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Proposing a new empirical adsorption isotherm known as Adejo-Ekwenchi isotherm

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Abstract: *The derivation of an adsorption isotherm is, largely, by empirical deductions on which basis isotherms like the Langmuir, Freundlich, Temkin, Frumkin, Flory-Huggins, El-Awady, Dubinin-Radushkevich, etc. were developed. We hereby propose yet another two-parameter empirical adsorption isotherm known as Adejo-Ekwenchi isotherm, derived from the data obtained from our corrosion inhibition of mild steel in 2 M* H_2SO_4 *using three plant extracts using weight loss method studied at the temperature between 303 and 315 K. The isotherm is centred on the fact that, for any adsorption process, the amount of adsorbate uptake from bulk concentration is, always, inversely proportional to the difference between the total available surface on the adsorbent and the fraction that is covered by the adsorbate at a given temperature, prior to the attainment of maximum value of surface coverage. Therefore, at any time during the adsorption process, (1 - θ) is the available surface and this decreases with increase in concentration, and thus;*

$$\frac{1}{(1-\theta)} \qquad \alpha \qquad C^b \tag{1}$$

"Equation 1" in a linear form is,

$$\log 1/(1-\theta) = \log K_{AE} + b \log C \tag{2}$$

"Equation 2" is known as Adejo-Ekwenchi isotherm. Results obtained therefrom the isotherm correlate very well with those obtained through other well-known isotherms.

Keywords: *Adsorption, Adsorption isotherm, Adejo-Ekwenchi isotherm, Physical and chemical adsorption mechanism, Surface coverage*

I. Introduction

The International Adsorption Society (2004) defines adsorption as the preferential partitioning of a substance from the gaseous or liquid phase onto the surface of a solid substrate. According to the Encyclopaedia Britannica (2013), adsorption is a capability of all solid substances to attract to their surfaces molecules of gaseous or solutions with which they are in contact. And the relationship between the amount of the adsorbed substance to the surface to its concentration in gas or solution phase at a particular temperature is known as adsorption isotherm.

Adsorption isotherm describes the phenomenon governing the retention or mobility of a substance from aqueous porous media or aquatic environment to a solid phase at constant temperature and pH [1]. Adsorption isotherms are critical for optimisation of the adsorption mechanism pathway, expression of the surface properties and capacities of adsorbents and effective design of the adsorption systems [2]. The earliest known adsorption isotherm equation obtained by empirical deductions, and which can be applied to non-ideal adsorption on heterogeneous surfaces as well as multilayer, was given by Freundlich in 1906 and Langmuir in 1916 developed a theoretical equilibrium isotherm [3]. The physicochemical parameters together with the underlying thermodynamic assumptions of an isotherm provide insight into the adsorption mechanism, surface properties and the degree of affinity of the adsorbents which are fundamentals in the characterization of adsorption process.

For any adsorption process, the rate of surface coverage, θ, depends on a number of factors; principally among which are the heat of adsorption of the surface and the rate at which the molecules strike the surface (that is, to the pressure of the gas, or concentration C in the case of molecules in liquid systems) [4].

II. Derivation of adsorption isotherm

Adsorption isotherms are of extreme importance in understanding of many processes. For example in corrosion inhibition process, the mechanism of inhibition can be better understood through the use of such isotherm [5, 6, 7]. The derivation of adsorption isotherm is largely by empirical deduction. For any adsorption process, the rate of surface coverage, θ, depends on a number of factors; principally among which are the heat of adsorption of the surface, the rate at which the molecules strike the surface (that is, to the pressure p of the gas, or concentration C in the case of molecules in liquid systems) [4]. The adsorbed molecules would bind first to the more attracting sites, that is, those with greatest binding power with high negative Gibb's free energy, ΔG_{ads}. As the surface gets fill up more active sites become used up and therefore at higher surface coverage, ΔG_{ads} would be less negative and the up take will decrease [8]. However, the free energy can be evaluated from the adsorption equilibrium constant, K_{ads}. Generally, K_{ads} has been obtained through a number of adsorption isotherms like the Langmuir, Freundlich, Temkin, Frumkin, Flory-Huggins, El-Awady, Dubinin-Radushkevich, etc. which were mostly developed empirically [9]. Kinetic, thermodynamic and potential approaches are always used in formulating an isotherm.

III. Methodology

Leaves and roots of *Portulaca oleracea*, *Cochlospermum tinctorium and Manihot esculentum* were collected, identified, shade-dried and ground into powder and the extracts obtained using 98% ethanol (BDH Chemicals Ltd, England) as reported elsewhere [5]. Stock solutions of concentrations of 0.1, 0.2, 0.3, 0.4 and 0.5 g/dm^3 of the extracts were prepared in 2 M H_2SO_4 (98%, Fiscons Chemicals Plc. England) using double distilled water. All reagents used were of analytical grade.

Coupons of dimension of 2 cm x 2 cm x 0.13 cm were prepared from the mild steel sample of composition (%W): Mn(0.56), P(0.04), C(0.27), Si(0.25), S(0.04). Each coupon was first weighed accurately using ae Adam AFP (d ±0.0001g) electronic weighing balance after degreasing in acetone (BDH Chemicals Ltd, England), with the surface prepared with different grade of emery papers. Each coupon was then suspended in 100 mL of the test solution, using a thread through a very thin hole borne at the edge, for a period of 8 hours in a thermostated water bath (Clifton: Nickel-Electro Ltd, England) without and with various concentrations of the extract at 303 K to 315K.. After the time interval the coupons were retrieved and the reaction terminated accordingly, and the coupons stored in a desiccator and reweighed afterwards [10, 11]. The inhibition efficiency, *IE%*, and surface coverage, θ, were calculated using "equations 1 and 2", respectively [10].

$$IE\% \quad = \quad (1 - \; W_{inh}/W_{uninh}) \times 100 \tag{3}$$

$$\theta \quad = \quad (1 \; - \; W_{inh}/W_{uninh}) \tag{4}$$

where W_{uninh} and W_{inh} are weight losses in absence and presence of inhibitor, respectively.

IV. Results

Tables 1 to 6 give the results of surface coverage as evaluated through "equation 4" from the studies of the corrosion inhibition of mild steel in the acid solution using the three plant extracts. Generally, it has been suggested that decrease in *IE%* (or surface coverage) with rise in temperature is indicative of physical adsorption mechanism, while increase in its value with rise in temperature signifies chemical adsorption mechanism [12, 13]. Following this assertion it means the inhibition process of the extracts of the leaves of *Portulaca oleracea*, leaves and root peels of *Manihot esculentum* and leaves of *Cochlospermum tinctorium* occurred through physical adsorption, while the roots of both Portulaca *oleracea* and *Cochlospermum oleracea* occurred through chemical adsorption mechanism.

Table 1. Surface coverage of the mild steel by extract of the leaves of Portulaca oleracea

Conc.	θ			
(g/dm^3)	303K	307K	311K	315K
0.1	0.2000	0.1758	0.1534	0.1334
0.2	0.3637	0.3067	0.2647	0.2105
0.3	0.4907	0.4336	0.3626	0.2719
0.4	0.6112	0.4811	0.4149	0.3417
0.5	0.6819	0.5866	0.5055	0.3771

Table 2. Surface coverage of the mild steel by extract of the roots extract of *Portulaca oleracea*

Conc.	θ			
(g/dm^3)	303K	307K	311K	315K
0.1	0.3200	0.3459	0.3512	0.3744
0.2	0.3440	0.3639	0.3847	0.3934
0.3	0.3613	0.3849	0.4282	0.4458
0.4	0.3728	0.3978	0.4338	0.4672
0.5	0.3946	0.4033	0.4851	0.4907

Table 3. Surface coverage of the mild steel of extract of the leaves of Manihot *esculentum*

Conc. (g/dm^3)	θ 303K	 307K	 311K	 315K
0.1	0.2155	0.1824	0.1736	0.1494
0.2	0.3944	0.2906	0.1986	0.1708
0.3	0.4429	0.3668	0.2885	0.2274
0.4	0.5727	0.5021	0.4416	0.3205
0.5	0.6983	0.5378	0.4870	0.3657

Table 4. Surface coverage of the mild steel by Extract of the Root Peels of *Manihot esculentum*

Conc. (g/dm^3)	θ 303 K	 307 K	 311 K	 315 K
0.1	0.1066	0.1048	0.0796	0.0757
0.2	0.1363	0.1204	0. 1162	0.1020
0.3	0.1778	0.1539	0.1352	0.1090
0.4	0.2000	0.1877	0.1423	0.1221
0.5	0.2324	0.2045	0.1527	0.1286

Table 5. Surface Coverage of Mild steel by Extract of the Leaves of *Cochlospermum tinctorium*

Conc. (g/dm^3)	θ 303K	 307K	 311K	 315K
0.1	0.7079	0.6571	0.5049	0.2100
0.2	0.7153	0.6762	0.5148	0.2400
0.3	0.7227	0.6952	0.5247	0.3000
0.4	0.7376	0.7047	0.5346	0.3400
0.5	0.7444	0.7142	0.5445	0.3800

Table 6. Surface coverage of the mild steel by extract of the root bark of *Cochlospermum tinctorium*

Conc. (g/dm^3)	θ 303 K	 307 K	 311 K	 315 K
0.1	0.0632	0.0793	0.1073	0.1495
0.2	0.1132	0.1273	0.1414	0.1682
0.3	0.1474	0.1628	0.2010	0.2281
0.4	0.1816	0.2008	0.2419	0.2628
0.5	0.2079	0.2317	0.2686	0.3022

However, some Authors tend to use value of ΔG_{ads} to distinguish between physical and chemical adsorption. It has been stated that the values below -20 kJ/mol are considered to be indicative of physical adsorption, while values above -40 kJ/mol are for chemical adsorption mechanism [1]. Therefore, going by values of ΔG_{ads} all the adsorption for the inhibition process occurred through physical adsorption as their values are all below -20 kJ/mol [4, 14]. Therefore, there is a bit of ambiguity in using solely both variation in *IE%* with temperature and values of ΔG_{ads} as strong criteria for distinguishing between physical and chemical adsorption. Our equation clearly resolves this ambiguity.

V. Proposing a new two-parameter adsorption isotherm known as *Adejo-Ekwenchi isotherm*

We hereby propose another two-parameter empirical adsorption isotherm to be known as ***Adejo-Ekwenchi isotherm***, taking into consideration the aforementioned approaches. The isotherm is centred on the fact that for an adsorption process, the amount of adsorbate uptake from bulk concentration is, usually, inversely proportional to the difference between the total available surface on the adsorbent surface and the fraction that is covered by the adsorbate at a given temperature, prior to the attainment of maximum value of surface coverage. That is the more the surface coverage the less the available surface. Thus;

$$\frac{1}{(1-\theta)} \quad \alpha \quad C^b$$

“Equation 1” can then be written as,

$$\frac{1}{(1-\theta)} = K_{AE} C^b \tag{5}$$

Linearisation of “equation 5” gives the proposed equation, that is, ***the Adejo-Ekwenchi isotherm.***

$$log\frac{1}{(1-\theta)} \quad = \quad logK_{AE} \; + \quad blogC$$

where C is the concentration of the adsorbate, K_{AE} and b are the isotherm parameters.

VI. Discussion

K_{AE} is the isotherm adsorption equilibrium constant known as Adejo-Ekwenchi constant. Just like any isotherm it is a temperature dependent parameter, which gives the adsorption strength. High value of it is indicative of favourable adsorption process. From Table 1 it can be seen that K_{AE} follows the expected trend in all cases.

The free energy of adsorption process can be evaluated using the "equation 6". K the adsorption equilibrium constant for an isotherm and can also be conventionally obtained through "equation 7" [15].

$$\Delta G_{ads} \quad = \quad -2.303RTlog(55.5Kads) \tag{6}$$

where

$$Kads \; = \frac{\theta}{(1-\theta)C} \tag{7}$$

Table 1 compares values ΔG_{ads} obtained through the proposed isotherm, Langmuir isotherm and conventional method where K_{ads} was obtained through "equation 7". As can be seen from the Table the new isotherm gives values which correlate very well with those obtained through the conventional method and other well-known adsorption isotherms [16, 17], giving credence to the formulation of yet another two-parameter adsorption isotherm. One important fact about the isotherm is that it seems to be followed by all adsorption processes, unlike many other isotherms. For instance, of six popular two-parameter isotherms of Langmuir, Freundlich, El-Awady, Flory-Huggins, Temkin and Frumkin tested using the data obtained for this work, the *Portulaca olerацea* leaves extract followed all the six, but its root extract only followed clearly four, while the *Manihot esculentum* leaves and roots followed two and five clearly, respectively and *Cochlospermum tinctorium* leaves and roots followed five and four clearly, respectively [18]. The accuracy of experimental result data was assessed based on the value of the coefficient of determination, R^2, [1], and most of the values obtained are close to unity. Therefore, we wish to term the isotherm a ***fundamental adsorption isotherm for adsorption process.***

Table 7. Evaluated Parameters of the New Isotherm at various Temperatures of each Extract

Extract	Temp (K)	R^2	Slope	Intercept	K_{ads}	b	$\Delta G_{ads(1)}$ (kJ/mol)	$\Delta G_{ads(2)}$ (kJ/mol)	$\Delta G_{ads(3)}$ (kJ/mol)
Portulaca oleracea (leaves)	303	0.9458	0.4991	0.5760	3.7670	0.4991	-13.46	-13.12	-12.20
	307	0.9784	0.3415	0.4174	2.6146	0.3415	-12.71	-12.48	-12.05
	311	0.9836	0.2682	0.3342	2.1587	0.2682	-12.38	-12.00	-11.82
	315	0.9545	0.1920	0.2456	1.7604	0.1902	-12.00	-11.25	-11.66
Portulaca oleracea (roots)	303	0.9958	0.0578	0.2246	1.6773	0.0578	-11.42	-12.02	-16.11
	307	0.9697	0.0598	0.2422	1.7466	0.0598	-11.68	-12.07	-17.21
	311	0.9580	0.1048	0.2908	1.9534	0.1048	-12.12	-12.99	-15.78
	315	0.9264	0.1187	0.3154	2.0673	0.1187	-12.42	-13.35	-1633
Manihot esculentum (leaves)	303	0.9384	0.4035	0.5009	3.1688	0.4035	-13.03	-13.10	Not Obeyed
	307	0.8906	0.2291	0.4001	2.5125	0.2291	-12.61	-12.27	
	311	0.7302	0.2530	0.3106	2.0446	0.2530	-12.24	-11.57	
	315	0.7729	0.1471	0.2042	1.6003	0.1471	-11.75	-10.98	
Manihot esculentum (roots)	303	0.9477	0.0805	0.1263	1.2375	0.0805	-10.85	-9.43	-10.81
	307	0.8519	0.0647	0.1094	1.2864	0.0647	-10.90	-9.26	-10.85
	311	0.9888	0.0525	0.0891	1.2277	0.0525	-10.92	-8.77	-11.45
	315	0.9827	0.0357	0.0703	1.1757	0.0357	-10.94	-8.46	-11.44
Cochlospermum tinctorium (leaves)	303	0.8578	0.0706	0.6008	3.9884	0.0706	-13.61	-15.96	-21.08
	307	0.9664	0.1029	0.5650	3.6728	0.1029	-13.57	-15.69	-20.38
	311	0.9571	0.0433	0.3470	2.2233	0.0433	-12.45	-14.17	-19.94
	315	0.8484	0.1303	0.1916	1.5545	0.1303	-11.68	-11.70	-13.11
Cochlospermum tinctorium (roots)	303	0.9844	0.0949	0.1214	1.3225	0.0949	-10.82	-8.80	-9.32
	307	0.9741	0.0988	0.1321	1.3555	0.0988	-11.03	-9.30	-10.01
	311	0.9229	0.1167	0.1598	1.4448	0.1167	-11.34	-10.01	-10.83
	315	0.8775	0.1031	0.1663	1.4666	0.1031	-11.52	-10.67	-11.95

$\Delta G_{ads(2)}$ are values obtained through the conventional equation

$\Delta G_{ads(3)}$ are values obtained through the Langmuir isotherm

b is a parameter we wish to call 'variation factor' and it relates the surface coverage by the adsorbate to the change of adsorbate bulk concentration. As stated above ΔG_{ads} is one of the criteria normally used to distinguish between physical and chemical adsorption. But as asserted by Popova and Co-workers [19] the use of this criteron only will be difficult to make such clear distinction, especially in the case when charged species are adsorbed due to possibility of coulombic interaction between charged species which can increase the value ΔG_{ads} even if no new chemical bonds are formed. Even many Authors observed that many adsorption processes which show clear chemical adsorption mechanism have their ΔG_{ads} values below -20 kJ/mol [13]. The value of the parameter b in this new isotherm clearly settles such ambiguity. A decrease in the value of b with rise in temperature is an indication of physical adsorption mechanism, while increase or fairly constant in its value with rise in temperature shows the mechanism of adsorption to be chemical adsorption. Also, low value of b signifies small variation of the adsorbate concentration (that is small change of performance) with increase in adsorbate concentration. That is, the ability of the adsorbate molecules to accumulate onto the surface of the adsorbent with change in concentration is small. High value of b is an indication that more of the adsorbate can accumulate on the adsorbent with change in its concentration. It does not, however, mean high value of b signifies good performance of the adsorbent. From Table 1 it can then be seen that extracts of leaves of *Portulaca oleracea* and leaves and roots of *Manihot esculentum* followed the physical adsorption mechanism, while those of roots of Portulaca oleracea and leaves and roots of *Cochlospermum tinctorium* followed the chemical adorption mechanism.

VII. Conclusion

We hereby submit yet another two-parameter adsorption isotherm. This isotherm, unlike the other known two- parameter isotherms, is followed by every adsorption process making it a fundamental adsorption isotherm and it unambiguously can show whether the adsorption process follows physical or chemical adsorption mechanism.

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