JOURNAL OF MARINE SCIENCES & ENVIRONMENTAL TECHNOLOGIES
Vol. 6, Issue No. 2 (December-2020)

ISSN (Print): 2413-5267
ISSN (Online): 2706-9966

Estimation of Adsorption Isotherm for Iron Ion on Three Different Active Carbon Types

Isam A.B. Salem[1, *], Abdulhameed O. Alshoukry[2], Bashaar F. Ismael[2] , and Abdulhakeem H. Imayof[2]

[1)] Chemical Engineering Department, Faculty of Engineering, University of Benghazi, Benghazi, Libya.
[2)] Chemical Engineering Department, Petrolibya Academy, Libya.

[*]**Corresponding author:** isam.salem@uob.edu.ly

تقدير الأيزوثرم الأنسب لعملية امتزاز أيون الحديد على ثلاثة أنواع مختلفة للكربون النشط

عصام عبد الكريم سالم[1، *]، عبد الحميد عمر الشكري[2]، بشار فتحي إسماعيل[2]، و عبد الحكيم حسين امعيوف[2]

[1)] قسم الهندسة الكيميائية، كلية الهندسة، جامعة بنغازي، بنغازي، ليبيا.

[2)] قسم الهندسة الكيميائية، أكاديمية بتروليبيا، ليبيا.

Received: 05 September 2020; Revised: 28 December 2020; Accepted: 30 December 2020.

Abstract

The purpose of this experimental study is to estimate a suitable isotherm for the adsorption of iron ions from an aqueous solution onto three different types of active carbon. Three types of active carbons were selected, they include granular activated carbon prepared from date stone (GACD), granular active carbon prepared from charcoal (GACCH), and granular active carbon bought from the market (GACM) used for home desalination unit. The experiments were performed in a batch system at a constant temperature 20 ºC and pH 7. Iron solutions of different concentrations were prepared from ferrous chloride. At equilibrium, linear forms of Langmuir isotherm, Freundlich isotherm, Timken isotherm, Dubinin-Radushkevich isotherm, and Elovich isotherm were tested with adsorption data to find the best-fit model. Freundlich and Langmuir were found to be good model for GACM, Freundlich isotherm was good model for GACCH and Langmuir isotherm best fits experimental data for GACD.

Keywords: *Activated carbon, Adsorption, Charcoal, Date stone, Iron ions, Market.*

الملخص

الغرض من هذه الدراسة التجريبية هو تقدير متساوي الحرارة المناسب [ايزوثرم] لامتزاز أيون الحديد من محلول مائي على ثلاثة أنواع مختلفة من الكربون النشط. تم اختيار ثلاثة أنواع من الكربون النشط، وهي الكربون النشط الحبيبي المحضر من نواة التمر (GACD)، والكربون النشط الحبيبي المحضر من الفحم (GACCH) والكربون النشط الحبيبي الذي تم شراؤه من السوق (GACM) والمستخدم لوحدة تحلية المياه المنزلية. تم إجراء التجارب في نظام دفعي عند درجة حرارة ثابتة 20 ºم وpH7. تم تحضير محلول الحديد بتركيزات مختلفة من كلوريد الحديدوز. في حالة التوازن، تم اختبار الأشكال الخطية من متساوي الحرارة لانجموير، متساوي فروندليش، متساوي الحرارة تيمكين، متساوي الحرارة دوبينين-رادوشكيفيتش وإيلوفيتش باستخدام بيانات الامتصاص للعثور على أفضل نموذج مناسب. تم العثور على منحنيات متساوي الحرارة لانجموير، متساوي فروندليش كنموذج جيد لـ GACM، وكان منحنى متساوي فروندليش نموذجًا جيدًا لـ GACCH ومنحنى متساوي الحرارة لانجموير يناسب البيانات التجريبية لـ GACD..

الكلمات الدالة: الكربون النشط، الامتزاز، الفحم، نواة التمر، أيونات الحديد، السوق.

ISSN (Print): 2413-5267
ISSN (Online): 2706-9966

1. Introduction

The problems of the ecosystem are increasing with developing technology. The industrial activity is the major source to the environmental pollution. Heavy metal pollution especially in industrial wastewaters is one of the main problems (Parmer and Thakur. 2013). Toxic metal compounds coming from industry can contaminate both the earth's waters (seas, lakes, ponds and reservoirs), and also underground water. Therefore, the earth's waters may contain various toxic metals. And because the Drinking water is obtained from earth's waters (seas, lakes, ponds and reservoirs), the treatment of the different pollutants including heavy metal containing wastewater is necessary prior to its discharge.

Many different treatment techniques such as adsorption, ion exchange, biodegradation, solvent extraction, and oxidation, have been used for removal of the different pollutants including heavy metal ions from industrial wastewaters. However, adsorption is considered as one of the most effective pollutant removal process, especially with pollutants removal at low concentrations from wastewater. Many researchers showed the ability of the carbon to remove pollutant like phenol, halogenated compounds, pesticides, caprolactam, chlorine (John Thomas and Crittenden, 1998), Copper ion (Alshuiref *et al.*, 2017), and H_2S (Lau *et al.*, 2016). The adsorption process has many Advantages like low cost, ease in handling, low consumption of reagents.

The aim of this paper is to prepare active carbon and use it as adsorbent to remove iron by adsorption technique and to estimate best isotherm (which is important in the design stage) for iron adsorption on each carbon type.

Three active carbon types were used in this study and each is tested with Langmuir isotherm, Freundlich isotherm, Timken isotherm, Dubinin-Radushkevich isotherm and Elovich isotherm (all are two parameter models) to estimate the best model for each carbon type (Hamdaouia and Naffrechoux, 2007; and Rania & Yousef, 2015).

These carbon types include Granular active carbon prepared from date stone, granular active carbon prepared from charcoal, and commercial active carbon brought from market.

2. Materials and Methods

2.1. Chemicals

Iron solution of six different concentrations prepared from ferrous chloride AR grade as in Table (1) and confirmed using laboratory equipment DR 900 COLORIMETER.

Phosphoric acid and hydrochloric acid used for activation are AR grade from BDH chemicals.

Table 1. Preparation of iron solution from ferrous chloride

Item	Value					
Concentration of iron solution in (mg/L).	4.5	15.6	33	58	73	98
Weight of Ferrous Chloride (mg) dissolved in one L of distilled water	16.1	55.815	118.071	207.519	261.188	350.636

ISSN (Print): 2413-5267
ISSN (Online): 2706-9966

2.2. Preparation of Activated Carbon

2.2.1. GACD (Granular active carbon from date stone) preparation

2.2.1.1. Cleaning and drying

Stones were collected and washed many times with water then left for enough time to dry.

2.2.1.2. Carbonation

The cleaned dry stones were put into oven at 100 ^oC for one hour in absence of oxygen. The carbonized stones were left to cool then crushed with mortar and pestle into granular form (Yahia, 2006).

2.2.1.3. Activation and sieving

Sieves are used to get granules of size 2000 μm. After that, the hydrochloric acid with concentration of 5 N as chemical activator. HCl 5N is added to granules and left 24 hours to ensure complete activation. After that, it was washed thoroughly well with distilled water to remove acidity with using PH paper as acidity indicator and filter paper for filtration.

2.2.1.4. Drying and pyrolysis

The activated carbon was left in drying oven for 24 hrs, then put in a furnace at 450 – 500 ^oC for two hours

2.2.2. GACH (Granular active carbon from charcoal) preparation

2.2.2.1. Crushing, grinding and sieving

Local ordinary charcoal of olive type from market was used. This charcoal was crushed and grinded using mortar and pestle. After that we used sieving equipment and selected size of 850 - 2000 μm as granular type.

2.2.2.2. Activation

Phosphoric acid was used to do activation. Granular carbons were immersed in a solution of 60% phosphoric acid and left for 24 hrs. This work has been done in glass beakers 250 mL.

2.2.2.3. Drying

The chemically activated carbon were washed well with distilled water to remove acid, finally we get pH 7 using PH paper and that mean all residual acid has been removed. After that, carbon has been dried using drying oven. The drying process was done at temperature of 100 ^oC for 24 hrs.

2.2.2.4. Pyrolysis

After drying 50 mg of carbon were placed in steel containers and placed in a furnace for purpose of pyrolysis. Temperature of furnace selected was 450 -500 C^0 for two hours.

2.3. Batch Adsorption Experiments

Experiments were performed by batch adsorption technique at constant temperature 20 ^oC and pH 7. Equal weights (6 No.) of 1.5 g have been taken from each of the three carbons, and have been placed in 18 flasks of 50 mL. 30 mL from solutions of different concentration (C_o) have been added to each flask including 4.5, 15.6, 33, 58, 73, 98 mg/L. These concentrations were prepared from ferrous chloride and then read by DR 900 COLORIMETER. Flasks left for enough time to reach equilibrium, and then concentration at equilibrium (C_e) have been taken using dilution then reading by DR900.

ISSN (Print): 2413-5267
ISSN (Online): 2706-9966

Amount of iron adsorbed in mg per gram of active carbon were calculated from mass balance equation (Eqn. (1));

$$q_e = \frac{V}{m}(C_0 - C_e) \quad \text{............... (1)}$$

Where; q_e : Amount of iron adsorbed per gram of adsorbent, (mg/g).
C_o : Initial concentration in (mg/L).
C_e : Concentration at equilibrium in (mg/L).
V : Volume, which is 30 mL (0.03 L).
m : Mass of adsorbent (1.5 g).

Five important known isotherms have been tested and compared with result data and checked which type of isotherm should these data follow by using Microsoft excel program, these isotherms are Langmuir isotherm, Freundlich isotherm (Richardson *et al.*, 2002), Timken isotherm (Tempkin and Pyzhev1940), Dubinin-Radushkevich isotherm (Dubinin 1960), and Elovich isotherm (Elovich and Larinov, 1962).

Linear form of each isotherm was used by plotting *x*-axis against *y*-axis of each isotherm, using Microsoft excel, the regression line and correlation for each data set was collected. Table (2) contain linear form and constants that can be calculated from slops and intercepts

Table 2. Linear forms of Langmuir, Freundlich, Timken, Dubinin-Radushkevich, and Elovich isotherms.

Isotherm Name	Linear form of isotherm	*x*-axis	*y*-axis	Constants and parameters calculated from slop and intercept
Langmuir	$\frac{1}{q_e} = \frac{1}{q_m\, K_L\, C_e} + \frac{1}{q_m}$	$\frac{1}{C_e}$	$\frac{1}{q_e}$	q_m maximum amount adsorbed, calculated from intercept ($^1/_{q_m}$). K_L langmuir equilibrium constant Measured from slop $\frac{1}{q_m\, K_L}$.
Freundlich	$lnq_e = lnK_F + \frac{1}{n}\, lnC_e$	lnC_e	lnq_e	K_F freundlich constant , measured from Intercept (lnK_F). n constant , measured from slop ($^1/_n$) .
Temkin	$q_e = BlnA_T + BlnC_e$ $B = \frac{RT}{b_T}$	lnC_e	q_e	b_T temkin isotherm constant, measured from slop RT/b_T. A_T constant measured from intercept $BlnA_T$
Dubinin–Radushkevich	$lnq_e = lnq_m - \beta\varepsilon^2$ $\varepsilon = RTln(1 + \frac{1}{C_e})$	ε^2	lnq_e	β D-R constant , measured from slop β. q_m maximum amount adsorbed, calculated from intercept lnq_m
Elovich	$ln\frac{q_e}{C_e} = lnK_E\, q_m - \frac{q_e}{q_m}$	q_e	$ln\frac{q_e}{C_e}$	q_m maximum amount adsorbed, calculated from slop($^1/_{q_m}$). K_E Elovich equilibrium constant, calculated from intercept $lnK_E\, q_m$.

ISSN (Print): 2413-5267
ISSN (Online): 2706-9966

3. Results and Discussion

Initial concentration C_o, concentration of iron at equilibrium C_e, and calculated values of q_e for the three types of active carbon are shown in Table (3).

Table 3. Initial concentration C_o, concentration of iron at equilibrium C_e, and calculated values of q_e for the three types of active carbons

No.	C_o (ppm)	GACM		GACCH		GACD	
		C_e (ppm)	q_e (mg/g)	C_e (ppm)	q_e (mg/g)	C_e (ppm)	q_e (mg/g)
1	4.5	0.3	0.084	4.5	0	0.15	0.087
2	15.6	3.29	0.2462	15.54	0.003	4.55	0.221
3	33	9.6	0.468	30	0.06	13.9	0.382
4	58	26.6	0.628	47	0.22	35.8	0.444
5	73	40.8	0.644	50.4	0.452	60	0.26
6	98	49	0.98	57	0.82	68	0.6

3.1. Estimation of isotherms for iron adsorption on GACM

The linear forms of Langmuir, Freundlich, Timken, Dubinin-Radushkevich, Elovich isotherms and constants for each one respectively are presented in Table (2). Adsorption isotherms calculations for iron on GACM are illustrated in Table (4).

Table 4. Adsorption isotherms calculations for GACM

C_e	q_e	$1/C_e$	$1/q_e$	$\ln (C_e)$	$\ln (q_e)$	ξ^2	$\ln(q_e/C_e)$
0.3	0.084	3.333	11.9	-1.20397	-2.47693	12,759,184	-1.2729
3.29	0.2462	0.30395	4.06	1.1909	-1.4016	386,995.9	-2.5925
9.6	0.468	0.1042	2.137	2.2617	-0.7592	58,267	-3.0210
26.6	0.628	0.03759	1.5923	3.2809	-0.4652	8,081.9	-3.7461
40.8	0.644	0.0245	1.552	3.7086	-0.441	3,479	-4.1487
49	0.98	0.020408	1.02	3.8918	-0.02020	409.163	-3.912

3.1.1. Langmuir isotherm plot

From Figure (1), the correlation coefficient (R^2) is 0.9688, which is an indication of good correlation.

ISSN (Print): 2413-5267
ISSN (Online): 2706-9966

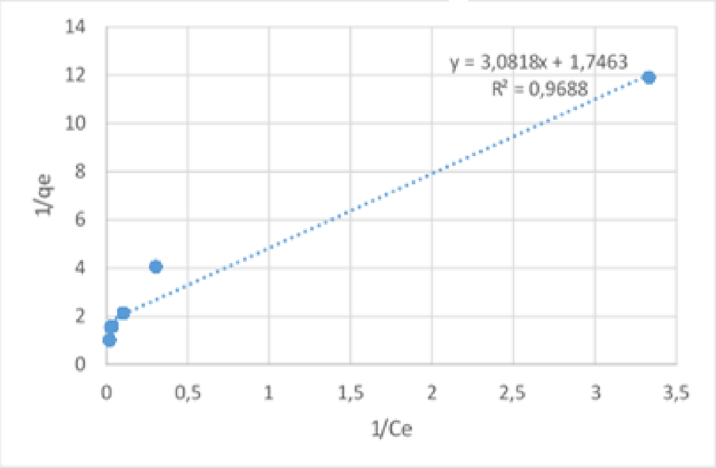

Figure 1. Langmuir isotherm plot for iron adsorption on GACM

3.1.2. Freundlich isotherm plot

From Figure (2), the correlation coefficient (R^2) is 0.9798, which is an indication of better fit than Langmuir.

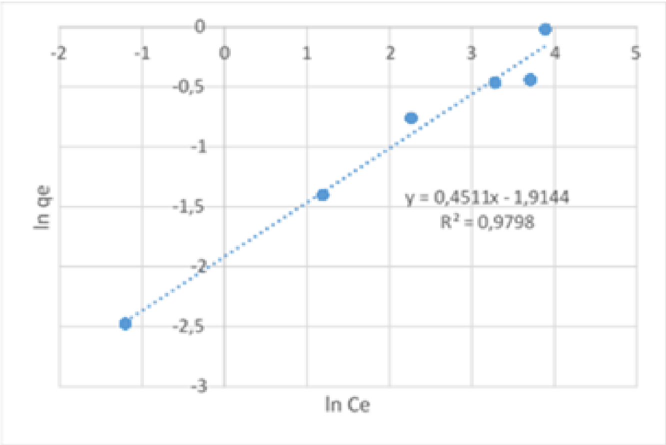

Figure 2. Freundlich isotherm plot for iron adsorption on GACM

3.1.3. Temkin isotherm plot

From Figure (3), the correlation coefficient (R^2) is 0.8425, which is an indication of less suitable fit than Langmuir.

ISSN (Print): 2413-5267
ISSN (Online): 2706-9966

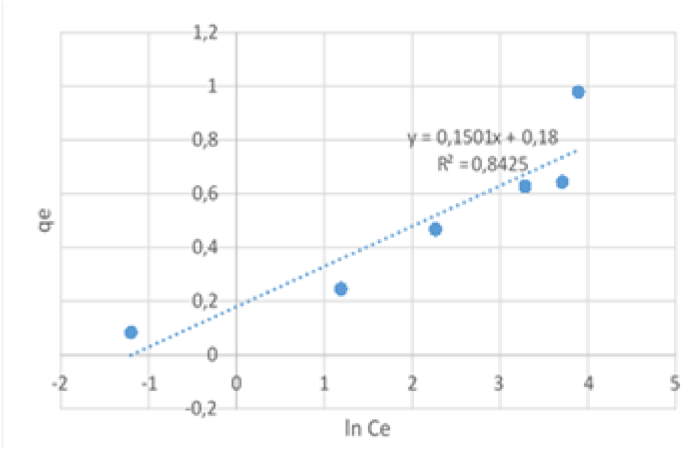

Figure 3. Temkin isotherm plot for iron adsorption on GACM

3.1.4. Dubinin-Radushkevich isotherm plot

From Figure (4), the correlation coefficient (R^2) is 0.7564, which is indication of bad fit.

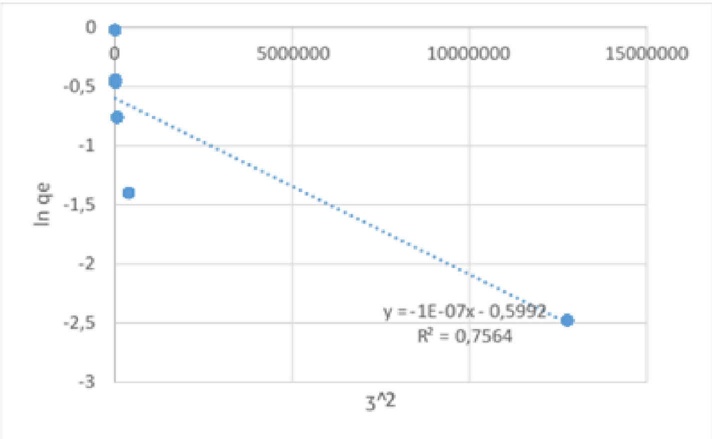

Figure 4. Dubinin-Radushkevich isotherm plot for iron adsorption on GACM

3.1.5. Elovich isotherm plot

From Figure (5), the correlation coefficient (R^2) is 0.7849, which is an induction of a bad fit.

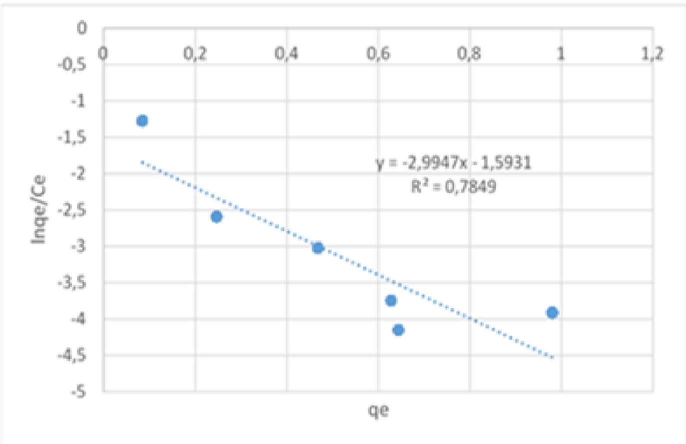

Figure 5. Elovich isotherm plot for iron adsorption on GACM

ISSN (Print): 2413-5267
ISSN (Online): 2706-9966

Therefore, by comparison, the order of the isotherm best fits experimental data for GACM is Freundlich > Langmuir > Temkin > Elovich > Dubinin-Radushkevich.
When apply Freundlich linear equation:

$$lnq_e = lnK_F + \frac{1}{n} lnC_e \qquad y=0.4511x - 1.9144$$

Slope was 0.4511, and n=2.2168, while Intercept was –1.9144, and K_F= 0.14743.

3.2. Estimation of isotherms for iron adsorption on GACCH

The linear forms of Langmuir, Freundlich, Timken, Dubinin-Radushkevich, Elovich isotherms and constants for each one respectively are presented in Table (2). Adsorption isotherms calculations for iron on GACCH are illustrated in Table (5).

Table 5. Adsorption isotherms calculations for GACCH

C_e	q_e	$1/C_e$	$1/q_e$	$\ln (C_e)$	$\ln (q_e)$	ξ^2	$\ln(q_e/C_e)$
15.54	0.003	0.06435	333.33	2.7434	-5.809	23,079.5	-8.5525
30	0.06	0.03333	16.6666	3.40119	-2.8134	6,380.18	-6.2146
47	0.22	0.021276	4.545	3.8501	-1.5141	2,630.26	-5.364
50.4	0.452	0.01984	2.21238	3.91999	-0.7941	2,290.59	-4.714
57	0.82	0.01754	1.2195	4.04305	-0.12783	1,041	-4.2415

3.2.1. Langmuir isotherm plot

From Figure (6), the correlation coefficient (R^2) is 0.9251. An indication of a good correlation.

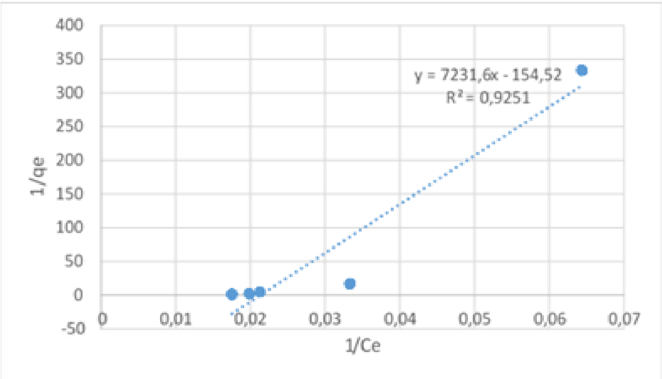

Figure 6. Langmuir isotherm plot for iron adsorption on GACCH

3.2.2. Freundlich isotherm plot

From Figure (7), the correlation coefficient (R^2) is 0.9887. It is better fit than Langmuir is.

ISSN (Print): 2413-5267
ISSN (Online): 2706-9966

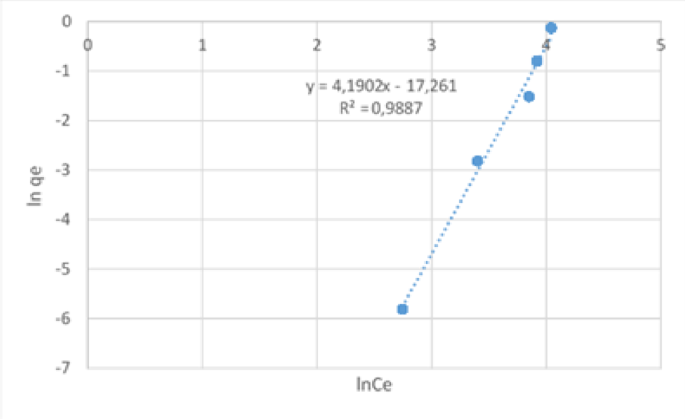

Figure 7. Freundlich isotherm plot for iron adsorption on GACCH

3.2.3. Temkin isotherm plot

From Figure (8), the correlation coefficient (R^2) is 0.6248, an indication of a bad fit.

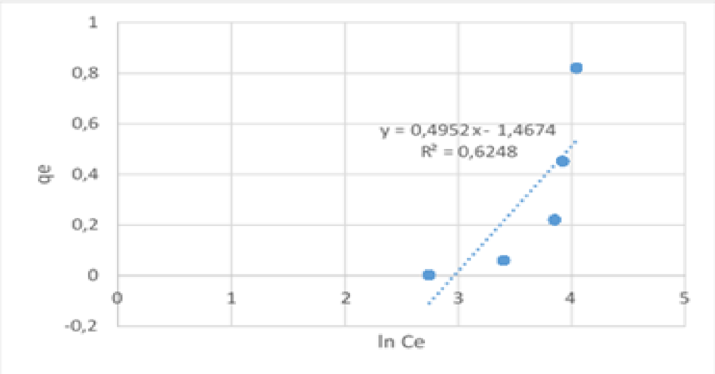

Figure 8. Temkin isotherm plot for iron adsorption on GACCH

3.2.4. Dubinin-Radushkevich isotherm plot

From Figure (9), the correlation coefficient (R^2) is 0.9374. It is good fit but less than Freundlich.

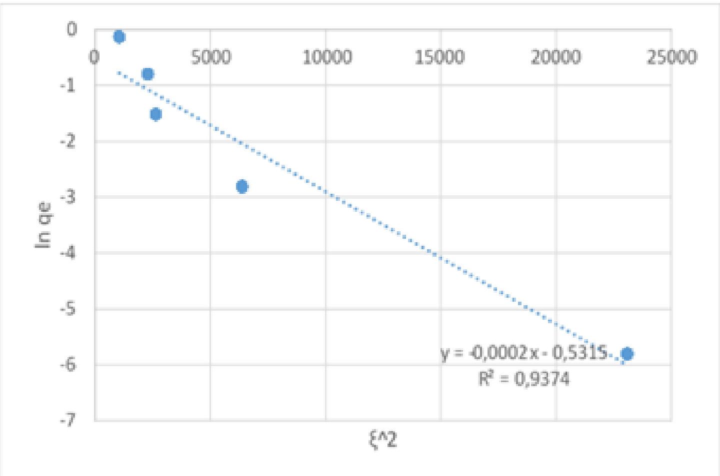

Figure 9. Dubinin-Radushkevich isotherm plot for iron adsorption on GACCH

ISSN (Print): 2413-5267
ISSN (Online): 2706-9966

3.2.5. Elovich isotherm plot

From Figure (10), the correlation coefficient (R^2) is 0.6722, an indication of a bad fit.

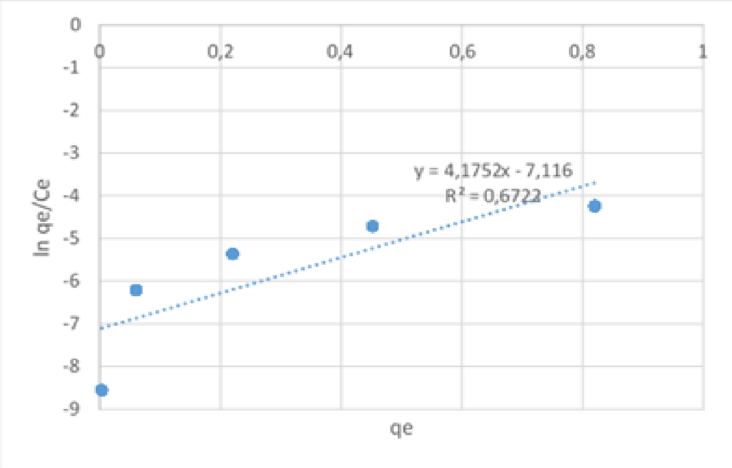

Figure 10. Elovich isotherm plot for iron adsorption on GACCH

By comparison, conclude that Freundlich isotherm best fits experimental data;

$ln q_e = ln K_F + \frac{1}{n} ln C_e$ $y=4.1902\, x - 17.261$

Slope was 4.1902, and n= 0.23865; while Intercept was –17.261, and K_F=3.1889×10^{-8}

3.3. Estimation of isotherms for iron adsorption on GACD

The linear forms of Langmuir, Freundlich, Timken, Dubinin-Radushkevich, Elovich isotherms and constants for each one respectively are presented in Table (2). Adsorption isotherms calculations for iron on GACD are illustrated in Table (6).

Table 6. Adsorption isotherms calculations for GACD

C_e	q_e	$1/C_e$	$1/q_e$	$\ln (C_e)$	$\ln (q_e)$	ξ^2	$\ln(q_e/C_e)$
0.15	0.087	6.6666	11.49425	-1.897	-2.4418	24,619,940.02	-0.5447
4.55	0.221	0.21978	4.52488	1.5151	-1.50959	234,219.4	-3.02472
13.9	0.382	0.07194	2.6178	2.6318	-0.9623	32,590.05	-3.5942
35.8	0.444	0.02793	2.2522	3.5779	-0.8119	4,503.98	-4.3898
60	0.26	0.016666	3.8461	4.0943	-1.347	1,621.3	-5.4414
68	0.6	0.014705	1.6666	4.2195	-0.5108	1,264.7	-4.73033

3.3.1. Langmuir isotherm plot

From Figure (11), the correlation coefficient (R^2) is 0.9267, an indication of a good correlation.

ISSN (Print): 2413-5267
ISSN (Online): 2706-9966

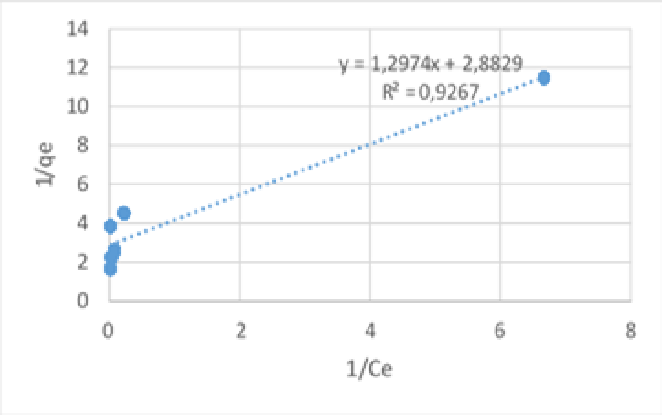

Figure 11. Langmuir isotherm plot for iron adsorption on GACD

3.3.2. Freundlich isotherm plot

From Figure (12), the correlation coefficient (R^2) is 0.8124.

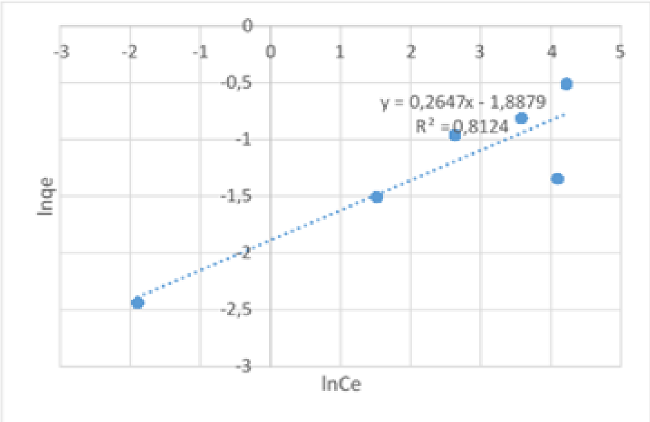

Figure 12. Freundlich isotherm plot for iron adsorption on GACD

3.3.3. Temkin isotherm plot

From Figure (13), the correlation coefficient (R^2) is 0.6242, it is a bad fit.

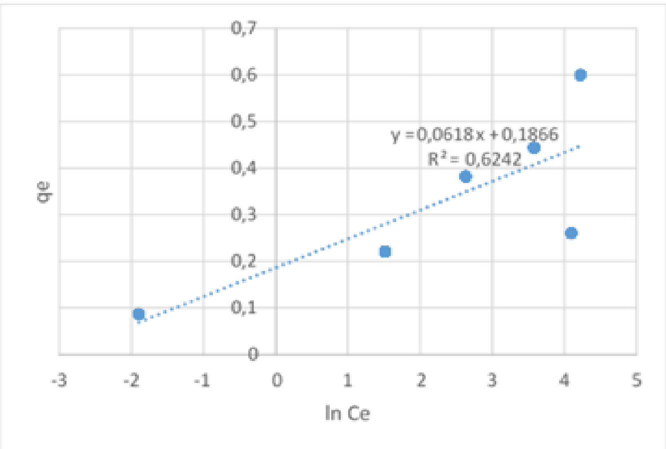

Figure 13. Temkin isotherm plot for iron adsorption on GACD

ISSN (Print): 2413-5267
ISSN (Online): 2706-9966

3.3.4. Dubinin-Radushkevich isotherm plot

From Figure (14), the correlation coefficient (R^2) is 0.7239.

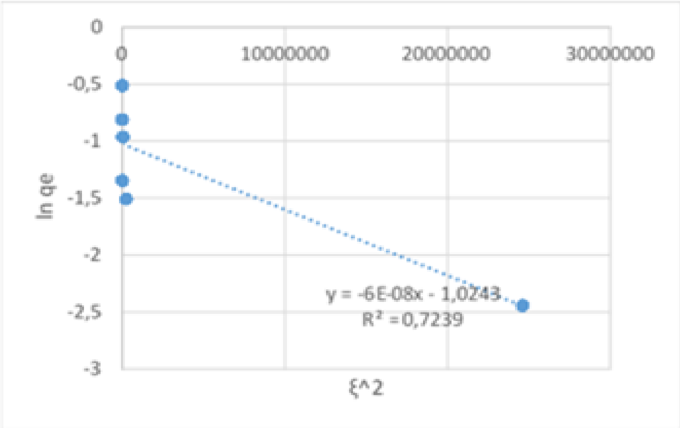

Figure 14. Dubinin-Radushkevich isotherm plot for iron adsorption on GACD

3.3.5. Elovich isotherm plot

From Figure (15), the correlation coefficient (R^2) is 0.4664, an indication of a bad fit.

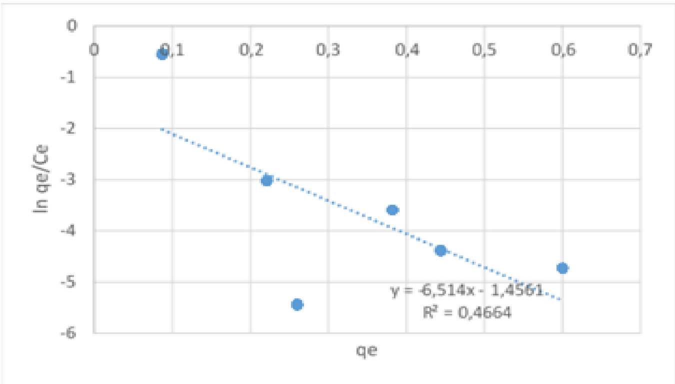

Figure 15. Elovich isotherm plot for iron adsorption on GACD

By comparison, conclude that Langmuir isotherm best fits experimental data;

$$\frac{1}{q_e} = \frac{1}{q_m\, K_L\, C_e} + \frac{1}{q_m} \qquad y=1.2974\, x + 2.8829$$

Intercept was 2.8829, and q_m= 0.346873, while Slope was 1.2974, and K_L=2.222.

4. Conclusion

In this study, activated carbon adsorbents were prepared from charcoal and date stones in addition to a commercial active carbon bought from market and applied for the adsorption of iron metal from wastewater. Investigation of adsorption isotherms were carried out at 20 ^{o}C and pH 7. The collected adsorption data sets were fitted into different two parameter models namely Langmuir, Freundlich, Temkin, Dubunin – Radushkevich and Elovich isotherms.

Freundlich model was good model for adsorption of iron on GACM, and GACCH. On the other hand, Langmuir isotherm best fits experimental data of GACD.

ISSN (Print): 2413-5267
ISSN (Online): 2706-9966

Acknowledgment

The researchers would like to thank the Research and Development Department in Aljouf Company for their complete and unlimited support provided for this research.

References

Alshuiref A.A., Ibrahim H.G., Ben Mahmoud M.M., and Maraie A.A. (2017). Treatment of Wastewater Contaminated with Cu(II) by Adsorption onto Acacia Activated Carbon. *Journal of Marine Sciences & Environmental Technologies*, 3(2):25-36.

Dubinin M.M. (1960). The potential theory of adsorption of gases and vapors for adsorbents with energetically non-uniform surface. *Chem. Rev.*, 60: 235–266.

Elovich S.Y., and Larinov O.G. (1962). Theory of adsorption from solutions of non-electrolytes on solid (I) equation adsorption from solutions and the analysis of its simplest form, (II) verification of the equation of adsorption isotherm from solutions. *Izv. Akad. Nauk. SSSR, Otd. Khim. Nauk.*, 2: 209–216.

Farouq R., and Yousef N. S. (2015). Equilibrium and Kinetics Studies of adsorption of Copper (II) Ions on Natural Biosorbent. *International Journal of Chemical Engineering and Applications*, 6(5): 319-324.

Hamdaouia O., and Naffrechoux E. (2007). Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon Part I. Two-parameter models and equations allowing determination of thermodynamic parameters. *J. Hazard. Mater.*, 147(1): 381-394.

John Thomas W., and Crittenden B. (1998). *Adsorption Technology and Design*, 1st ed. Oxford: Butterworth-Heinemann, UK

Lau L.C., MohamadNor N., Lee K.T., and Mohamed A.R. (2016). Adsorption isotherm, kinetic, thermodynamic and breakthrough curve models of H_2S removal using CeO_2/NaOH/PSAC. *International journal of petrochemical science and engineering*, 1(2): 1-10.

Parmar M., andThakur L.S. (2013). Heavy metal Cu, Ni and Zn: Toxicity, health hazards and their removal techniques by low cost adsorbents: A short overview. *Int. J. Plant. Anim. Environ. Sci.*, 3(3): 143-157.

Richardson J.F., Harker J.H., and Backhurst J.R. (2002). Coulson and Richardson’s Chemical Engineering, 5th ed. Vol. (2), Oxford: Butterworth-Heinemann, UK.

Tempkin M.I., and Pyzhev V. (1940). Kinetics of ammonia synthesis on promoted iron catalyst. *Acta Phys. Chim.*, 12: 327–356.

Yahia A. Alhamed. (2006), Activated Carbon from Dates' Stone by $ZnCl_2$ Activation, *JKAU: Eng. Sci.*, 17(2): 75–100.