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Inhibitory Effect of *Solenostemon monostachyus* Leaf Extract on Mild Steel Corrosion in H_2SO_4 Solution

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ABSTRACT
Solenostemon monostachyus leaf extract was studied for its inhibitory effect on mild steel corrosion in H_2SO_4 solution using weight loss and hydrogen evolution methods. The inhibition efficiency increased with increase in extract concentration and temperature. The highest inhibition efficiency of 80.35% occurred at 4.0 g/L *Solenostemon monostachyus* leaf extract at 60°C by the weight loss measurements. Chemisorption of the extract on mild steel surface has been proposed. The obtained thermodynamic parameters reveal that the adsorption of *Solenostemon monostachyus* leaf extract on mild steel surface was both endothermic and spontaneous. The adsorption of *Solenostemon monostachyus* leaf extract on mild steel conformed to the Freundlich adsorption isotherm.
Keywords: *Solenostemon monostachyus,* mild steel, Freundlich isotherm, Chemisorption, Corrosion.

1. INTRODUCTION
The corrosion of metals in aggressive media such as high concentrations of acids or alkalis has been a problem to scientists and industrialists for years. The need for the control or reduction of metallic corrosion led to the discovery of organic compounds containing nitrogen, sulphur, oxygen and/or phosphorus atoms as corrosion inhibitors. Many efficient corrosion inhibitors that have been in use for years are inorganic and synthesised organic compounds. The need for their replacement in recent times have become imperative due to their bio-toxicity (Al-Otaibi et al., 2014; Abakedi and Asuquo, 2016a).
Research efforts by scientists have paid off by the discovery and extraction of efficient eco-friendly metallic corrosion inhibitors from natural products. Plants, for instance, contain phytochemicals which are rich sources of organic nitrogen, sulphur and oxygen in the combined form (Abakedi et al., 2016a). Several leaves extracts have been reported as potential inhibitors of mild steel corrosion in acidic media (Okafor et al.,2010; Cang et al., 2013; Ejikeme et al., 2015; Okewale and Olaitan, 2017; Sivakumar and Srikanth, 2017).This work is our contribution to the global search for efficient eco - friendly corrosion inhibitors.
Solenostemon monostachyus is an aromatic, medicinal plant that belongs to the family Lamiaceae. In English language, it is called Monkey potato. Its names among some ethnic groups in Nigeria include Ntorikwot (Ibibio) and Olojogbodu (Yoruba). The use of *Solenostemon monostachyus* plant in traditional medicine by the people of Nigeria has been documented (Ekundayo and Ezeogu, 2006; Ajibesin et al., 2008; Amazu et al., 2015). The phytochemical screening of *Solenostemon monostachyus* leaf extract revealed the presence of saponins, tannins, cyanogenic glycosides, flavonoids and alkaloids (Obichi et al., 2015). Previous studies (Abakedi, 2017) showed that Solenostemon *monostachyus* leaf extract is a good inhibitor of aluminium corrosion in acidic medium. The aim of this work was to assess the inhibitory effect of *Solenostemon monostachyus* leaf extract on mild steel corrosion in H_2SO_4 solution.

2. MATERIALS AND METHODS

2.1Test Materials

The mild steel used for this study had the following chemical composition (weight %): Mn (0.85), S (0.06), P (0.05), Si (0.09), C (0.12) and Fe (98.83). It was mechanically press - cut into 4 cm x 5 cm coupons, and polished to mirror finish using different grades of silicon carbide papers. Further treatment of the coupons involved degreasing in absolute ethanol, dipping in acetone before air-drying. The cleaned coupons were then stored in a moisture – free desiccator before use in corrosion studies (NACE, 1984).

2.2 Preparation of *Solenostemon monostachyus* leaf extract

Fresh mature *Solenostemon monostachyus* leaves were collected from a farm in Etinan, Akwa Ibom State, Nigeria and authenticated by a plant taxonomist in the Department of Botany and Ecological Studies, University of Uyo, Nigeria. They were washed and oven – dried at 50°C to a constant weight before grinding to powder. *Solenostemon monostachyus* leaf extract was prepared as reported previously (Abakedi, 2017).

2.3 Weight loss method

Mild steel coupons, which were previously cleaned and weighed, were suspended with the aid of glass hooks and rods and completely immersed in 100 cm^3 of 1 M H_2SO_4 solution (blank) and in 1 M H_2SO_4 solution containing 1.0 g/L – 4.0 g/L *Solenostemon monostachyus* leaf extract (inhibitor) in open beakers. Each beaker contained one mild steel coupon. The temperatures of the experiment were maintained at 30°C, 40°C, 50°C, and 60°C, respectively, using a thermostatic water bath. The mild steel coupons were retrieved from the test solutions after four (4) hours and scrubbed with bristle brush under running water. They were dipped in acetone and air - dried before reweighing.

The inhibition efficiency I_{WL}(%) was calculated using the formula (Abakedi et al., 2016b):

$$I_{WL}(\%) = \left(\frac{W_0 - W_1}{W_0}\right) \times 100 \qquad (1)$$

where W_0 and W_1 are the weight losses of the mild steel coupons in the absence and presence of extract, respectively, in 1 M H_2SO_4 at the same temperature.

The corrosion rate (CR) of mild steel in H_2SO_4 solution was calculated using the equation (Abakedi, 2016):

$$CR\ (mg\ cm^{-2}hr^{-1}) = \left(\frac{W}{At}\right) \qquad (2)$$

where W is the weight loss (mg), A is the total surface area (cm^2) while t is the exposure time (hours).

2.4 Hydrogen Evolution Method

The instrumentation and procedure for the hydrogen evolution tests are as described in literature (Onuchukwu and Mshelia,1985). Mild steel coupon weighing 8.0 g was dropped into the reaction vessel containing 100 cm^3 of 1 M H_2SO_4 solution (blank). The volume of H_2 gas evolved from the corrosion reaction was recorded every 60 seconds for 60 minutes. The same experiment was repeated in the presence of 1.0 g/L – 4.0 g/L *Solenostemon monostachyus* leaf extract in 1 M H_2SO_4 solution.

The inhibition efficiency I_{HE}(%) was calculated using the equation (Abakedi, 2017):

$$I_{HE}(\%) = \left(\frac{R_{H0} - R_{H1}}{R_{H0}}\right) \times 100 \qquad (3)$$

where R_{H0} and R_{H1} are the hydrogen evolution rates in the absence and presence of inhibitor, respectively, at a specified time.

3. RESULTS AND DISCUSSION

3.1 Effect of *Solenostemon monostachyus* leaf extract concentration on inhibition efficiency

Fig. 1 shows that *Solenostemon monostachyus* leaf extract significantly inhibited the corrosion of mild steel in H_2SO_4 solution by weight loss measurements. At a particular temperature, the inhibition efficiency increased with increase in the leaf extract concentration. Fig. 2 reveals a reduction in the volume of hydrogen gas evolved in the presence of *Solenostemon monostachyus* leaf extract compared to the blank. Furthermore, it is observed that the higher the extract concentration, the lower the volume of hydrogen gas evolved. The lower the hydrogen evolution rate, the higher the inhibition efficiency (Table 1). Similar results have been reported previously (Abakedi and Asuquo, 2016b; Abakedi et al., 2016b). The weight loss and hydrogen evolution results followed a similar trend. An increase in the inhibition efficiency with increase in the extract concentration indicates a strong interaction between mild steel surface and the inhibitor (Ita et al., 2013).

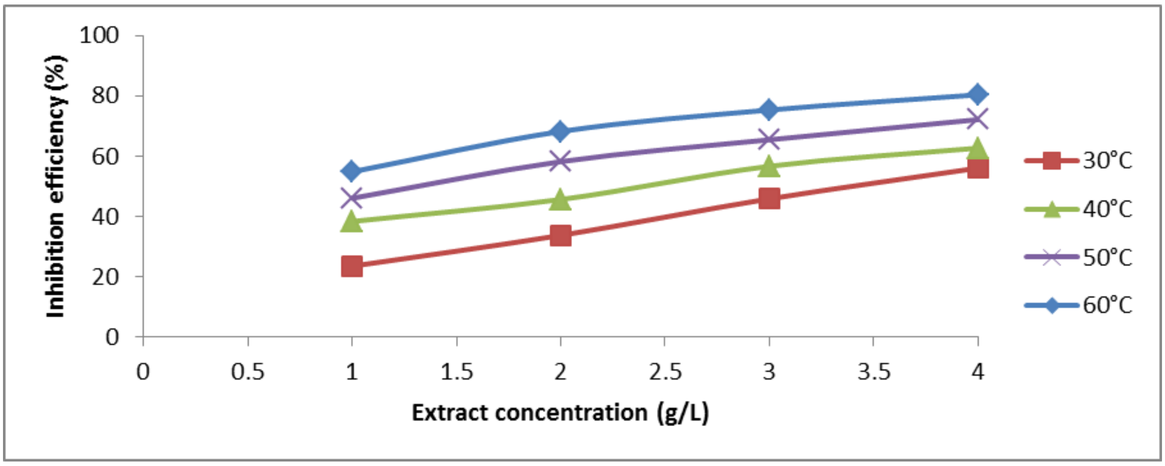

Fig. 1. Effect of *Solenostemon monostachyus* leaf extract concentration on the inhibition efficiency of mild steel corrosion in 1 M H_2SO_4 at different temperatures

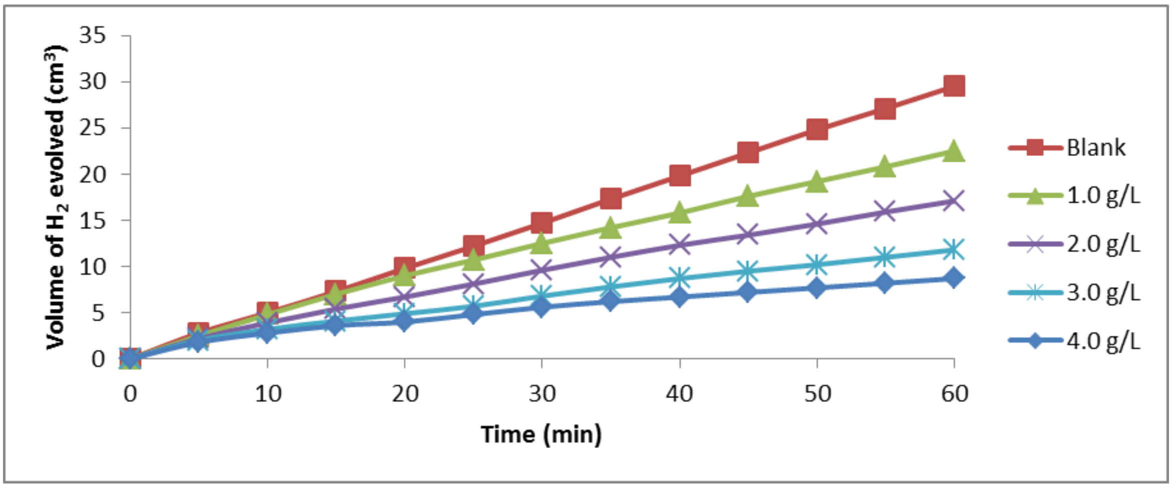

Fig. 2. Variation of volume of H_2 gas evolved (cm^3) with time (min) for mild steel corrosion in 1 M H_2SO_4 in the absence and presence of *Solenostemon monostachyus* leaf extract at 30°C

Table 1. Effect of *Solenostemon monostachyus* leaf extract concentration on hydrogen evolution rate and inhibition efficiency of mild steel in 1 M H_2SO_4 solution at 30°C (Hydrogen evolution measurements)

Extract concentration (g/L)	H_2 evolution rate (cm^3 min^{-1})	Inhibition efficiency (%)
Blank	**0.492**	**-**
1.0	**0.375**	**23.78**
2.0	**0.285**	**42.07**
3.0	**0.197**	**59.96**
4.0	**0.145**	**70.53**

3.3 Effect of temperature on inhibition efficiency

Temperature was found to have a great influence on the inhibition efficiency of *Solenostemon monostachyus* leaf extract on mild steel corrosion in H_2SO_4 solution. Table 2 shows an increase in inhibition efficiency with increase in temperature. This indicates that *Solenostemon monostachyus* leaf extract was more effective as an inhibitor at higher temperatures than at lower ones. Furthermore, an increase in the inhibition efficiency with increase in temperature indicates that the extract adsorbed chemically onto mild steel surface.

Table 2. Weight loss data for mild steel corrosion in 1M H_2SO_4 in the absence and presence of different concentrations of *Solenostemon monostachyus* leaf extract

Extract conc. (g/L)	Weight loss (g)				Corrosion rate (mg cm^{-2} hr^{-1})				Inhibition efficiency (%)			
	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
1M H_2SO_4	0.314	0.563	1.407	2.046	1.963	3.519	8.794	12.788	-	-	-	-
1.0	0.240	0.347	0.759	0.924	1.500	2.169	4.744	5.775	23.57	38.37	46.05	54.83
2.0	0.200	0.306	0.588	0.650	1.300	1.913	3.675	4.063	33.76	45.65	58.21	68.21
3.0	0.170	0.244	0.486	0.505	1.063	1.525	3.038	3.156	45.86	56.66	65.46	75.32
4.0	0.138	0.210	0.392	0.402	0.863	1.313	2.450	2.513	56.05	62.70	72.14	80.35

The values of the activation energy (E_a) for mild steel corrosion in 1 M H_2SO_4 solution in the presence and absence of *Solenostemon monostachyus* leaf extract, respectively, were obtained using the equation
(Abakedi and Moses, 2016):

$$\ln CR = \frac{-E_a}{RT} + \ln A \qquad (4)$$

where T is the temperature in Kelvin, R is the gas constant, CR is the corrosion rate and A is the pre-exponential factor.

The activation energies (E_a) of mild steel corrosion in 1M H_2SO_4 solution, in the absence and presence of *Solenostemon monostachyus* leaf extract, were obtained from the gradients of ln CR vs. 1/T plots (Fig. 3).The E_a values so calculated are contained in Table 3**.** The E_a values in the presence of the leaf extract were lower than the E_a value of the blank (54.363 kJ mol^{-1}). A decrease in the E_a values in the presence of the extract compared to the blank could be interpreted as an indication of physical adsorption mechanism while the reverse could be regarded as signifying chemical adsorption mechanism (Awad, 2006). Therefore, the adsorption of *Solenostemon monostachyus* leaf extract on mild steel surface has been proposed to occur by a chemical adsorption mechanism.

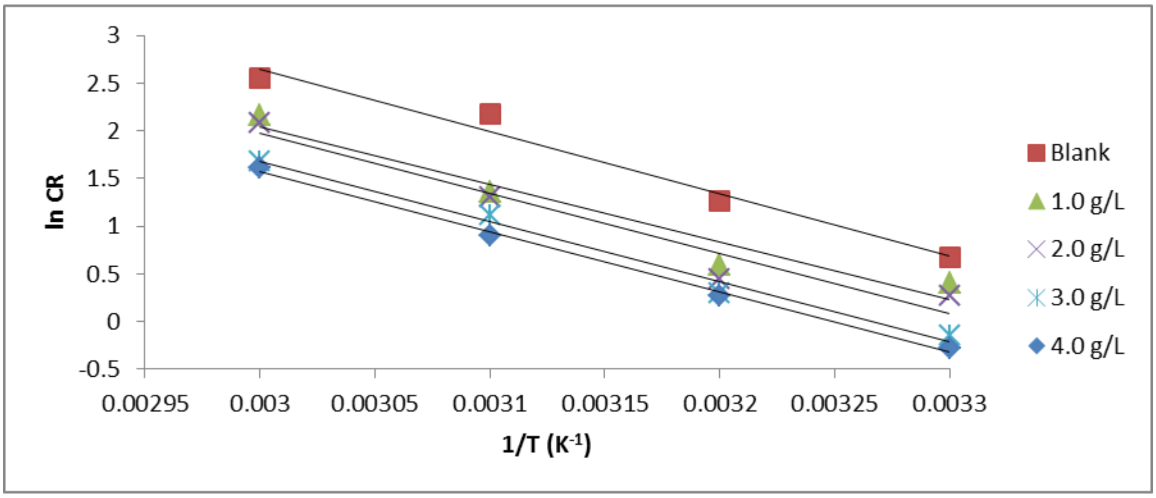

Fig. 3. Arrhenius plot for mild steel corrosion in 1 M H_2SO_4 in the absence and presence of *Solenostemon monostachyus* leaf extract

The values of enthalpy of activation (ΔH°_{ads}) and entropy of activation (ΔS°_{ads}) were obtained from an alternative formulation of the transition state equation (Abakedi and Asuquo, 2016b):

$$\ln\left(\frac{CR}{T}\right) = \left[\ln\left(\frac{R}{Nh}\right) + \frac{\Delta S^\circ_{ads}}{R}\right] - \frac{\Delta H^\circ_{ads}}{RT} \qquad (5)$$

where N is the Avogadro's number, A is the Arrhenius pre-exponential factor and R is the universal gas constant; h is the Planck's constant, CR is the corrosion rate, and T is the absolute temperature. Linear plots of ln (CR/T) vs. 1/T (Figure 4) with gradients of ($-\Delta H^\circ_{ads}/R$) and intercepts of [ln (R/Nh) + $\Delta S^\circ_{ads}/R$] were used in calculating values of ΔH°_{ads} and ΔS°_{ads} presented in Table 3. Endothermic process is implied for mild steel corrosion inhibition in the presence of the extract since ΔH°_{ads} values are positive. Also, there was a decrease in the disorderliness of the system, since the values of ΔS°_{ads} obtained are negative. Negative values of ΔS°_{ads} indicate that *Solenostemon monostachyus* leaf extract probably formed an ordered layer on mild steel surface.

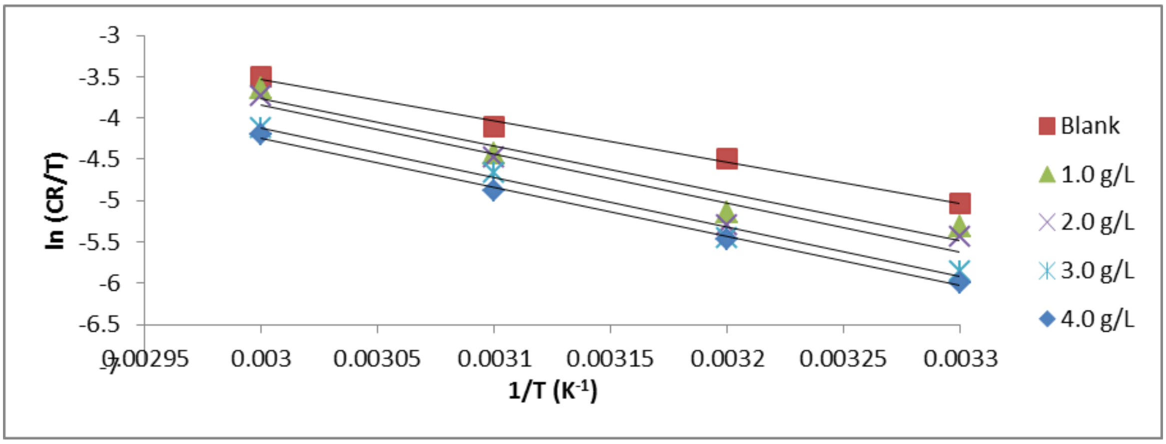

Fig. 4.Transition state plot for mild steel corrosion in 1 M H_2SO_4 solution in the absence and presence of *Solenostemon monostachyus* leaf extract

Table 3. Thermodynamic parameters for mild steel corrosion in 1 M H_2SO_4 solution in the absence and presence of *Solenostemon monostachyus* leaf extract

Extract concentration	E_a (kJ mol^{-1})	ΔH°_{ads} (kJ mol^{-1})	ΔS°_{ads} (J K^{-1} mol^{-1})
1 M H_2SO_4 (Blank)	54.363	51.746	- 68.605
1.0 g/L	40.128	37.516	- 117.932
2.0 g/L	33.865	31.251	- 139.486
3.0 g/L	32.885	30.267	- 144.397
4.0 g/L	31.858	29.241	- 149.295

Adsorption isotherm

The best fit for the adsorption of *Solenostemon monostachyus* leaf extract on mild steel surface was obtained by the Freundlich adsorption isotherm defined as (Al-Bonayan, 2015):

$$\log\theta = n\log C + \log K_{ads} \qquad (6)$$

where C is the inhibitor concentration, θ is the degree of surface coverage, n is the interaction parameter and K_{ads} is the equilibrium adsorption constant. Linear plots of log θ vs. log C (Fig. 5) with intercept of log K_{ads} obtained confirm that the adsorption of *Solenostemon monostachyus* leaf extract on mild steel surface in 1M H_2SO_4 solution obeyed the Freundlich adsorption isotherm.

The Gibb's free energy of adsorption (ΔG°_{ads}) was calculated using the formula (Zang et al., 2010):

$$K_{ads} = 1/55.5\exp\left(-\Delta G^\circ_{ads}/RT\right) \qquad (7)$$

where 55.5 is the molar concentration of water in the solution in mol dm^{-3}.

The negative values of ΔG°_{ads} (Table 3) for the adsorption process in the presence *of Solenostemon monostachyus* leaf extract reveal that the mild steel corrosion inhibition process by the extract occurred spontaneously.

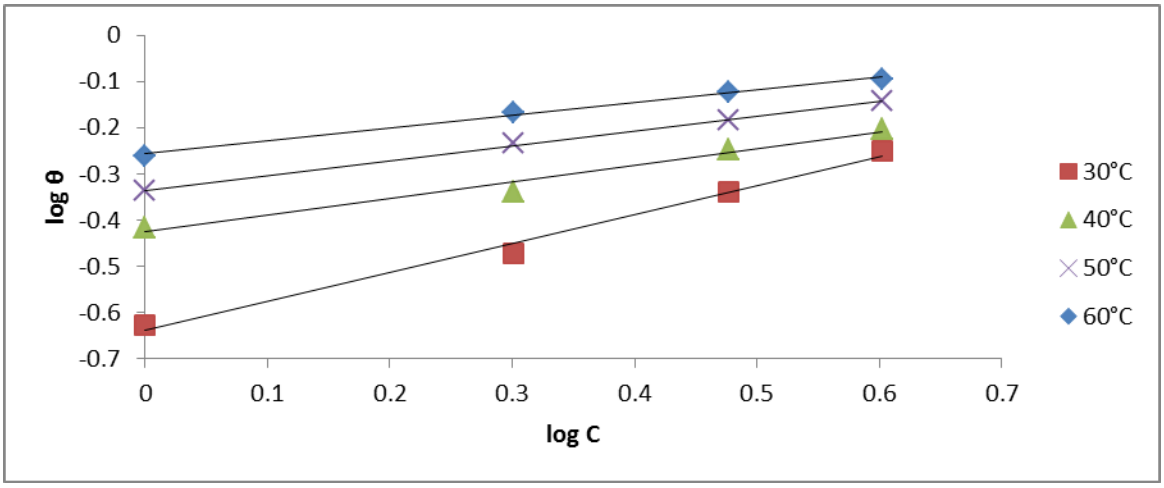

Fig. 5. Freundlich isotherm plot for mild steel corrosion in 1 M H_2SO_4 solution containing *Solenostemon monostachyus* leaf extract

Table 4. Freundlich adsorption isotherm parameters for mild steel corrosion in 1 M H_2SO_4 solution containing *Solenostemon monostachyus* leaf extract

Temperature	R^2	n	log K_{ads}	K_{ads}	$\Delta G°_{ads}$ (kJ mol^{-1})
303K	0.9915	0.63	-6.38 x 10^{-1}	2.30 x 10^{-1}	-6.42
313K	0.9735	0.36	-4.26 x 10^{-1}	3.75 x 10^{-1}	-7.90
323K	0.9991	0.32	-3.35 x 10^{-1}	4.62 x 10^{-1}	-8.71
333K	0.9939	0.28	-2.57 x 10^{-1}	5.53 x 10^{-1}	-9.48

CONCLUSION

On the basis of this study, the following conclusions could be drawn:

1. *Solenostemon monostachyus* leaf extract inhibited the corrosion of mild steel in H_2SO_4 solution by both the weight loss and hydrogen evolution methods.
2. The inhibition efficiency of the leaf extract increased with increase in extract concentration and temperature.
3. The adsorption of *Solenostemon monostachyus* leaf extract onto mild steel surface obeyed the Freundlich adsorption isotherm.
4. Chemical adsorption (chemisorption) has been proposed for the adsorption of *Solenostemon monostachyus* leaf extract onto mild steel surface because the inhibition efficiency increased with increase in temperature in addition to a decrease in the activation energy in the presence of the extract relative to the blank.

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