 446.5 | 454.95 | 453.78 | $(q)_{ex}$ | Pseudo Second-Order |
| 454.54 | 476.19 | 464.54 | $(q)_{cel}$ | |
| 0.0121 | 0.0053 | 0.0161 | $K_2$ | |
| 0.9991 | 0.998 | 0.999 | $R^2$ | |
| 157.29 | 160.16 | 161.93 | $K_p$ | Molecular Influence |
| 73.56 | 63.663 | 75.84 | I | |
| 0.8024 | 0.848 | 0.8021 | $R^2$ | |

Among the synthesized nanocomposites, metal-organic framework nanocomposite ($NiFe_2O_4$@ $SiO_2$@HKUST-1) with a 30% weight percentage showed better absorption. As a result, the kinetics of adsorption for this metal-organic framework nanocomposite are calculated in different concentrations of

curcumin solution. To find the kinetic absorption of this nanocomposite, all three models mentioned above were examined.

### 3.2.5 Study of isothermal absorption models

In this study, to evaluate the isotherms of adsorption on the desired adsorbent under optimal conditions, the three absorption isotherms of Langmuir, Freundlich and Tamkin were examined (Fig. 9).

Fig. (9): Investigation of adsorption isotherms, a) Langmuir isotherm b) Freundlich isotherm c) Temkin isotherm.

In isothermal absorption, it is assumed that the drug is placed on the adsorbent as a single-layer coating. According to the calculation, the $R^2$ obtained from the isotherm is the absorption of Langmuir (0.948), which indicates that there is a single molecular absorption of curcumin on the target adsorbent. Freundlich adsorption isotherm is widely used for multilayer absorption modeling on heterogeneous adsorbent surfaces and it is not limited to the formation of a single layer on the surface in addition absorption functions can also be described using the Freundlich isotherm parameters. As can be seen from the calculations, $R^2$ is obtained from the calculations of this isotherm (0.995). Also, the value (1/n) obtained indicates that the adsorption conditions of curcumin on the adsorbent are optimal and the curcumin groups are adsorbed on the heterogeneous adsorbent surface. Using the Temkin adsorption isotherm, the ratio of the surface covered to the total available surface can be obtained for the adsorbent and in this isotherm, $R^2$ is equal to (0.945). This indicates that almost a large area of the adsorbent is available to absorb curcumin and is covered with curcumin.

Table (7): Investigation of different types of isotherms of absorption and presentation of their parameters

Adsorbent

| F-S-MOF30% Concentration(mg/L) 30 | F-S-MOF30% Concentration(mg/L) 30 | Parameter Concentration(mg/L) 30 | Model |
|---|---|---|---|
| 358 | $(q)_{ex}$ | $(q)_{ex}$ | Langmuir |
| 222.330 | $(q)_{m}$ | $(q)_{m}$ | |
| 0.397 | $K_L$ | $K_L$ | |
| 0.948 | $R^2$ | $R^2$ | |
| 358 | $(q)_{ex}$ | $(q)_{ex}$ | Freundlich |
| 370.37 | $K_F$ | $K_F$ | |
| 0.1045 | 1/n | 1/n | |
| 0.995 | $R^2$ | $R^2$ | |
| 124.64 | $K_T$ | $K_T$ | Temkin |
| 45.706 | $B_1$ | $B_1$ | |
| 0.945 | $R^2$ | $R^2$ | |

According to the data in Table (7), the correlation coefficients ($R^2$) of all three adsorption isotherms of Langmuir, Freundlich and Temkin and compliance are close to one, but the correlation coefficient of Freundlich absorption is the highest. This indicates that the isotherm was the dominant isotherm of the Freundlich. This means that the adsorption process has been multi-layered on heterogeneous surfaces, as a result, this model describes experimental data well. Therefore, the mechanism of adsorption of curcumin on the nanocomposite of the magnetic metal-organic framework and a filling of the available absorbent surface of curcumin.

### 3.3 The mechanism of absorption of curcumin on $NiFe_2O_4$@$SiO_2$)@HKUST-1 x (x=30%wt)

Based on the analysis of experimental data, the mechanism of adsorption of curcumin on the metal-organic framework nanocomposite adsorbent are attributed to (π-π) bonds, hydrogen bonds and electrostatic interactions between the curcumin functional groups and the metal-organic framework. These high adsorption capacities were obtained at pH = 7, where curcumin molecules are natural or neutral. In addition, coordinate

bonds have been established between $Cu_2+$ open sites within the HKUST-1 metal-organic framework and CO- and O-groups in curcumin molecules. Hydrogen bonds are also formed between Cu-O-Cu molecules in HKUST-1 and OH in curcumin. On the one hand, curcumin molecules can form covalent bonds with the Si-O group in nanocomposites through silica-oxygen bonds in D-ketones [29, 52, 53]. On the other hand, curcumin binds strongly to most metal ions, because curcumin has acted as a ligand and are attached to the central metals that act as the core of the metal-organic framework and create stable complexes [54-57].

## 4. Conclusion

Currently, the drug curcumin has been absorbed and examined using metal-organic framework nanocomposites. Magnetic metal-organic framework nanocomposites with ferrite nickel weight ratios of 30, 10 and 50 to silica matrix were synthesized by the in-situ self-arrangement method. These magnetic metal-organic nanocomposites were identified by XRD, TEM, SEM, VSM and BET analysis and from their comparison with the authorities, the accuracy of the synthesis was obtained. To study the nanocomposites of the synthesized magnetic metal-organic framework as the adsorbent and drug interaction of curcumin, absorption parameters such as adsorbent type, adsorbent dose and drug dose were investigated. Finally, the optimal conditions were introduced using these metal-organic frameworks nanocomposites. Magnetic metal-organic frameworks nanocomposite with ferrite nickel ratio of 30% by weight to silica matrix acted as the best adsorbent with the highest capacity to absorb curcumin. The results of drug uptake and interaction by this nanocomposite showed a synthesized magnetic metal-organic framework in an environment with pH=7, contact time 8 hours, the dose of drug 10 ppm and the amount of adsorbent double of the dose of the drug are the optimum values for achieving the maximum absorption capacity of the drug curcumin by magnetic metal-organic frameworks nanocomposite with a weighted ratio of 30% of ferrite nickel to the synthesized silica matrix. To determine the adsorption isotherm, adsorption isotherms of Langmuir, Freundlich, and Temkin were examined. The results showed that absorption and drug interaction on the synthesized adsorbent with the isothermal model of Freundlich absorption has a better match and most of the absorption process is chemical. To examine the kinetics of adsorption, synthetic models of quasi-first and second-order molecular absorption were used that kinetic relations showed, the process of drug uptake and interaction of curcumin follows second-order kinetics. Based on the obtained results, $NiFe_2O_4$@$SiO_2$@HKUST-1 magnetic metal-organic frameworks nanocomposite is a good option for absorbing and interacting with curcumin.

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