

Modelling Azadirachta Indica (Neem) Seed Extract-inhibited Corrosion of Mild steel and Copper in H₂SO₄ Medium

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Abstract— Corrosion inhibition of mild steel and copper using Azadirachta indica (neem) seed extract in 0.5M, 1.0M and 1.5M H₂SO₄ was investigated using the gasometric method. The data obtained were fit to Zero order, half order and first order models based on volume of hydrogen evolved. These results show that the kinetics of corrosion of mild steel and copper in H₂SO₄ medium, based on volume of hydrogen evolved, can be modeled using a zero order kinetic model and inhibition reduces the instantaneous volume of hydrogen evolved (V₀) and the kinetic rate constant (k). The results from the gasometric method also indicated that corrosion rate was higher in solutions involving the use of mild steel than those of copper.

Keywords— Corrosion; gasometric; Azadirachta indica; kinetics; hydrogen evolution; mild steel; Copper.

INTRODUCTION

Mild steel is an alloy that has enormous number of applications in the Engineering field due to certain characteristics it possesses which include its versatility, cost-effectiveness, weldability, ductility, recyclability, strength, availability, machinability, malleability and high impact and tensile strength while copper is a naturally occurring metal that is soft, malleable, ductile and has high electrical and thermal conductivity. However, despite the importance of these metals, the problem associated with corrosion still remains a source of concern to Engineering practitioners. The study of corrosion inhibition has become of importance, in order to curb the increasing rate of metal failure and corrosion in general. Several inhibitors in use are either produced from cheap raw materials or chosen from compounds having heteroatoms in their aromatic or long-chain carbon system. However, most of these inhibitors are toxic to the environment and this has prompted the search for green corrosion inhibitors [1, 2, 3, 4].

Green corrosion inhibitors are obtained from plants and animals. They are nontoxic and do not contain heavy metals or other toxic substances. These green inhibitors are relatively cheap and can be easily produced and purified. In addition, they are biodegradable. In view of these, several extracts of plants have been successfully utilized for the inhibition

of the corrosion of metals in acidic, neutral or alkaline media.

Reference [5] and [6] gave a summary of some plant extracts used as corrosion inhibitors. Reference [7] studied the inhibition efficiency of acetone extract of red onion skin on Aluminium in 2M hydrochloric acid solutions. The effect of naturally occurring Emilia sonchifolia (ES) as corrosion inhibitor for mild steel in 1.0M H₂SO₄ using gravimetric measurement at 30°C and 60°C was investigated by [8]. Reference [9] carried out an experiment on the Corrosion Inhibition of Mild Steel in Hydrochloric acid by acid extracts of Eichhornia crassipes using gasometric method of corrosion inhibition analysis. The volume of gas that was evolved when an inhibitor was added to the solution was less than that evolved when it was blank.

Several other plant extracts have been used in recent times as corrosion inhibitors, but, of special interest in the present study is the use of Azadirachta indica extracts as corrosion inhibitors for metals. The extracts of the leaves of Azadirachta indica have been reported to effectively inhibit the acidic corrosion of metals [10, 11, 12, 13, 14]. Reference [15] carried out a study on the inhibitive action of leaves (LV), root (RT) and seeds (SD) extracts of Azadirachta indica on mild steel corrosion in 2M H₂SO₄ solutions using weight loss and gasometric techniques. The results obtained indicate that the extracts functioned as good inhibitors in H₂SO₄ solutions. Inhibition efficiency was found to increase with extracts concentration and temperature, and followed the trend: SD > RT > LV. Reference [16] carried out the corrosion inhibition of Azadirachta indica leaves extract as a green corrosion inhibitor for Zinc in H₂SO₄ and found out that the corrosion rate for Zinc at 303K was 1.18, 1.32, 1.48 mg/cm²hr for 0.5M, 1.0 and 2.0 molar concentrations of the acid respectively. They also found out that the corrosion rate increased with an increase in temperature.

The present work tries to determine models based on order of reaction that best fit hydrogen gas evolution during corrosion of mild steel and copper in 0.5M, 1M and 1.5M H₂SO₄ solutions inhibited with Azadirachta indica seeds extract as corrosion inhibitor using gasometric methods.

MATERIALS AND METHODS

Materials: The materials used in the present work include, reflux condenser, retort stand, burner,

beakers, weighing balance, burette, volumetric cylinder, round-bottom flask, stop clock, soft towels, hard brushes, paper tape, hand gloves, sand paper, thread, bulk solution of tetraoxosulphate (VI) acid (H₂SO₄), distilled water, acetone solution, ethanol solution (2.5L) and Vaseline.

Inhibitor Preparation: The neem seeds were obtained from a tree located at the Federal University of Technology, Owerri, Imo State, Nigeria. The seeds were bone-dried and the moisture content was determined. They were then ground to fine powder. 100g of the ground seeds was weighed into a round bottom flask containing 400ml of ethanol. The concentration of the inhibitor obtained was 0.25g/ml or 0.25g/cm³. Both substances were then mixed thoroughly. The equipment for refluxing was then setup to heat for 1 hour. The chaff was filtered afterwards. The filtrate obtained served as the inhibitor.

Gasometric Method: The electrolyte was prepared using 200 ml each of 0.5M, 1.0M, and 1.5M molar solutions of H₂SO₄ acid + 10 ml of the inhibitor. The mild steel coupons (2cm x 2cm x 0.2cm) were weighed using the electric weighing balance. A control experiment was setup (without the corrosion inhibition solution). The gasometric apparatus was then setup. The mild steel coupon was inserted into the conical flask of the apparatus containing the acid plus inhibitor and the stop clock was switched on. The experiment was carried out at ambient or room temperature which was an average of about 28°C or 301K on daily basis. Measurement of the gas evolved was noted at different points in time through the readings on the calibrated cylinder. The values were then recorded and tabulated. The above procedure was repeated for the copper coupon.

The spontaneous dissolution of mild steel in acidic media is accompanied by the cathodic reduction of hydrogen ions as shown in equation 1;

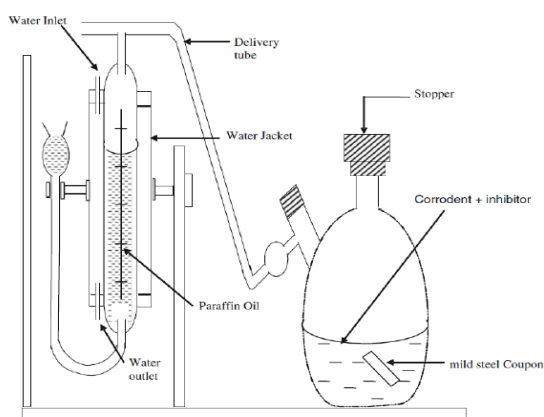


Figure 1: Gasometric Experiment Setup for Measuring Hydrogen Gas Evolved [17]

Mathematical Methodology

If the rate of evolution of hydrogen is a function of the concentration (volume) of hydrogen in the set up, we have:

$$\frac{dV}{dt} = kV^n \quad (2)$$

where V is volume of hydrogen in set up, t is time, k (rate constant) and n (order of reaction) are model constants. At time t = 0, let V₀ be the volume of hydrogen in the set up, then solving the above relation for zero order (n = 0), half order (n = 1/2) and first order (n = 1) processes, we have:

$$\text{Zero Order: } V = V_0 + kt \quad (3)$$

$$\text{Half Order: } V = \frac{k^2}{4} t^2 + k\sqrt{V_0}t + V_0 \quad (4)$$

$$\text{First Order: } V = V_0 \exp(kt) \quad (5)$$

The three model equations (eqn. 3, 4 and 5) will be fit to the experimental data to determine the model that best fit the data and thus the order of reaction based on volume of hydrogen evolved.

The inhibition efficiency was calculated using the equation below:

$$IE = \frac{V_0 - V_I}{V_0} \times 100 \quad (6)$$

where IE is inhibition efficiency, V₀ and V_I are volumes of hydrogen evolved for the uninhibited and inhibited samples respectively.

DISCUSSION OF RESULTS

The graphical fit results (fig. 2 and fig. 3) for Mild steel in 0.5 M H₂SO₄ medium, for the uninhibited and inhibited cases respectively, and the associated numerical fit results (Tables 1a & 1b) reveal that the experimental data fits best to the zero order kinetic models. The corrosion therefore does not depend of volume of hydrogen evolved. Inhibition however reduces the instantaneous amount on hydrogen evolved (V₀) and the model rate constant (k) by about 50% and 12% respectively.

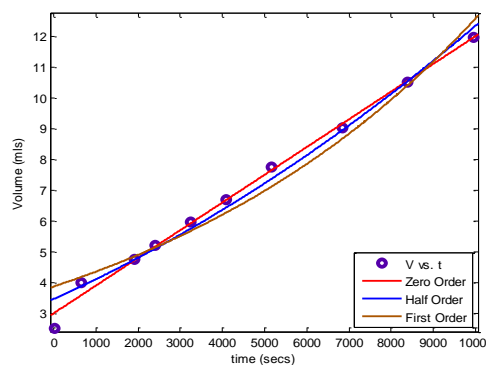


Fig. 2: Mild Steel in 0.5M H₂SO₄ (Uninhibited)

Table 1a: Numerical fit results to all models for mild steel in 0.5M H₂SO₄

Model	Uninhibited			
	V ₀	k	R ²	Adj. R ²
Zero order	2.9880	9.010e-4	0.9941	0.9934
Half order	3.4522	3.308e-4	0.9830	0.9809
First order	3.8620	1.181e-4	0.9616	0.9568

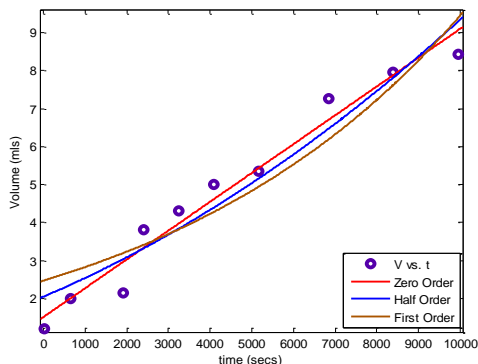


Fig. 3: Mild Steel in 0.5M H₂SO₄ (Inhibited)

Table 1b: Numerical fit results to all models for mild steel in 0.5M H₂SO₄

Model	Inhibited			
	V ₀	k	R ²	Adj. R ²
Zero order	1.5040	7.593e-4	0.9657	0.9614
Half order	2.0449	3.252e-4	0.9322	0.9237
First order	2.4700	1.342e-4	0.8881	0.8741

The graphical fit results (fig. 4 and fig. 5) for Mild steel in 1.0M H₂SO₄ medium, for the uninhibited and inhibited cases respectively, and the associated numerical fit results (Tables 2a & 2b) reveal that the experimental data fits best to the zero order kinetic models. The corrosion therefore does not depend on volume of hydrogen evolved. Inhibition however reduces the instantaneous amount of hydrogen evolved (V₀) and the model rate constant (k) by about 100% and 22% respectively.

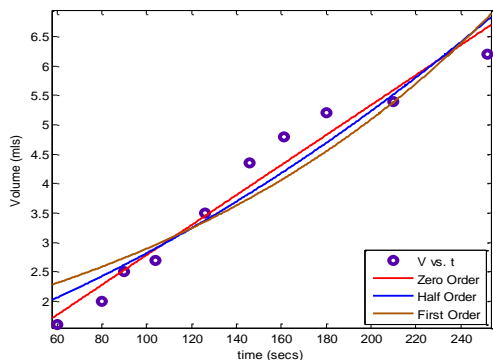


Fig. 4: Mild Steel in 1.0M H₂SO₄ (Uninhibited)

Table 2a: Numerical fit results to all models for mild steel in 1.0M H₂SO₄

Model	Uninhibited			
	V ₀	k	R ²	Adj. R ²
Zero order	0.2350	2.548e-2	0.9605	0.9555
Half order	1.1428	1.218e-2	0.9253	0.9160
First order	1.6440	5.646e-3	0.8817	0.8669

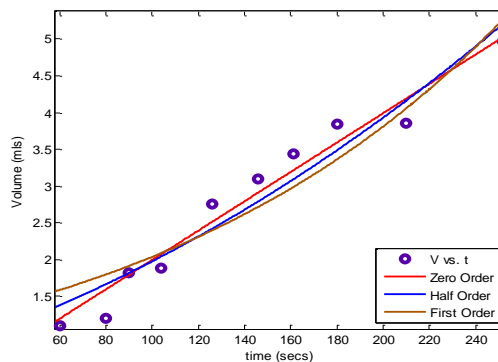


Fig. 5: Mild Steel in 1.0M H₂SO₄ (Inhibited)

Table 2a: Numerical fit results to all models for mild steel in 1.0M H₂SO₄

Model	Inhibited			
	V ₀	k	R ²	Adj. R ²
Zero order	0	1.994e-2	0.9639	0.9639
Half order	0.6876	1.153e-2	0.9362	0.9282
First order	1.0900	6.253e-3	0.8976	0.8848

The graphical fit results (fig. 6 and fig. 7) for Mild steel in 1.5 M H₂SO₄ medium, for the uninhibited and inhibited cases respectively, and the associated numerical fit results (Tables 3a & 3b) reveal that the experimental data fits best to the zero order kinetic models. The corrosion therefore does not depend of volume of hydrogen evolved. Inhibition however reduces the instantaneous amount of hydrogen evolved (V₀) and the model rate constant (k) by about 16% and 26% respectively.

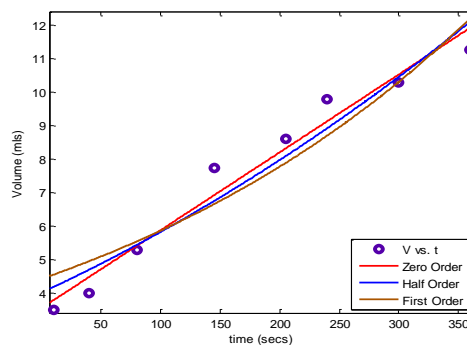


Fig. 6: Mild Steel in 1.5M H₂SO₄ (Uninhibited)

Table 3a: Numerical fit results to all models for mild steel in 1.5M H₂SO₄

Model	Uninhibited			
	V ₀	k	R ²	Adj. R ²
Zero order	3.555	2.324e-2	0.9671	0.9617
Half order	4.020	8.189e-3	0.9393	0.9292
First order	4.427	2.816e-3	0.9047	0.8888

Table 3b: Numerical fit results to all models for mild steel in 1.5M H₂SO₄

Model	Inhibited			
	V ₀	k	R ²	Adj. R ²
Zero order	2.9870	1.728e-2	0.9579	0.9509
Half order	3.3160	6.854e-3	0.9306	0.9190
First order	3.6080	2.659e-3	0.8969	0.8797

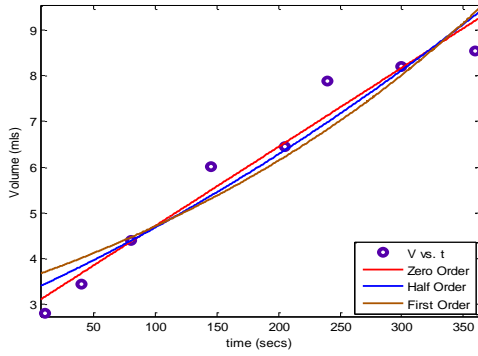


Fig. 7: Mild Steel in 1.5M H₂SO₄ (Inhibited)

The graphical fit results (fig. 8 and fig. 9) for Copper in 0.5 M H₂SO₄ medium, for the uninhibited and inhibited cases respectively, and the associated numerical fit results (Tables 4a & 4b) reveal that the experimental data fits best to the zero order kinetic models. The corrosion therefore does not depend of volume of hydrogen evolved. Inhibition however reduces the instantaneous amount of hydrogen evolved (V₀) and the model rate constant (k) by about 63% and 1.5% respectively.

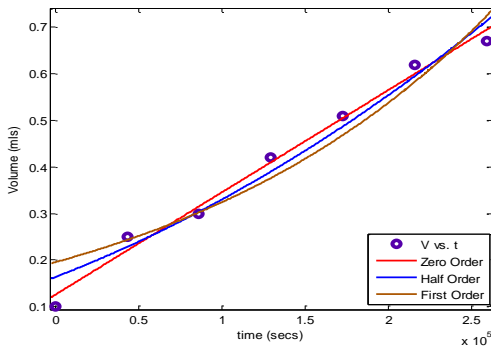


Fig. 8: Copper in 0.5M H₂SO₄ (Uninhibited)

Table 4a: Numerical fit results to all models for Copper in 0.5M H₂SO₄

Model	Uninhibited			
	V ₀	k	R ²	Adj. R ²
Zero order	0.1249	2.2e-6	0.9886	0.9863
Half order	0.1631	3.404e-6	0.9668	0.9602
First order	0.1950	5.068e-6	0.9326	0.9191

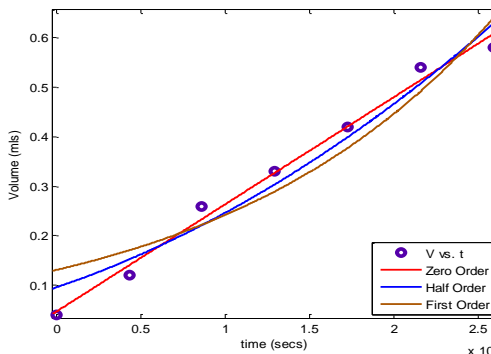


Fig. 9: Copper in 0.5M H₂SO₄ (Inhibited)

Table 4b: Numerical fit results to all models for Copper in 0.5M H₂SO₄

Model	Inhibited			
	V ₀	k	R ²	Adj. R ²
Zero order	0.04631	2.167e-6	0.9895	0.9875
Half order	0.0955	3.736e-6	0.9588	0.9506
First order	0.1305	6.134e-6	0.9123	0.8947

The graphical fit results (fig. 10 and fig. 11) for Copper in 1.0 M H₂SO₄ medium, for the uninhibited and inhibited cases respectively, and the associated numerical fit results (Tables 5a & 5b) reveal that the experimental data fits best to the zero order kinetic models. The corrosion therefore does not depend of volume of hydrogen evolved. Inhibition however reduces the instantaneous amount of hydrogen evolved (V₀) and the model rate constant (k) by about 57% and 5.7% respectively.

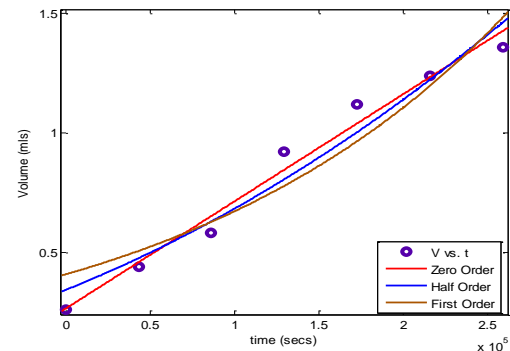


Fig. 10: Copper in 1.0 M H₂SO₄ (Uninhibited)

Table 5a: Numerical fit results to all models for Copper in 1.0M H₂SO₄

Model	Uninhibited			
	V ₀	k	R ²	Adj. R ²
Zero order	0.2626	4.499e-6	0.9796	0.9755
Half order	0.3415	4.831e-6	0.9552	0.9463
First order	0.4070	4.998e-6	0.9165	0.8999

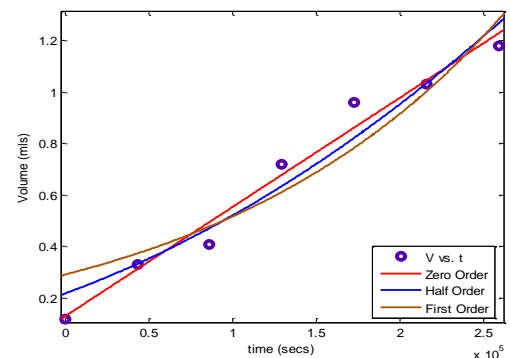


Fig. 11: Copper in 1.0 M H₂SO₄ (Inhibited)

Table 5b: Numerical fit results to all models for Copper in 1.0M H₂SO₄

Model	Inhibited			
	V ₀	k	R ²	Adj. R ²
Zero order	0.1287	4.242e-6	0.9775	0.9730
Half order	0.2178	5.091e-6	0.9504	0.9404
First order	0.2916	5.719e-6	0.9059	0.8871

The graphical fit results (fig. 12 and fig. 13) for Copper in 1.5 M H₂SO₄ medium, for the uninhibited and inhibited cases respectively, and the associated numerical fit results (Tables 6a & 6b) reveal that the experimental data fits best to the zero order kinetic models. The corrosion therefore does not depend of volume of hydrogen evolved. Inhibition however reduces the instantaneous amount of hydrogen evolved (V₀) and the model rate constant (k) by about 32% and 11.4% respectively.

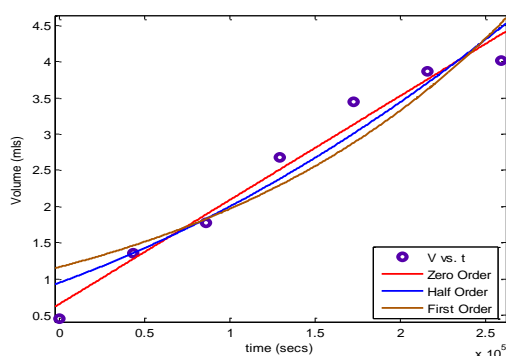


Fig. 12: Copper in 1.5 M H₂SO₄ (Uninhibited)

Table 6a: Numerical fit results to all models for Copper in 1.5M H₂SO₄

Model	Uninhibited			
	V ₀	k	R ²	Adj. R ²
Zero order	0.6478	1.439e-5	0.9708	0.9650
Half order	0.9454	8.822e-6	0.9319	0.9182
First order	1.1620	5.255e-6	0.8821	0.8586

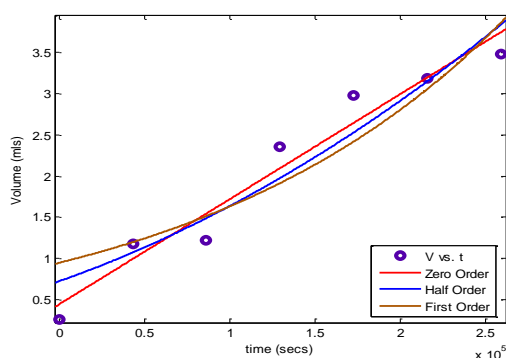


Fig. 13: Copper in 1.5 M H₂SO₄ (Inhibited)

Table 6b: Numerical fit results to all models for Copper in 1.5M H₂SO₄

Model	Inhibited			
	V ₀	k	R ²	Adj. R ²
Zero order	0.4415	1.275e-5	0.9521	0.9425
Half order	0.7234	8.558e-6	0.9122	0.8946
First order	0.9474	5.442e-6	0.8613	0.8335

It can also be observed generally that the instantaneous volume of hydrogen evolved (V₀) and the rate constant (k) for corrosion of mild steel increased with concentration of H₂SO₄ in the medium to a maximum at 1.0M and then begins to reduce, while these two quantities increased continuously with concentration of H₂SO₄ in the medium for corrosion of copper.

Table 7 reveals that the inhibition efficiency (maximum or average) of Azadirachta indica (neem) seed extract reduces with increase in concentration of H₂SO₄ in the medium. The maximum inhibition efficiency of Azadirachta indica (neem) seed extract is higher for Copper than Mild steel, though the average Inhibition efficiency is higher for Mild steel. Generally more hydrogen is evolved in the corrosion of Mild steel as compared to Copper. The reason is that copper is more electropositive and thus has a lower tendency to corrode. Hence, mild steel corroded faster and more hydrogen gas was evolved.

Table 7: Maximum and average values of Inhibition Efficiency at varying Concentrations

Conc. of H ₂ SO ₄	Mild steel		Copper	
	Maximum	Average	Maximum	Average
0.5M	0.5474	0.3409	0.6000	0.2725
1.0M	0.4000	0.2817	0.5358	0.2491
1.5M	0.2500	0.2028	0.4222	0.2044

CONCLUSION

Azadirachta indica seed extract can serve as a good corrosion inhibitor for mild steel and copper. The kinetics, based on volume of hydrogen evolved, can be modeled using a zero order kinetic model. The highest inhibition efficiency occurred when the concentration of the acid was the least (0.5M H₂SO₄) while the lowest occurred for the highest acid concentration (1.5M H₂SO₄). This is not out of place since the tendency for corrosion to occur is higher in a more acidic environment than in a less acidic one. The reason why copper generally had lower corrosion rate values than mild steel can be explained in terms of electrochemical potential. The more electropositive an element is, the less likely it is to corrode. Copper has an electrochemical potential of +0.02V while that of mild steel is -0.440V.

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