A comparative Adsorption Study for Fe in Ferrosam and Hemavit Drugs on Iraqi Bentonite clay

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الخلاصة:

يستخدم طين البنتونايت على مدى واسع في الصناعات الصيدلانية والتطبيقات الدوائية. تمت الدراسة باختلاف امتزاز الحديد في دوائي الفيروسام والهيمافيت على طين البنتونايت العراقي وبطريقة الوجبة. وصلت نسبة امتزاز الحديد في الفيروسام (Q%) الى (96.2-96.6) عند المدى الحراري (303-323) كلفن بينما وصلت هذه النسبة الى (71.3-80.7) في حالة امتزاز الحديد في الهيمافايت في نفس المدى الحراري. بينت ايزوثيرمات الامتزاز بانها من نوع لبنكماير بالنسبة لامتزاز الفيروسام ومن نوع فريندلش بالنسبة لامتزاز الهيمافيت. تم حساب القيم الثرموداناميكية والحركية لامتزاز الدوائين بالتفصيل، ودلت كل المؤشرات على ان الحديد (بالهيئة اللاعضوية) اي الفيروسام هو اكثر امتزازا من الحديد (بالهيئة العضوية) اي الهيمافيت.

Abstract:

Bentonite clay is widely used in pharmaceutical industry and medical applications. A batch adsorption system has been applied to study the differences between the adsorption of Fe in ferrosam ($FeSO_4.7H_2O$) and Fe in hemavit ($C_4H_2FeO_4$) on the Iraqi bentonite. The adsorption percentage (Q%) of Fe in ferrosam reached to (96.2 - 96.6)% while the percentage for hemavit reached to (71.3- 80.7)% at the temperature range (303-323) K.

The adsorption isotherms for ferrosam was a Langmuir type while the adsorption isotherm for hemavit was Freundlich type. Thermodynamics and kinetics parameters of the adsorption of two drugs has been calculated in details. The results were shown that higher adsorption of Fe in ferrosam as (inorganic formula) than the adsorption of Fe in hemavit as (organic formula).

Introduction:

Bentonite is clay that is used in for many different purposes, it is used in animal foods, since it slows down the digestion of food, thus it enables more nutrients to be absorbed by the body [1-2]. Bentonite is used medicinally due to its healing properties and in the synthesis of drugs as filler [3]. Bentonite is used as filler in pharmaceuticals, and due to its absorption /adsorption functions it allows paste formation, such application include industrial protective creams, calamine lotion, wet compresses, and anti-irritants for eczema. In medicine bentonite is used as anti-dote in heavy metal poisoning.

Iron is one of most abundant metals on the earth, it is essential for the life and to normal human physiology. Iron is an integral part of many proteins and enzymes that maintain good health, in humans, iron is an essential component of proteins involved in oxygen transport [4-5]. It is also essential for the regulation of cell growth and differentiation [6-7]. A deficiency of iron limits oxygen delivery to cells, resulting in fatigue poor work performance and decreased immunity [3,8-9]. On the other hand, excess amounts of iron can result in toxicity and even death [10].

Almost two-thirds of iron in the body is found in hemoglobin, the protein in red blood cell that carries oxygen to tissue. Smaller amounts of iron are found in myoglobin, a protein that helps supply oxygen to muscle and in enzymes that assist biochemical reactions [11].

Iron is also found in proteins that store for future needs and that transport iron in the blood. Iron stores are regulated by intestinal iron absorption [4,12].

In this paper two Fe sources drugs are used to study the adsorption of Fe on Iraqi bentonite to shed light on the possibility of using Iraqi bentonite to remove iron poisoning and to study the extent of adsorption of Fe in ferrosam and hemavit drugs on the surface of bentonite clay.

1. Materials and methods

The cheap widely available sorbent used in the study was bentonite clay supplied by geological survey directorate – Baghdad. It has the following formula:

$Mg_2Al_{10}Si_{24}O_{60}(OH)_{12}[Na, Ca]$

The bentonite clay had the following composition with particle size less than 75 µm:

Table 1- The composition of Iraqi bentonite clay.

Constituent	SiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O	Fe_4O_3	L.O.I	Total
% (wt/wt)	56.77	15.67	4.48	3.42	0.6	1.11	5.02	12.49	99.66

The sorbent used in all experiments was ferrosam drug (150 mg $FeSO_4.7H_2O$) and hemavit drug (200 mg $C_4H_2FeO_4$), both drugs were supplied by Egyptian pharmaceutical industries (EPI) – Egypt. Stock solutions (100 ppm) of drugs were prepared. The stock solution was then diluted using distilled water to give standard solution of the appropriate concentration that ranging from (10-50 ppm). Then 10 ml of aliquots of these standard solutions were placed in around bottom 250 ml flask and equilibrated using a magnetic stirrer with (0.1 g) of bentonite clay at constant temperature. Thereafter the solutions were filtered and the concentration of Fe (II) in supernatant were analyzed at 248 nm using an atomic absorption spectrophotometer (GBC-933 plus) model.

The amounts of adsorption were calculate based on difference of Fe (II) concentration in aqueous solutions before and after adsorption, the volume of aqueous solution 10 ml and the weight of the clay (0.1 g) according to:

Adsorption capacity $Q_e=(C_o - C_e)\ V/W$ …..(1)

Where C_o is the initial Fe (II) concentration (p.p.m), C_e is the final or the equilibrium Fe(II) concentration (p.p.m), V is the volume of the Fe(II) solution (ml), and W is the weight of the clay (g).

For batch kinetic studies, 0.1 g of clay were equilibrated under optimum conditions as mentioned earlier. The clay and 10 ml of Fe(II) solution were placed in 250 ml round bottom flasks and stirred by a magnetic stirrer. The sorption time was varied between 5 to 30 minutes at four constant temperatures (303-313-318-323 K). At predetermined times the solution in the beakers was separated from the clay by filtration. After, the concentrations of Fe (II) in supernatant were determined at wavelength 248 nm.

2. Results and discussion

2.1 sorption isotherm:

The Langmuir and Freundlich isotherms have been used by various workers for the sorption of variety compounds. Hemavit and ferrosam adsorption isotherms were shown in figure (1), and the data were in the tables 2 and 3.

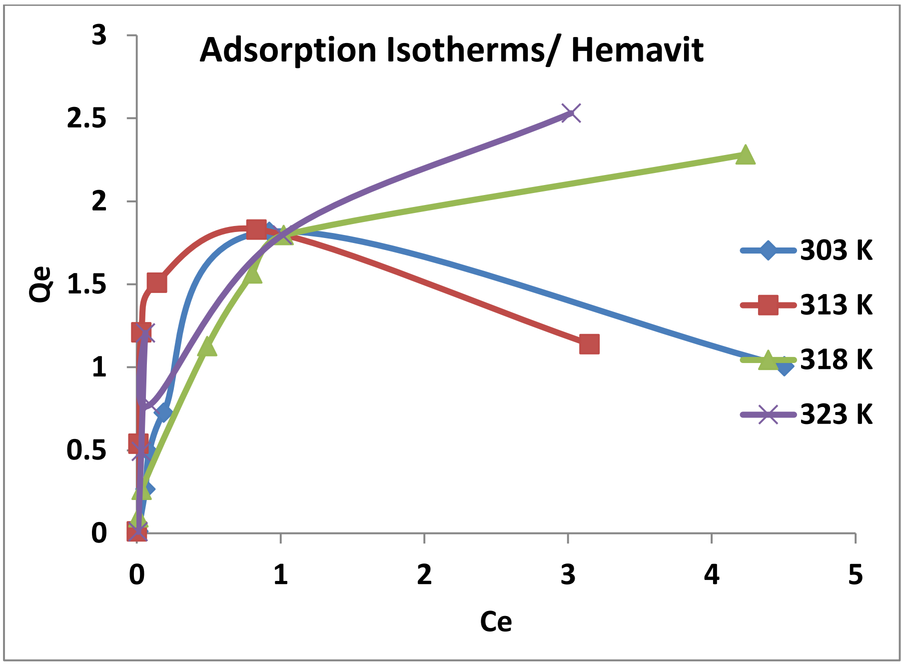


Figure 1: The adsorption isotherms of ferrosam and hemavit at different temperatures.

Table 2: The values of C_e, and Q_e at different initial concentration of ferrosam and hemavit at dfferent temperatures.

For ferrosam									For hemavit									
303 K			313K		318 K		323 K		303 K			313K		318 K		323 K		
C_o	C_e	Q_e	C_e	Q_e	C_e	Q_e	C_e	Q_e	C_o	C_e	Q_e	C_e	Q_e	C_e	Q_e	C_e	Q_e
0.934	0.006	0.237	0.004	0.237	0.001	0.237	0.007	0.2374	0.056	0.01	0.011	0.0001	0.011	0.011	0.096	0.009	0.0094
2.376	0.014	0.349	0.018	0.350	0.012	0.350	0.024	0.349	2.496	0.06	0.266	0.01	0.54	0.032	0.263	0.03	0.4932
3.521	0.019	0.459	0.021	0.35	0.018	0.458	0.028	0.352	6.124	0.086	0.487	0.03	1.21	0.49	1.127	0.06	1.2076
4.598	0.037	0.596	0.039	0.596	0.08	0.452	0.049	0.591	5.544	0.186	0.727	0.139	1.51	0.803	1.566	0.092	0.7757
6	0.1655	0.716	0.153	0.718	0.16	0.7174	0.190	0.709	10	0.921	1.816	0.832	1.83	1.02	1.796	1.012	1.7976
8.667	0.294	0.837	0.31	0.836	0.29	0.7174	0.33	0.834	15.675	4.504	1.006	3.15	1.14	4.236	2.282	3.022	2.531

Table 3: The values of C_e, and C_e/Q_e at different temperatures.

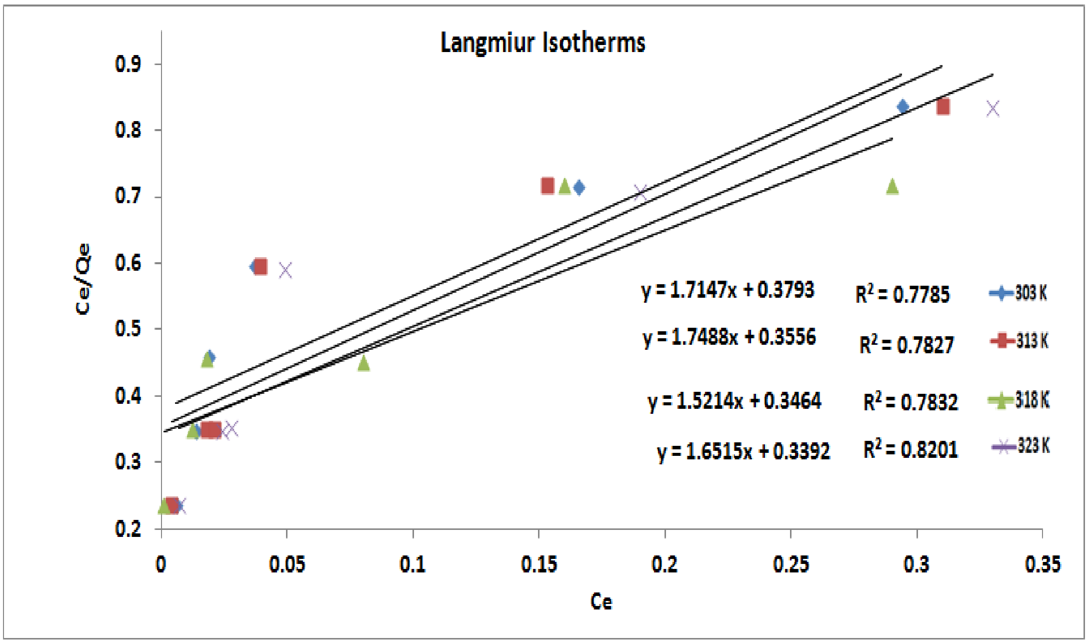
	For ferrosam								For hemavit							
	303 K		313K		318 K		323 K		303 K		313K		318 K		323 K	
C_o	C_e	C_e/Q_e	C_e	C_e/Q_e	C_e	C_e/Q_e	C_e	C_e/Q_e	C_e	C_e/Q_e	C_e	C_e/Q_e	C_e	C_e/Q_e	C_e	C_e/Q_e
0.934	0.006	0.237	0.004	0.237	0.001	0.237	0.007	0.2374	0.01	0.091	0.0001	0.009	0.011	1.146	0.009	0.09
2.376	0.014	0.349	0.018	0.350	0.012	0.350	0.024	0.349	0.06	0.123	0.01	0.0185	0.032	0.122	0.03	0.061
3.521	0.019	0.459	0.021	0.35	0.018	0.458	0.028	0.352	0.086	0.204	0.03	0.0246	0.49	0.435	0.06	0.0712
4.598	0.037	0.596	0.039	0.596	0.08	0.452	0.049	0.591	0.186	0.256	0.139	0.0918	0.803	0.847	0.092	0.1183
6	0.1655	0.716	0.153	0.718	0.16	0.7174	0.190	0.709	0.921	0.507	0.832	0.454	1.02	0.658	1.012	0.563
8.667	0.294	0.837	0.31	0.836	0.29	0.7174	0.33	0.834	4.504	4.477	3.15	2.76	4.236	1.868	3.022	1.194

Tables 2 and 3 show the adsorption data for hamavit and ferrosam respectively. The linear form of Langmuir isotherm is given by the following equilibrium:

$$C_e/Q_e = 1/b\, q_{max} + C_e/q_{max} \quad .....(2)$$

Where Q_e is the amount of adsorbed species at equilibrium (mg. g^{-1}), C_e the equilibrium concentration of the adsorbate in solution (mgL^{-1}), q_{max} , b are the Langmuir constant related to the maximum capacity of adsorption and energy of adsorption, respectively.

Where C_e/Q_e was plotted against C_e straight lines with slope of $1/q_{max}$ were obtained as shown in figure 2. The adsorption data for iron ion were also analyzed by Freundlich model figure 3, but the data better fit the Langmuir model in case of ferrosam and better fit the Freundlich model in the case of hemavit. So the inorganic Fe ions from ($FeSO_4.7H_2O$) adsorbed as monolayer while the organic Fe form ($C_4H_2FeO_4$) adsorbed as multilayer [13].



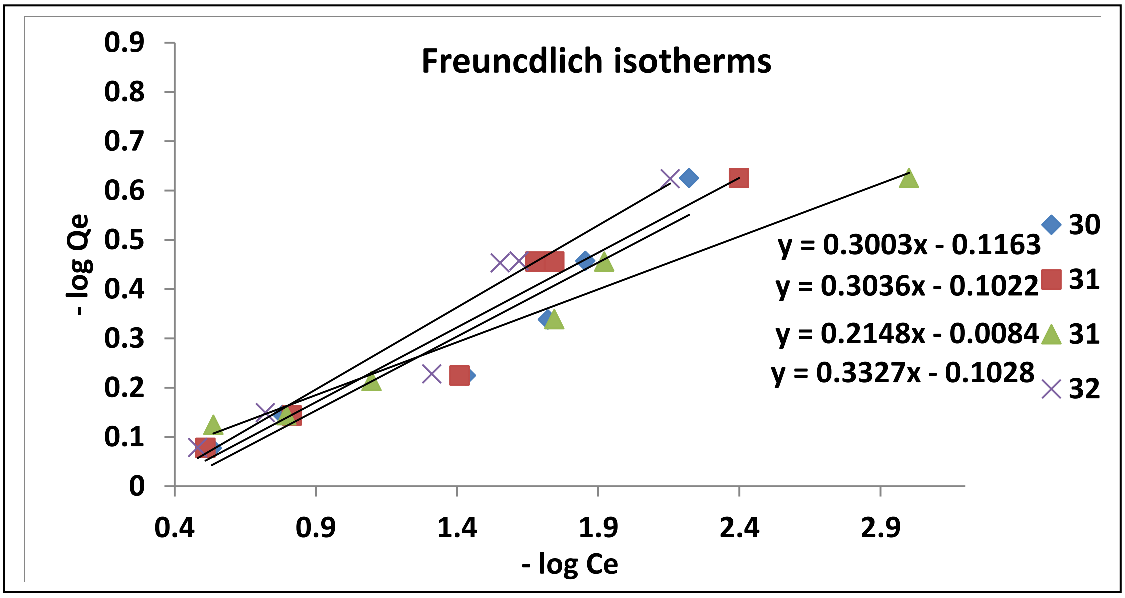


Figure 3: Freuncdlich isotherms for hemavit at different temperatures.

2.2 Thermodynamic Parameters of sorption:

According to the following equations it is possible to calculate Gibbs energy changes for the sorption process at different temperatures [14-15].

b= a exp (-ΔH/RT)………………...(3)

ln b = ln a -(ΔH/R). 1/T ……(4)

ln a = ΔS/R…………………(5)

ΔG= ΔH-TΔH……………….(6)

Where b is the maximum adsorption quantity for the different C_e concentration on bentonite and could be obtained from figure 2.

Table 4: The values of ln b and 1/T for ferrosam and hemavit at different temperatures.

	Ferrosam		Hemavit	
T	**1/T**	**ln b**	**1/T**	**ln b**
303	0.0033	-0.177	0.0033	0.0059
313	0.0032	-0.179	0.0032	0.1327
318	0.00314	-0.189	0.00314	0.6011
323	0.0031	-0.181	0.0031	0.9286

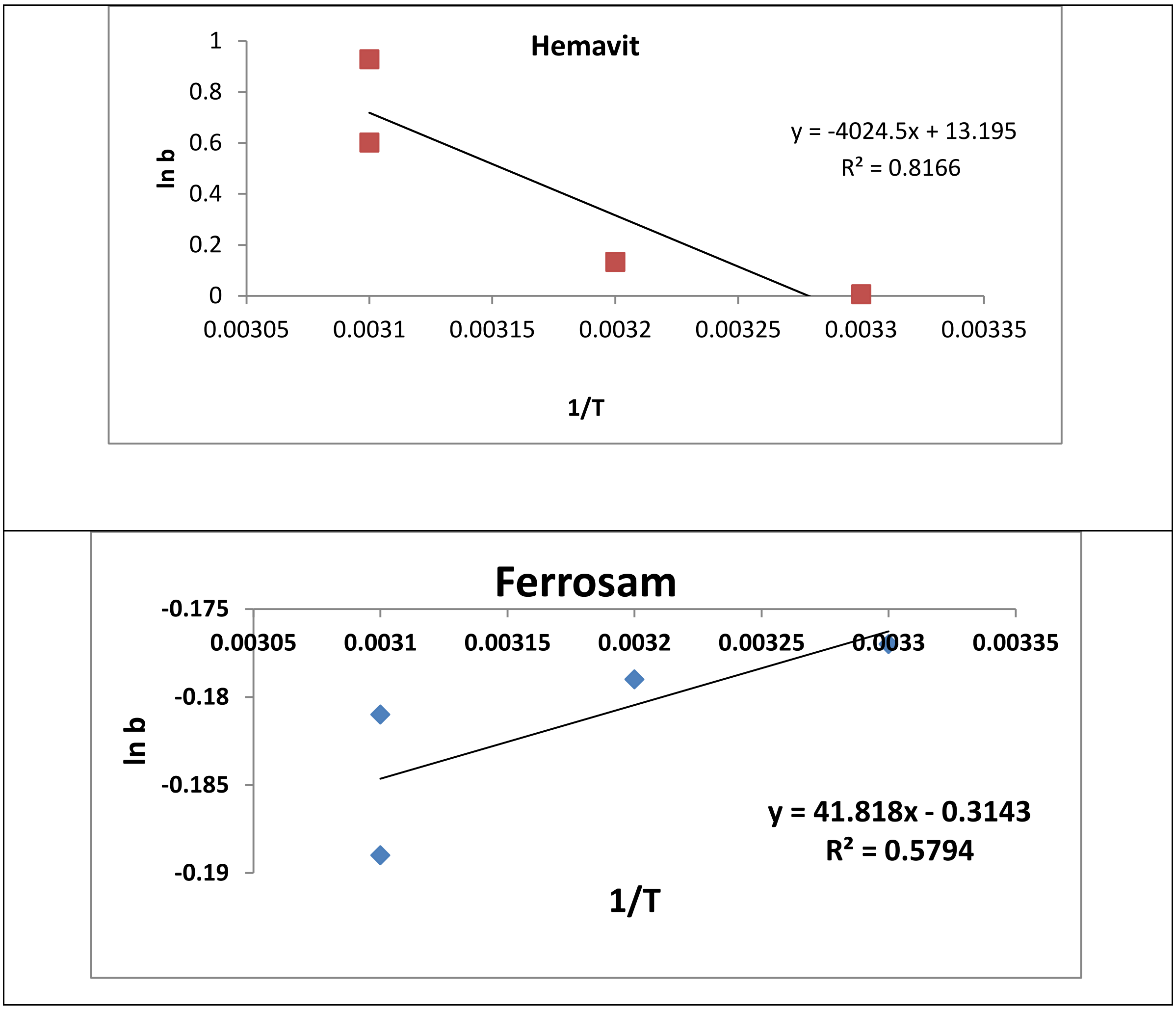


Figure 4: The plot of ln b versus 1/T.

Figure 4 and table 4 showed a linear relationship and the slope represents (-ΔH/R), R is the gas constant (8.314 J. K^{-1} mol^{-1}), and the ΔH values were calculated as shown in table 5.

Table 5: Thermodynamic parameters of drugs.

Drugs	ΔH (J. K^{-1} mol^{-1})	ΔS (J. K^{-1} mol^{-1})	ΔG (J. K^{-1} mol^{-1})
Ferrosam	0.14926	-1.97	0.77572
Hemavit	-38.354	125.6	-78.326

The ΔH value indicates that the sorption is a combination of adsorption is an exothermic process and absorption as an endothermic process. The negative sign means the overcome of adsorption while the positive sign means the overcome of absorption.

3.3 Effect of temperature on sorption percentage:

The origin of Fe, organic or inorganic forms effect on the Q% (sorption percentage), the Q% values had been calculated by using the following formula [11]:

$$Q\% = [(C_o - C_e)/ C_o] \times 100 \quad \ldots\ldots(7)$$

The effect of temperature had been studied and a plot of Q% against temperature showed a higher sorption percentages for ferrosam than that for hemavit as shown below in figure 5 and table 6.

Table 6: The values of adsorption percentages and temperatures.

Ferrosam		Hemavit	
T (K)	Q%	T (K)	Q%
303	96.6	303	71.26
318	96.4	318	79.9
313	96.5	313	72.8
323	96.2	323	80.72

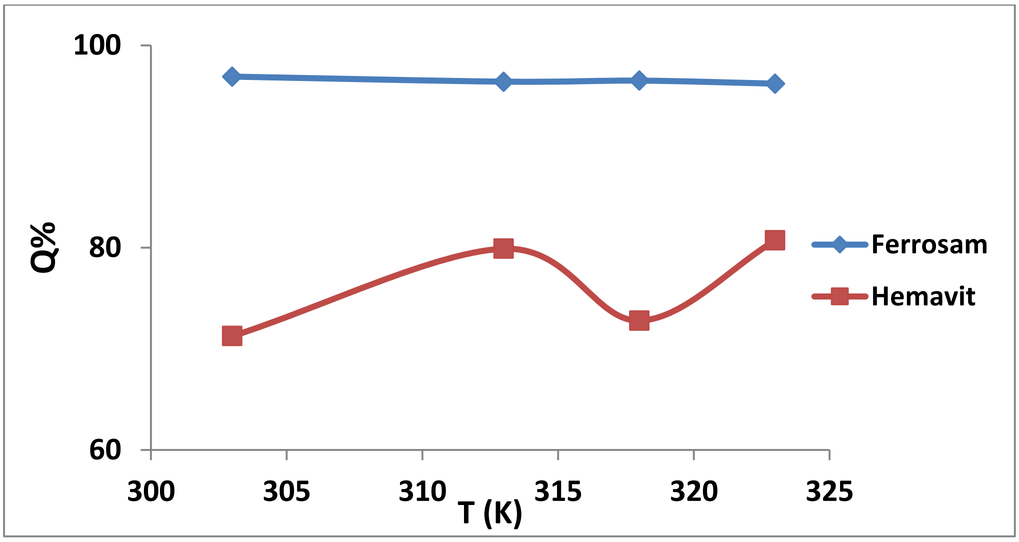


Figure 5: Effect of temperature on Q%.

Conclusion:

In the light of the present study it clear that the bentonite under study is an effective sorbent for iron ions removal from aqueous solution. This removal was enhanced in the iron of inorganic form. Sorption capacity strongly dependant on the applied conditions such as temperature, concentrations of sorbate. The Langmuir model fitted the experimental data for ferrosam better than Freundlich models, while the Freundilch fitted for hemavit.

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