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Thermodynamic study of adsorption of a mixture of Nolvadex and nanoparticle ferric oxide that prepared on the surface of activated charcoal

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Abstract

The research included preparing nanoparticle ferric oxide and then diagnosing it with several techniques including scanning electron microscopy technology (SEM) and transmission electron microscopy (TEM) and Energy-dispersive X-ray (EDX), and this research also included a thermodynamic study of adsorption of a mixture of nolvadex with nano ferric oxide prepared on a surface of Activated charcoal, as it was found that the equilibrium time was 40-50 minutes and an appropriate weight of the adsorbent 0.1 g, The study was carried out at four different temperatures (290.65-320.65 K), as it was found that the adsorption process was Spontaneous (ΔGo = -) and Exothermic (ΔH= -) A few Random (ΔSo =-).

Keywords: nanoparticle Ferric oxide, adsorption, Nolvadex, adsorption.

Introduction

Nanotechnology is an active and new field of research, which is studied by many scientists around the world because of this technology has many applications and dating in various sectors, which means more efficiency and optimal use of resources (1) Nanoscience is defined as the science that deals with Substances where their dimensions or one of their three dimensions are within the nanoscale, so that they do not exceed 100 nm (2).

Activated charcoal was defined as black powder, with a high carbon content, tasteless and odourless, nontoxic, with high porosity, and it is the name of a large family of charcoal materials that do not have a specific chemical structure (3).

Adsorption is considered a relatively old phenomenon, and this process has received the attention of a large number of researchers in this field due to the need for it and its wide applications, and adsorption is a phenomenon that collects fine particles of a substance in the form of particles, atoms or ions on the surface of another substance, these micro-molecules are called Adsorbent, and the surface on which adsorption occurs is called the adsorbent surface (4).

During the past years, researchers increased interest in preparing and studying nanopartic metal oxides due to their increasing applications (5), and it was found that these different properties of these oxides change significantly at the nanoscale compared to the conventional scale, where they reach a complete change in properties (6).

Super Magnetized Nanoxide is an interesting mineral oxide due to its many applications in advanced technologies. Where it is widely used in many important medical and biological applications such as image reversal in magnetic resonance technology (7) tissue restoration (8) detoxification from Bio-fluids (9) and as postulates for medicines within Bio-systems (10) and removal of heavy elements ions (11) and others of uses.

The aim of the research

1- Preparation and diagnosis of nanopartic ferric oxide using several techniques including (SEM), (EDX) and (TEM).

2- Calculation of thermodynamic functions for adsorption of a mixture of Nolvadex nanoparticle and ferric oxide on the surface of activated charcoal.

Experimental part

- **Preparation of nanoparticle ferric oxide:**

1. 100 mL of iron sulfate (II) solution (0.2 molar) was mixed with 100 ml ferric chloride (lll) solution (0.4 molar).
2. Sodium hydroxide (2 molar) is added dropwise until a pH equal to (11) is obtained

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with constant stirring using a magnetic motor for one hour at room temperature.

3. A black precipitate is formed that is washed with deionized water several times, then dried in the oven for three hours at a degree of 100 C°, then ground and placed in a sealed container away from moisture.

- **Determining (λ_{max}) and building a standardization curve for Nolvadex**

The maximum wavelength (λ_{max}) at which the highest absorption of Nolvadex solution is obtained is determined by using the visible - ultraviolet spectroscopy apparatus and for a standardization curve preparing 10 dilute aqueous solutions within the range (10^{-4} x 0.5 - 10^{-4} x 4 molar). In a 10 ml volumetric flask of standard solution for Nolvadex, The absorbance values of each of these diluted solutions were measured after Reset the apparatus using the solvent (water) as a reference (Blank) at the greatest wavelength, which was drawn based on (Lambert Beer Law). Then, some factors affecting adsorption such as concentration, temperature, and others were studied.

- **Estimating the amount of adsorbed material**

The terms adsorption capacity and adsorption efficiency (percentage of adsorption) are used to express the amount of adsorbed material by calculating the amount of residual material from the drug in the adsorption solution using the titration curve of the drug and then calculating the amount of adsorption from the difference between the initial concentration of the drug and the rest of it, and it can be calculated The percentage or the so-called adsorption efficiency using the following equation: -

$$\%\text{Adsorption} = \frac{C_o - C_e}{C_o} \times 100 \text{ .... } (1)$$

Whereas, C_o represents the value of the initial concentration of the drug in the liquid phase (mg / L) and C_e the concentration of the drug in the solution at equilibrium (mg / L), while the adsorption capacity of activated charcoal can be expressed by the following formula [11]: -

$$Q_e = \frac{C_o - C_e}{M} \times V \text{ .... } (2)$$

Whereas, M represents the weight of the adsorbent (activated charcoal) in grams, and V is the volume of the drug solution used when studying adsorption in liters.

- **Calculation of Thermodynamic Function**

The values of the equilibrium constant for the adsorption process (K_{eq}) are calculated at different temperatures, upon reaching equilibrium state through the ratio between the amount of adsorbent material and the residue in the solution according to the formula:

$$K_{eq} = \frac{X_{eq}}{a - X_{eq}} \text{ ... ... } (3)$$

Where **a** = the initial concentration of the adsorbent substance (mg / L), $\mathbf{X_{eq}}$ = the concentration of the adsorbent material at equilibrium (mg / L), a-x_{eq} = the remaining concentration of the adsorbent material at equilibrium, and the value of Δ H of the ln$\mathbf{K_{eq}}$ drawing was calculated against an inverted The temperature is based on the following (Vant-Hoff Equation) [12]:

$$\ln Keq = (\ \Delta H/RT) + C \text{ ……………………..} (4)$$

–

(Since Keq = equilibrium constant for adsorption process, ΔHº = enthalpy of standard adsorption ($J.mol^{-1}$), R = general constant of gases ((8.314 J / mol.K), C= constant of Vant-Hoff Equation, T = absolute temperature in Kelvin) We will get a straight line with a slope equal to (- ΔH/ R) and from it we will get ΔHº, as the values of ΔGº and ΔSº are calculated according to the following equations:

$$\Delta G^o = -RT \ln Keq \text{ ………………………….…. } (5)$$

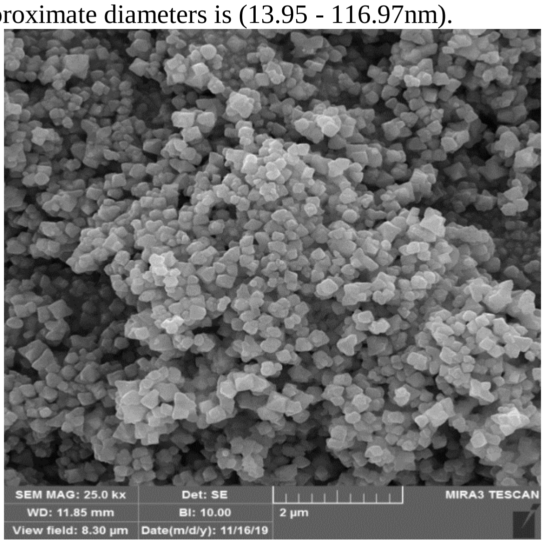
$$\Delta S^o = (\Delta H - \Delta G^o)/T \text{ ……………………………} (6)$$

Since ΔSº = entropy (randomness) standard ($J.mol^{-1}.K^{-1}$), ΔGº = standard free energy ($J.mol^{-1}$).

Results and discussion:

- **Diagnosis of prepared nanoparticle ferric oxide**

From Figure (1), the scanning electronic microscopy (SEM) nano ferric oxide is shown at a different magnifying force with a micro and nano scale and it is clear that the material is formed in the form of semi-spherical or square particles and the size of their approximate diameters is (13.95 - 116.97nm).



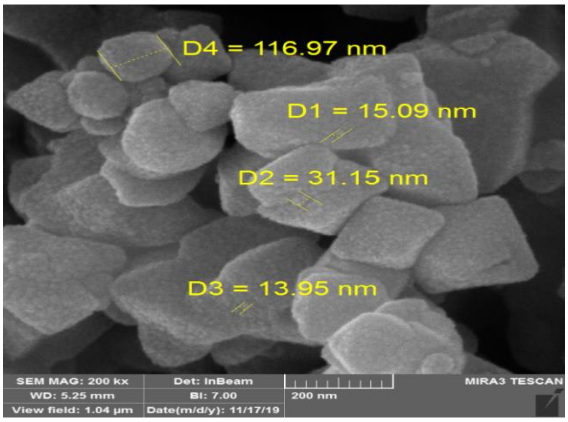


Figure 1: Image of a scanning electron microscope (SEM) of prepared nanoparticles Ferric oxide at a different magnification force of 1.64μm, 8.33μm.

And the diagnosis of prepared ferric oxide under transmission electron microscopy (TEM) shows the results, as shown in Figure 2 at the magnification force of 100nm. The prepared ferric oxide particles within the nanoscale have a spherical or semi-square shape.

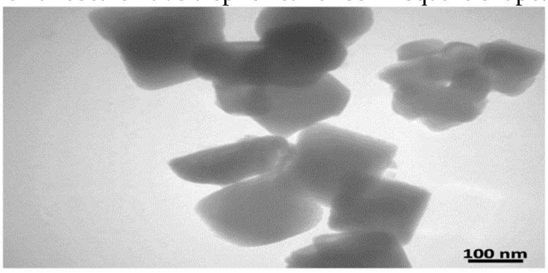


Figure (2): Measurement of transmission electron microscopy (TEM) of ferric oxide nanoparticles at a magnification force of 100 nm.

As the prepared ferric oxide was diagnosed with X-ray dispersion technology and Figure (3) shows that the highest percentage is for the iron element by (49.50%), followed by the oxygen element (47.87%), while the lowest percentage is for the carbon element by (2.63%) and table (1) Shows the proportions of the sample components.

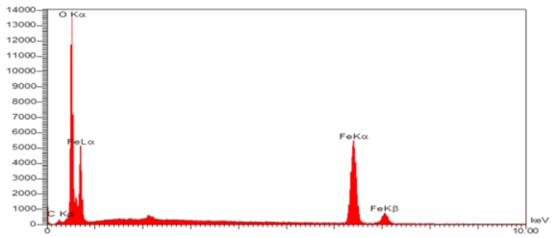


Figure (3): X-ray dispersion spectrum of nanoparticle ferric oxide

Table (1) the proportions of the constituent elements of nanoparticle ferric oxide

Element	Weight%	Atomic%
Fe	49.50	21.63
O	47.87	73.02
C	2.63	5.34
Totals	100.00	100.00

-Determination of equilibrium time:

The results showed that the adsorption process reached the equilibrium state during a period of time ranging between 40-50 minutes as in Tab. 2 which gave the highest Adsorption Efficiency (Abs. %) . In the case of Equilibrium, we note that the increase in the Equilibrium time (t) did not enhance the adsorption process of the drug (Nolvadex) due to the lack of pores of adsorption . Which leads to return to the solution because, of the extortion process.

Tab. 2 Determination of equilibrium time and adsorption efficiency (Abs.%)

Time (t) (min.)	Abs.	$C_{Abs.}$ (mg/g)	Abs. %
10	0.16	1.91	82.5
20	0.15	1.94	84.0
30	0.13	1.98	85.4
40	0.10	2.05	88.6
50	0.10	2.05	88.6
60	0.18	1.77	80.9

-Thermodynamic study: The results show that, as in Table (3), the equilibrium constant (K_{eq}) decreases with increasing temperatures due to a decrease in the adsorbent concentration of the drug, it corresponds to the residual concentration with increasing temperature.as the (K_{eq}) values have been calculated by the ratio between the amount of adsorbed material to the residue in the solution, we note the inverse proportion between the temperature and the equilibrium constant.

Among the values of (ΔG^o) and (ΔH) that are calculated by the Vant-Hoff curve (Equation No. 4) that we obtain by drawing ($\ln K_{eq}$) with the reverse of the temperature as in Figure (4), the values of (ΔG^o) are calculated by Equation 5. the values of (ΔS^o) is then estimated from equation 6.

It is worth noting that this study was conducted at optimal conditions for adsorption using the best concentration of Nolvadex (0.000025), molar and (0.000015 molar) of nanoparticle ferric oxide and the best weight of the adsorbent material (0.1 g) and at equilibrium time (40-50) minutes and thermodynamic values fixed in Table No. (2).

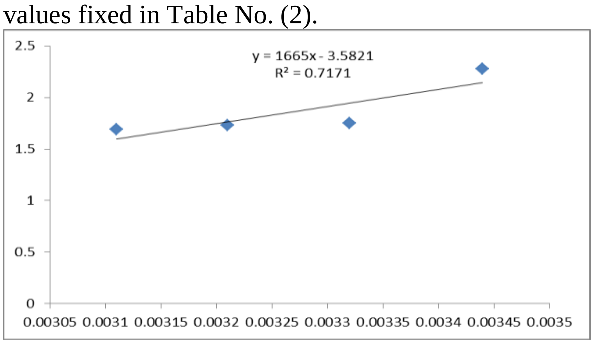


Fig.4 Drug adsorption on the surface of activated carbon using the Vantt-Hoff equation

Table 3: Thermodynamic values for drug adsorption on activated carbon at different temperatures

T (K)	1/T (K^{-1})	K_{eq}	ln K_{eq}	HΔ ($kJ.mole^{-1}$)	G°Δ ($kJ.mole^{-1}$)	S°Δ (J/mole.K)
290.65	0.00344	9.840	2.286	-13.842	-5.524	-28.621
300.65	0.00332	5.763	1.751	-13.842	-4.376	-31.485
310.65	0.00321	5.692	1.793	-13.842	-4.491	-30.102
320.65	0.00311	5.465	1.698	-13.842	-4.526	-29.053

The negative value of the enthalpy (ΔH) indicates that the adsorption of the mixture of Nolvadex and ferric oxide on the surface of the prepared activated charcoal is a Exothermic process as it indicates that the physical adsorption means that the forces responsible for the occurrence of the adsorption process are weak forces, and the values of the change in Negative free energy (ΔG°) adsorption occurs spontaneous The decrease in the values of the change in free energy confirms the nature of the exothermic adsorption process, and the change in negative entropy (ΔS°) values indicates that the occurrence of the adsorption process reduces the randomness of the system under study because the particles that suffer from adsorption become constrained due to their attachment to the adsorbent surface, that is, it will be lost its freedom compared to the state she was in before the adsorption [14,15].

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