ANTICORROSION ACTIVITY OF *LAUNAEA TARAXACIFOLIA* LEAVES ON MILD STEEL IN ACID MEDIUM

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ABSTRACT
The effectiveness of *Launaea taraxacifolia* leaf extract (LTLE), ethanol leaf extract as a green anti-corrosive inhibiting agent for mild steel corrosion in 0.5 mol/dm^3 HCl was investigated using the gravimetric techniques at temperatures ranging from 303 to 333 K. The results demonstrated LTLE's ability to inhibit corrosion in acidic conditions, with higher inhibition efficiency (95.41%) observed at lower temperatures (303K) and higher extract concentrations (5% v/v). For instance, even at a 5% v/v concentration, inhibition rates reached approximately 95.41 % at 303 K and 85.76 % at 333 K. Thermodynamic parameters, including ΔG_{ads}, were determined using the Langmuir adsorption isotherm, confirming a monolayer adsorption of the inhibiting agent on the mild steel surface. The ethanol extract of *L. taraxacifolia* leaves proved to be an effective anti-corrosive inhibiting agent due to its composition rich in essential oils, steroids, triterpenes, and a variety of complex flavonoids, chalcones, and flavones.

Keywords: *Launaea taraxacifolia,* Inhibiting agent, acidic conditions, Corrosion, Mild steel

1.0 INTRODUCTION

Corrosion is the process where a material placed in a specific environment undergoes degradation, which may involve chemical or electrochemical factors and may or may not be coupled with mechanical stresses. In metals, this degradation is linked to their tendency to revert from the natural state of lower internal energy (El-Hajjaji, et al., 2019; Olasunkanmi & Ebenso, 2020). This reversion can lead to the formation of corrosion products, weakening the material's structural integrity and potentially compromising its functionality over time (Dahmani et al., 2021; Olasunkanmi & Ebenso, 2020). Notably, metals and their alloys are highly susceptible to this phenomenon. An example is mild steel, widely employed in various sectors and recognized as one of the most extensively manufactured materials globally (Mo, Luo & Li, 2017; Dahmani et al., 2021). Several methods are used to remove rusting and imperfections of the outermost layer of mild steel (MS), but the most common one is acid washing (Obot, Umoren & Obi-Egbedi, 2011; Lgaz et al., 2019; Mo et al., 2017). Putting mechanisms in place to slow down the rate at which metal dissolves is essential. Among the methods that have been suggested for this purpose are anodic and cathodic protection, corrosion preventatives, and anti-corrosion coatings (Leili & Mohammad, 2018; Mobin, Basik & Shoeb, 2019). In combating corrosion, anti-corrosion agents emerge as a particularly promising approach. These agents are designed to inhibit or slow down the corrosion process by interfering with the chemical or electrochemical reactions that lead to material degradation. They can be applied through various methods such as coatings, and inhibitors added directly to the environment or integrated into the material's composition during manufacturing.

For example, anti-corrosion coatings prevent damage from direct contact and slow down the pace of corrosion by forming a layer of protection between the material and an acidic environment. Conversely, inhibitors function by changing the material's or the corrosive medium's electrochemical characteristics, which lessens the possibility that corrosive reactions will occur.

The effectiveness of anti-corrosion agents is subject to the type of material, the nature of the environment, and the specific mechanisms driving corrosion in that environment. Anti-corrosion includes the development of advanced coatings, environmentally friendly inhibitors, and smart materials capable of self-healing or self-monitoring corrosion. By leveraging anti-corrosion agents, industries can prolong the lifespan of materials, reduce maintenance costs, improve safety, and enhance the overall performance of equipment and structures operating in corrosive environments. To choose an appropriate anti-corrosive inhibiting agent three key parameters must be considered: cost-effectiveness, sustainability, binding efficiency, and shielding proficiency (Palanisamy et al., 2018; El-Hajjaji et al., 2019). Inhibitors that effectively sequester heteroatoms such as P, S, and N, along with multiple bonds in their molecules, hold considerable significance in their binding to the mild steel surface of the anti-corrosive group, including charge concentration at donor atom, conformational flexibility, solubility, the electron arrangement and so on (Prabakaran et al., 2016; Peimani and Nasr-Esfahani, 2018).

Despite the commendable anticorrosive prowess exhibited by numerous synthetic compounds, a significant drawback surfaces many of them pose elevated toxicity perils to both human safety and ecosystem stability (Prabakaran et al., 2016; Mo et al., 2017; Verma, Olasunkanmi & Ebenso, 2018). This realization has led to constraints on the utilization of chemical inhibitors, primarily propelled by increasingly stringent environmental regulations (Obot & Obi-Egbedi, 2009; Lebrini, Robert & Roos, 2010). The potential to induce transient or irreversible impairment to organ systems, particularly impacting the liver or heart, and interference with biochemical processes or enzyme systems during both the synthesis and application of these compounds, underscores the toxicity concerns (Saleh, Mahmoud & Abd El-Lateef, 2019; Shrestha et al., 2019). Consequently, a heightened awareness of the hazardous effects linked to synthetic corrosion inhibitors has catalyzed a shift toward investigating natural products as promising alternatives for corrosion inhibition (Alibakhshi et al., 2018; Tamalmani & Husin 2020). Synthetic corrosion inhibitor refers to a chemically engineered compound utilized to shield metals against rusting. Its mechanism requires the formation of a protective barrier on the mild steel surface.

More environmentally friendly anti-corrosion agents have recently surfaced as substitutes for conventional hazardous corrosion-inhibiting agents (Prabakaran et al., 2016; Alibakhshi et al., 2018). Plant-based extracts are generally inexpensive, biocompatible, and biodegradable; they are extracted from leaves, fruits, and seeds (Alibakhshi et al., 2018; Tamalmani and Husin 2020). These extracts are likely to exhibit robust corrosion inhibition properties, especially when it comes to protecting metal surfaces in acidic environments because they contain donor electron components including heteroatoms and aromatic groups (Saleh et al., 2019; Singh et al., 2020)

Launaea taraxacifolia, also called "African lettuce" or "wild lettuce," serves diverse purposes. It is a common leafy vegetable in specific African areas, offering nutritional benefits. In traditional medicine, certain plant parts are utilised for potential healing properties, addressing concerns like digestive issues and skin conditions. In this study, our objective was to assess the inhibitory effectiveness of LTL extract in mitigating corrosion for MS immersed in a 0.5mol/dm^{3}HCl medium. Electrochemical techniques, including EIS and polarization, were utilised to examine the rust-inhibiting features of this compound (*L. taraxacifolia*).

2.0 MATERIALS AND METHODS

Collection and Preparation of Plant Extract

L. taraxacifolia, leaves were collected from the botanical garden of the Department of Science Laboratory Technology, Federal Polytechnic Ilaro, Ogun State. After cleaning with distilled water, the leaves were dried at room temperature and subsequently powdered. To make the extract, 500 ml of absolute ethanol was added to the 20g powdered *L. taraxacifolia,* leaves, and the mixture was permitted to stand unaltered for 48 hrs., the mixture was sieved through Whatman filter paper. The liquid obtained was concentrated using a rotary evaporator. (Prabakaran et al., 2016; Leili Rassoulia, Mohammad-Mahdavain, 2018; Benahmed, et al., 2020).

Preparation of Mild Coupon

The study utilised distinctive mild steel coupon specimens with the following composition: Carbon = 0.01 %, manganese = 0.34 %, phosphorus = 0.08 %, and iron = 99.51 %. The mild steel coupons, measuring 15 × 15 × 2 mm, underwent degreasing in absolute ethanol, rinsing in distilled water, and rapid drying in acetone before being stored in a desiccator for further use.

Sample Preparation

Mild steel plates acted as the operative electrode. A solution of 0.5 mol/dm^3 HCl was prepared by diluting hydrochloric acid with distilled water. Various grades of silicone carbide paper (400 - 1000) were employed to eliminate surface scales, followed by cleaning with analytical-grade acetone. Subsequently, different concentrations of *L. taraxacifolia,* leaves extract (0, 1, 2, 3, 4 and 5 %v/v) were readied for weight loss measurements, considering the solubility of LT LE.

Weight loss Experiment

Weight loss assessments were conducted in a temperature-controlled water bath at 303–333 K utilizing 500 ml glass beakers filled with 250 ml of 0.5 mol/dm^3 HCl solution. The analyses were done under complete immersion. With the use of a rod and hook, the mild steel coupons were weighed and suspended in the beaker. The coupons were gradually extracted every one-hour interval for five hours at 303 - 333 K. They were then extensively cleaned with a bristle brush in distilled water, dehydrated in acetone, and weighed again Prabakaran et al., 2016; Mo et al., 2017; Verma et al., 2018). The variations between the overall weight of the mild steel coupons before and afterwards submerged in various test solutions were calculated employing an electronic weighting device to measure the weight loss, expressed in grammes. The tests were carried out again at various temperatures. To achieve high reproducibility, duplicate experiments were conducted. The current study's parallel triple experiment standard deviation values were determined to be less than 6 %, showing a high degree of reliability. The corrosion rate (C_R) in g/cm²/h was determined using equation 1. (Verma et al., 2018; Benahmed et al., 2020):

$$CR = \frac{\Delta W}{At} \text{.................. Eqn. (1)}$$

A denotes the total area of a single mild steel specimen, t represents the duration of immersion, and W indicates the average weight loss of three mild steel sheets. After calculating the corrosion rate, the inhibition efficiency (%I) was then assessed using Equation 2. (Verma et al., 2018; El-Hajjaji et al., 2019):

$$\eta = \frac{Cr(ab) - Cr\,(pr)}{Cr\,(ab)} \times 100 \text{...........Eqn. (2)}$$

Where Cr (ab) represents the corrosion rate of the mild steel coupons in the absence of *L. taraxacifolia*, and Cr (pr) represents the corrosion rate in its presence.

3.0 RESULTS AND DISCUSSION

The most widely used technique for assessing inhibition is the gravimetric (weight loss) approach (Verma et al., 2018; Feng, Yang & Wang, 2011). The weight loss method's measurement is so straightforward and dependable that it is frequently used as the standard approach in corrosion monitoring programmes (Verma et al., 2018; Olasunkanmi & Ebenso, 2020). The weight loss method shows a similar agreement with other widely recognized corrosion monitoring techniques., including the polarisation technique (Qiang, Li & Lan, 2020), electrochemical impedance spectroscopy (Varshney, Chen & Li, 2012), gasometric (Singh et al., 2020), thermometric (Zang, Pang & Gao, 2019), and atomic absorption spectroscopy (Tan et al., 2018), has been documented by several researchers.

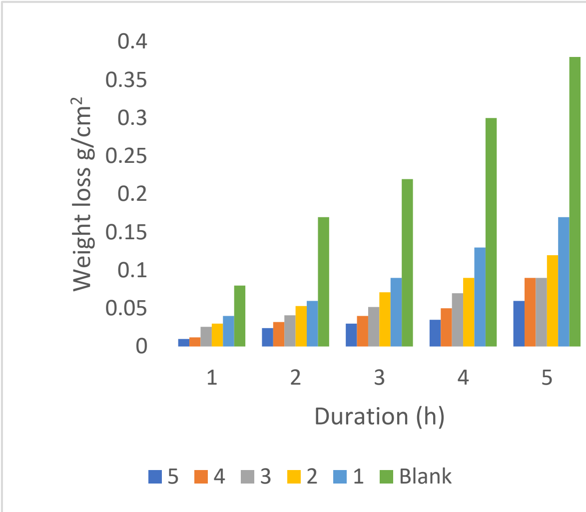

Figure 1. Impact of contact duration on weight loss of mild steel in 0.5 mol/dm^3 HCl at 303 K

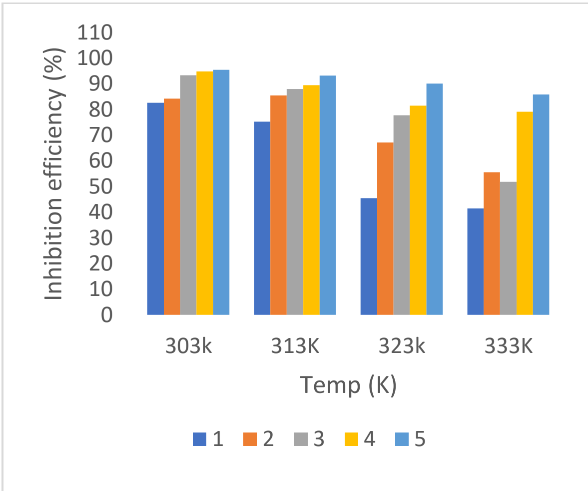

Figure 2. Changes in inhibition efficiency with varying concentrations at varying temperatures.

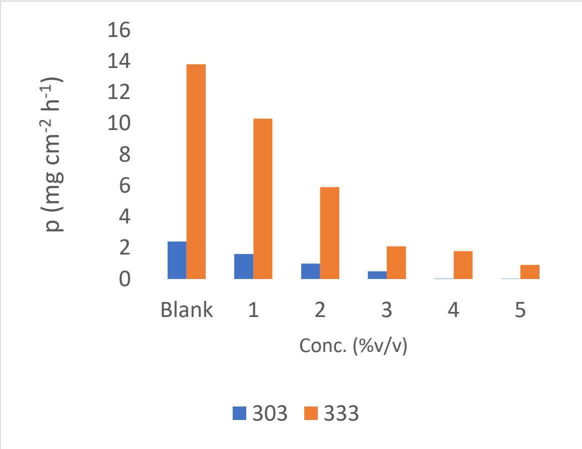

Figure 3. The change in corrosion rate with different concentrations of the inhibiting agent for mild steel in 0.5 mol/dm^3 HCl with *L. taraxacifolia* at temperatures of 303 K and 333 K.

The weight loss method is significant in corrosion studies because it provides direct and tangible evidence of material degradation due to corrosion. By measuring the weight loss of a material over time, researchers can quantify the extent of corrosion and evaluate the effectiveness of corrosion inhibitors or protective coatings (Verma et al., 2018; Shahini, Ramezanzadeh & Ramezanzadeh, 2020). Figure 1 shows the findings from weight loss evaluations regarding the corrosion tendencies of mild steel in a 0.5 mol/dm^3 HCl solution infused with *L. taraxacifolia* across the concentration span of 1% to 5% v/v. Additionally, Figure 2 illustrates the corrosion rate and inhibition effectiveness for mild steel in 0.5 mol/dm^3 HCl, plotted against extract concentration at temperatures of 303 and 333 K. Since there is an overall reduction in the mild steel corrosion rates upon completion of the corrosion monitoring process, these results demonstrate that the tested extract prevents the corrosion of mild steel in 0.5 mol/dm^3 HCl at all concentrations of LTLE utilized in this research. The corrosion-inhibitory impact rises as LTLE concentration rises, demonstrating that the concentration of LTLE in the corroding medium affects the inhibition mechanism (Mo et al., 2017; Verma et al., 2018; Shahini, Ramezanzadeh & Ramezanzadeh, 2020).

According to an analysis of the results, the corrosion rates increased as the temperature rose in the acid (0.5 mol/dm^3 HCl) conditions with and without LTLE. Additionally, a decrease in inhibitory capacity was observed as temperature increased, which suggested that the quantity of material loss was also shown to be dependent on the LTLE by preventing mild steel from corroding in HCl. Figure 3 illustrates the plot of inhibition effectiveness with LTLE concentration for mild steel in 0.5 mol/dm^3 HCl. It shows that inhibition effectiveness increases as extract concentration rises, attaining a maximum value of 95.41 and 85.76% at 303 and 333 K, respectively. The binding and adsorption of the LTLE components onto the steel surface are responsible for the inhibitive activity of LTLE towards the corrosion of mild steel. Initial corrosion inhibition is caused by the adsorbed water molecules being displaced by the type of inhibitor that causes particular adsorption on the metal surface (Varshney, Chen & Li, 2012; Tan et al., 2018). According to reports, *L. taraxacifolia* contains several significant chemical components, including steroids, tannins, alkaloids, and carbohydrates (Prabakaran et al., 2016; Mo et al., 2017; Tan et al., 2018); essential oils, triterpenes, and a variety of complex flavonoids, chalcones, and flavones (Adinortey et al., 2018).

These biochemical molecules are heterogeneous organic compounds that have molecular structures that include nitrogen, oxygen, sulphur, as well as aromatic rings. It has been observed that these elements present in organic heterogeneous compounds contribute to the inhibition of mild steel (Shahini, Ramezanzadeh & Ramezanzadeh, 2020). The suppression of the corrosion reaction is therefore thought to be primarily brought about by the adsorption of these chemicals on the mild steel surface. Nonetheless, the extract's remarkable inhibitory efficacy might be attributed to the interactions between its phytochemical constituents (Tan et al., 2018; Shrestha, et al., 2019; Olasunkanmi & Ebenso, 2020). It is also evident from Fig. 1 that as temperature rises, inhibition strength decreases. This phenomenon can be elucidated by the physical adsorption of phytochemical molecules onto the mild steel surface, which causes some of the adsorbed phytochemical molecules to desorb from the surface of steel when the temperature increases. However, the interactions among its phytochemical ingredients may account for the extract's exceptional inhibitory activity.

Immersion Time

Using the duration of immersion is vital in corrosion inhibition investigations because it affects how the inhibitor interacts with the mild steel surface over time (Thamaraiselvan, Michael & Oren, 2018; Tan et al., 2019; Olasunkanmi & Ebenso, 2020). In a gravimetric approach, we studied the corrosion response of mild steel in 0.5 mol/dm^3 HCl with and without LTLE across durations ranging from 1 to 5 hours. The goal was to ascertain the impact of immersion duration on the corrosion inhibition impact of LTLE. Figure 1 presents the acquired results. The plot shows that, in the presence and absence of low and high concentrations of LTLE (1 - 5 %v/v) in an acidic medium (0.5 mol/dm^3 HCl) solution, the corrosion rate intensified with prolonged immersion periods. The development of a protective coating on the mild steel surface, which is dependent on time, is responsible for the increase in inhibitory efficiency observed in HCl solution over prolonged immersion times (Verma et al., 2018; Tan et al., 2018; Olasunkanmi & Ebenso, 2020). Prolonged immersion times in inhibitor solutions often lead to the establishment of persistent, two-dimensional films of inhibitor molecules on metal surfaces. This phenomenon, observed and discussed by Tan et al. in 2019, is crucial in understanding the behaviour of corrosion inhibition over extended periods. According to Olasunkanmi and Ebenso, (2020), the decline in inhibitory efficacy during lengthy immersion times can be attributed to several factors. Firstly, the barrier formed by the inhibitor molecules may become unstable over time. This instability could result from the desorption of certain constituents of the inhibitor, weakening the defensive barrier on the mild steel surface. Additionally, the diffusion process passing through the interface protective layer may contribute to its degradation, allowing corrosive agents to reach the mild steel surface more easily.

Adsorption Process

The prevailing opinion in the existing research on corrosion inhibition is that adsorption onto the metal surface is the first stage of an inhibitor's activity in acidic conditions (El-Hajjaji et al., 2019; Olasunkanmi & Ebenso, 2020; Benahmed, et al., 2020). This is predicated on the idea that corrosion reactions are stopped from happening across the portion of the metal surface where inhibitor molecules had been adsorbed, while the inhibitor-free region saw typical corrosion responses (Zahra Sanaei et al., 2019; Singh et al., 2020; Benahmed, et al., 2020). The degree of surface covering (θ) is crucial in elucidating the mechanism of adsorption. Its value was calculated from the weight loss measurements for various LTLE concentrations at the temperatures (303, 313, 323 and 333 K) under investigation. $\eta\% = \theta \times 100$ (presuming a direct correlation between inhibition efficacy and surface coverage) and thereafter hypothetically fitted to various adsorption isotherms. The best-matched isotherm was identified using the correlation coefficient (R^2) value (Zhang et al., 2020; Vorobyova & Skiba, 2021). Using the Langmuir adsorption isotherm model, the best outcome was achieved. The graphical representation of C/θ against C is displayed in Figure 4. Linear graphs were produced, demonstrating that the Langmuir adsorption isotherm is followed by the adsorption of LTLE elements onto mild steel surfaces. The Langmuir adsorption isotherm is distinguished by equation 3:

$$\frac{C}{\theta} = \frac{1}{K} + C \text{……….…..} \quad \text{Eqn. (3)}$$

where C is the concentration, θ is the surface coverage, and K_{ads} is the adsorption process equilibrium constant that is connected to the conventional Gibbs free energy of adsorption by the following equation:

$$K_{ads} = \frac{1}{55.5} \exp\left(\frac{-\Delta G\ ads}{RT}\right) \text{…………………} \text{Eqn. (4)}$$

where T is the absolute temperature, R is the molar gas constant, and 55.5 is the water concentration in mol dm^3.

Table 1. A few variables from the Langmuir isotherm model for mild steel in 0.5 mol/dm^3 HCl in the presence of LTLE.

Temperature (K)	R^2 Value	Slope	K (L/ml)	ΔG^o_{ads} (KJ/mol)
303	0.989	0.968	2.98	-12.78
313	0.996	0.985	3.75	-13.89
323	0.999	0.973	2.74	-13.52
333	1.000	1.063	2.86	-13.91

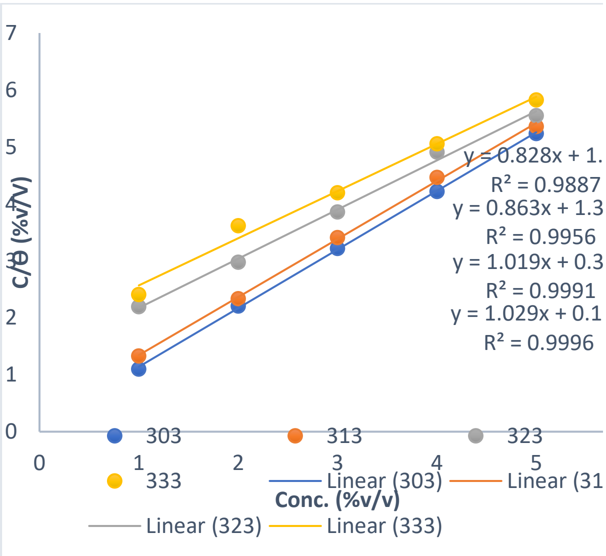

Figure 4. Langmuir adsorption isotherm plots for LTLE on mild steel in 0.5 mol/dm^3 HCl.

Table 1 in the Additional Information presents crucial adsorption parameters derived from the plotted data. A notable trend observed is that as the temperature increases, the K_{ads} values, representing the inhibitor's binding affinity to the metal surface, tend to decrease. This trend provides valuable insights into the impact of temperature on corrosion inhibition mechanisms.

The influence of elevated temperatures on corrosion inhibition can be understood through the phenomenon of desorption, where certain adsorbed components from the extracts detach from the mild steel surface. This aligns with the principles of the physisorption mechanism, where molecules attach and detach based on weak physical forces (Zahra Sanaei et al., 2019; Zhang, Hou & Zhang, 2017). The driving force behind this desorption process is the free energy of adsorption, typically ranging from –10.0 to –19.72 kJ/mol under such conditions. This range indicates that the extracts predominantly act by physically adhering to the metal surface to inhibit corrosion (Mo et al., 2017; Verma et al., 2018; Vorobyova & Skiba 2021).

Analyzing adsorption energies provides further clarity. Values up to –20 kJ/mol generally indicate physical adsorption or electrostatic interactions between charged molecules and the mild steel surface. Conversely, values exceeding –40 kJ/mol suggest chemisorption, a more intricate interaction involving charge transfer to form coordinate bonds with the mild steel surface, thereby enhancing corrosion inhibition (Olasunkanmi & Ebenso, 2020; Benahmed, et al., 2020; Singh et al., 2020).

The data in Table 1 also reveals a significant deviation from unity in the slope observed during mild steel corrosion in 0.5 mol/dm^3 HCl. This deviation implies potential deviations from strict adherence to the isotherm, highlighting the complexity of interactions and mechanisms involved in corrosion inhibition processes. These findings underscore the need for a comprehensive understanding of the interplay between temperature, adsorption energies, and corrosion inhibition mechanisms to develop effective strategies for corrosion control (Qiang et al., 2020; Singh et al., 2020).

4.0 CONCLUSION

It has been found that LTLE effectively prevents mild steel corrosion in a 0.5 mol/dm^3 HCl solution, with the inhibition impact dependent on concentration. The highest inhibitory efficiency in 0.5 mol/dm^3 HCl was achieved at a 5.0% v/v extract concentration. Additionally, immersion time impacts corrosion inhibition, with increased extract concentration leading to improved inhibitory efficacy. This improvement is attributed to LTLE components adsorbing onto mild steel surfaces, following the Langmuir adsorption isotherm and inhibiting corrosion. The trend of increasing inhibitory efficiency with rising temperature, supported by kinetic parameter values from experimental data, aligns with the theory of physical adsorption.

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