# Evaluation of *Abutilon indicum* as Mild Steel Corrosion Inhibitor in 1 M HCl and 0.5 M H₂SO₄ by Electrochemical Techniques

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The present study reports on performance of acid extracts of *Abutilon indicum* as mild steel corrosion inhibitor in 1 M HCl and 0.5 M H₂SO₄ solutions studied by electrochemical techniques. The inhibition efficiency was found to be greater than 95 % in acid media and potentiodynamic polarization study revealed that inhibitor as a mixed type of inhibitor in both HCl and H₂SO₄ acid media controlling anodic and cathodic reactions. Linear polarization study showed increase in resistance and the electrochemical impedance study showed a decrease in double layer capacitance as the adsorption of inhibitor caused structural changes at electrode-solution interface.

**Key Words: Corrosion inhibition, *Abutilon indicum*, Potentiodynamic polarization, Linear polarization and electrochemical impedance.**

## INTRODUCTION

The use of natural products as corrosion inhibitor for various metals in different environments is a recently emerging robust field. The plant products being biodegradable, readily available and renewable sources of materials are widely recognised as corrosion inhibitors and are well documented. The extracts prepared using leaves, barks, seeds, fruits and roots of plants are found to comprise of mixtures of organic compounds containing nitrogen, sulphur and oxygen atoms. Some of the plant extracts reported as effective for mild steel corrosion inhibition are aloe vera[1] and *Phyllanthusamarus*[2], mango (*Mangifera indica*)[3] thyme, coriander, hibiscus, anis, black cumin and *Garden cress*[4]. *Eucalyptus hibiscus* and Agaricus[5] *Murraya koenigii*[6], *Medicago sativa*[7], *Dacryodis edulis*[8], *Nyctanthes arbortristis* (Night Jasmine, Coral Jasmine)[9], *Azadirachta indica*[10], *Tributes terrestris* L[11], *Acalypha indica* L[12], *Justicia gendarussa*[13], bitter leaf[14], *Emblica officianalis*[15], Pennyroyal mint[16], *Combretum bracteosum*[17], *Kopsia singapurensis*[18], *Eclipta alba*[19], *Citrus aurantifolia*[20], *Jasminum grandflorum*[21], *Hibiscus sabdariffa*[22] and *Eucalyptus*[5]. Nature has rich varieties of flora and fauna and yet a large portion of the kingdom has not been explored for our benefit. Inspired by the woks reported on natural inhibitors, the weed variety *i.e.*, leaves of *Abutilon indicum* has been selected for screening as mild steel corrosion inhibitor in two different acid media. *Abutilon indicum* (vernacular name Thuti) is a small annual Shrub, which generally distributed throughout the plains of India. The phytochemical components of *Abutilon indicum* have been extensively studied and reported to have steroids, carbohydrates, alkaloids, amino acid, fatty acids, flavonoids and tannins[23]. These compounds have been known for their medicinal properties like antifungal, antibacterial, antioxidant and most likely responsible for inhibiting corrosion. In this study, inhibition effect of *Abutilon indicum* as mild steel corrosion inhibitor in each 1.0 M HCl and 0.5 M sulphuric acid is evaluated by electrochemical techniques such as potentiodynamic polarization, linear polarisation and electrochemical impedance spectroscopy (EIS) as these techniques are known for rapidity, accuracy and reliability.

## EXPERIMENTAL

**Preparation of mild steel specimens:** Rectangular mild steel samples of area 5 cm × 1 cm have been cut from a sheet of commercial grade mild steel bought from local market. The elemental analysis was carried out with Vacuum Emission Spectrometer of Model: BAIRD-DV4 and found to contain the following percentage composition of: C = 0.039, S = 0.028, Si = 0.19, P = 0.017, Mo = 0.006, Ni = 0.012, Mn = 0.272, Cr = 0.021and remaining Fe.

The samples were polished with various grade emery papers, degreased in acetone, washed with distilled water and lacquered so as to expose an area of 1 cm².

**Preparation of acid solutions:** The aggressive solutions (1 M HCl and 0.5 M H₂SO₄) were prepared using commercial grade HCl and H₂SO₄ with double distilled water.

**Preparation of stock solution of plant extract:** The plant extract in each acid solution (HCl and H₂SO₄) was prepared by refluxing 50 g of shade dried *Abutilon indicum* leaves powder in 500 mL of each acid for 3 h, filtered and made up to 500 mL using the same acid solution and taken as stock solution. Solutions of various concentrations of 0.1, 0.5, 1, 5, 10 % (v/v) were prepared using each stock solution.

**Potentiodynamic polarisation technique:** Polarization experiments were carried out in the three electrode polarization cell containing platinum auxiliary electrode, saturated calomel reference electrode and polished mild steel specimen as working electrode. All the measurements were carried out using Solartron 1280 B-electrochemical work station. 100 mL of electrolytic solution in the absence and presence of various concentrations of the *Abutilon indicum* extract was taken in the electrochemical cell. The polished electrode was then introduced and held for 5 min to attain a constant potential. The electrode was placed between -0.45 to -0.5 V as its open circuit potential. Potentiodynamic anodic and cathodic polarization curves were obtained by polarizing anode or cathode by applying voltage with a scan rate = 2 mV/s. By Tafel extrapolation method, plots of applied potential *vs.* log current were made and extrapolation of linear portion to the corrosion potential gave the corrosion current in the linear polarization method, current *versus* voltage curve is recorded very near to the open circuit potential (10 mV). A numerical fit of the curve yields polarization resistance $R_p$.

The inhibition efficiency (IE) was evaluated from the potentiodynamic polarization data by using the formulae (1 and 2).

$$IE\ (\%) = \frac{I^0_{corr} - I_{corr}}{I^0_{corr}} \times 100 \qquad (1)$$

where, $I^0_{corr}$ and $I_{corr}$ are the corrosion current densities in the absence and the presence of the inhibitor.

**Linear polarization resistance method:**

$$IE\ (\%) = \frac{R_p - R^0_p}{R_p} \times 100 \qquad (2)$$

where, $R_p$ and $R^0_p$ are the linear polarization resistance values in the presence and absence of the inhibitor, respectively.

**Electrochemical impedance spectroscopy:** The usefulness of impedance spectroscopy lies in the ability to distinguish the dielectric and electric properties of individual contributions of components under investigation. Electrochemical impedance spectroscopy (EIS) was carried out with the same solution using a frequency response analyzer 1280 B (Solartron) with inbuilt IBM personal computer. After the determination of steady state current at a given potential, sine wave voltage (10 mV) peak to peak, at frequencies between 10 kHz and 0.1 Hz were superimposed on the rest potential. Computer programs (Z plot and Z-view) automatically controlled the measurements performed at rest potentials after 10 min of exposure. The Nyquist plots were analyzed by fitting the experimental data to a simple equivalent circuit model which includes solution resistance ($R_s$), double layer capacitance $C_{dl}$, which are placed in parallel to the charge transfer resistance $R_{ct}$ (Fig. 1).
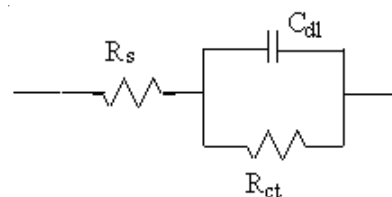


Fig. 1. Simple equivalent circuit with one time constant

$R_{ct}$ values were calculated from the difference in impedance at low and high frequencies. The value of $R_{ct}$ is a measure of impedances exerted by the solution (in the absence and presence of the extract) to electron transfer across the surface and is inversely proportional to the corrosion rate. The double layer capacitance was calculated at the frequency $f_{max}$ at which the imaginary component of impedance is high.

The inhibition efficiency (IE) was calculated from the charge-transfer resistance using eqn. 3

$$IE\ (\%) = \frac{R_{ct} - R^0_{ct}}{R_{ct}} \times 100 \qquad (3)$$

where, $R_{ct}$ and $R_0^{ct}$ are the change-transfer resistance values in the presence and absence of the inhibitor and from $C_{dl}$ values IE % is calculated using the eqn. 4

$$IE\ (\%) = \frac{C^0_{dl} - C_{dl}}{C^0_{dl}} \times 100 \qquad (4)$$

where, $C_{dl}$ and $C^0_{dl}$ are the double layer capacitance in the presence and absence of the inhibitor.

## RESULTS AND DISCUSSION

**Potentiodynamic polarization data:** Fig. 2(a) and Fig. 3(a) show the polarization curves for mild steel corrosion in 1 M HCl and 0.5 M H₂SO₄ solutions in the presence of different concentrations of *Abutilon indicum* extract. Electrokinetic's corrosion parameters such as corrosion current density ($I_{corr}$), corrosion potential ($E_{corr}$), linear polarization resistance ($R_p$) and inhibition efficiencies (IE %) calculated using $I_{corr}$ values and $R_p$ values for different concentrations of *Abutilon indicum* in 1 M HCl and 0.5 M sulphuric acid (Table-1).

Fig. 2a and Fig. 3a are polarization curves for mild steel corrosion in HCl and sulphuric acid, respectively. It is clear
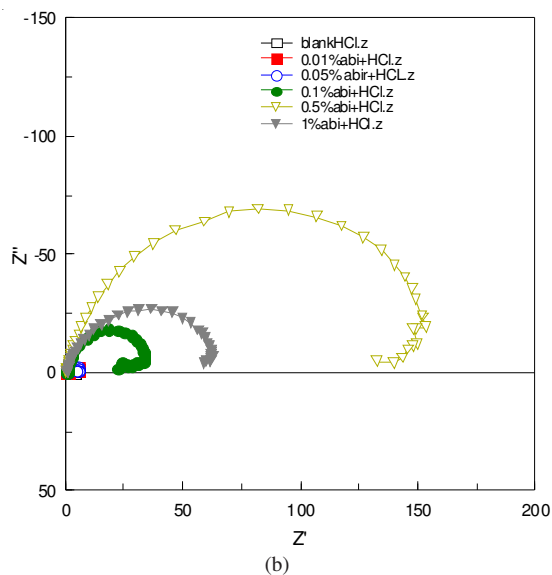


(a)
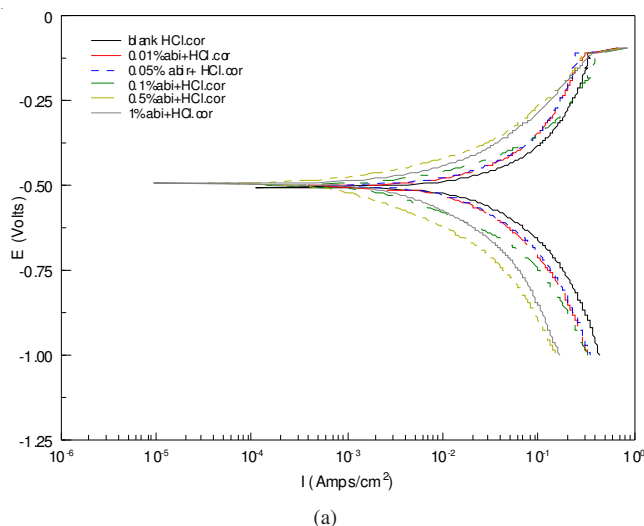
Fig. 2.  (a) Potentiodynamic polarisation curves and (b) Nyquist plots for mild steel corrosion of in 1 M HCl with out and with different concentrations of *Abutilon indicum* extract
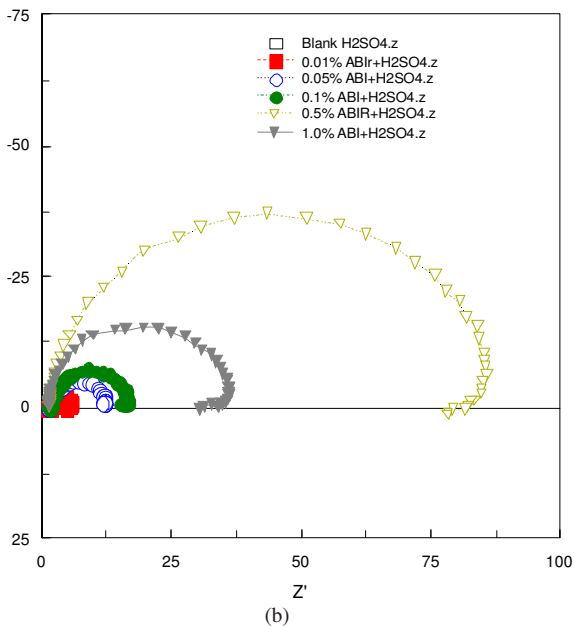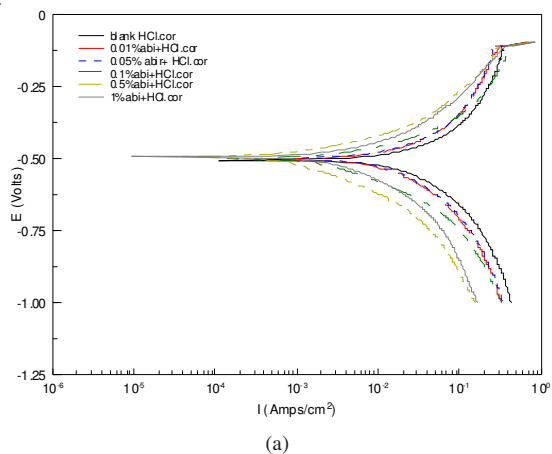


Fig. 3.  (a) Potentiodynamic polarisation curves and (b) Nyquist plots for mild steel corrosion in 0.5 M sulphuric acid with out and with different concentrations of *Abutilon indicum* extract

from these figures that additions of *Abutilon indicum* extracts to the acid solutions shift both the anodic polarization and cathodic polarization curves to lower values of current density ($I_{corr}$) indicating mixed mode of inhibition controlling both the anodic and cathodic reactions. It is noticed from Table-1 that the presence of *Abutilon indicum* does not change the $E_{corr}$ values, which indicates *Abutilon indicum* extract acts as a mixed type inhibitor. Generally, if the displacement in $E_{corr}$ is > 85 mV with respect to $E_{corr}$ in uninhibited solution, the inhibitor can be seen as a cathodic or anodic type. In this study, the maximum displacement of $E_{corr}$ is 33.65 mV in sulphuric acid medium. It is noted that the corrosion current densities were significantly reduced in the presence of *Abutilon indicum* inhibitor with increasing concentration and became only 1.06 mAmp $cm^{-2}$ (1 M HCl ) and 0.908 mAmp $cm^{-2}$ (0.5 M $H_2SO_4$) at 5 % v/v concentration shows decrease in metal dissolution. An increase in $R_p$ value with concentration shows good resistance offered by the solution. Inhibition efficiencies (IE %) were calculated using $R_p$ and $I_{corr}$ values and are given in the Table-1. Inhibition efficiency (%) calculated using $I_{corr}$ and $R_p$ values were found increasing with increasing concentrations till 5 % (v/v) and the maximum IE % ($I_{corr}$) obtained are 95.82 and 95.11 % for *Abutilon indicum* extracts in 1 M HCl and 0.5 M $H_2SO_4$, respectively.

**Electrochemical impedance measurements:** The electrochemical impedance spectroscopy provides a new method to characterize the film coverage on the electrode, which is related to charge transfer resistance ($R_{ct}$) and double layer capacitance ($C_{dl}$).

The Nyquist plots obtained for mild steel in 1 M HCl and 0.5 M $H_2SO_4$ with various concentrations of *Abutilon indicum* extract are shown as in Fig. 2(b) and Fig. 3(b), respectively. The impedance response consisted of characteristic semicircles for various acid solutions containing inhibitor whose size increases with inhibitor concentrations, shows that the dissolution of mild steel occurs under charge transfer control and these semicircles shown in the Nyquist plots are not perfect which may be attributed to the frequency dispersion as result of roughness and in homogeneity of the electrode surface[24-26]. It is clear from the plots that the impedance responses of mild steel in the HCl and $H_2SO_4$ solutions have significantly changed after the addition of *Abutilon indicum* extract to these corrosive solutions. The characteristic parameters associated to the impedance diagrams, $R_{ct}$, $C_{dl}$ and IE (%) are given in the Table-2.

The values of $R_{ct}$, $C_{dl}$ and inhibition efficiency for mild steel corrosion in 1 M HCl and 0.5 M $H_2SO_4$ are given in Table-2. The $R_{ct}$, charge transfer resistance increases while the value of $C_{dl}$ decreases with increase in inhibitor concentration and inhibition efficiency (IE %) is increasing with increase in concentration up to the concentration of 5 % (v/v) and then decreases at 10 % (v/v) in both the acid solutions.

The increase in impedance ($R_{ct}$) is due to the presence of phytochemical constituents at the metal-solution interface, which are organic in nature with low dielectric constant. When these organic molecules replaced the water molecules of high dielectric constant at the metal solution interface the relative dielectric constant decreases. Moreover the bulky phytochemical constituent's increases double layer thickness due to adsorption and resulting in high impedance to electron transfer.

TABLE-1
POTENTIODYNAMIC POLARISATION PARAMETERS FOR THE CORROSION OF MILD STEEL IN HCl
AND 0.5 M SULPHURIC ACID SOLUTIONS CONTAINING DIFFERENT CONCENTRATIONS OF ABI EXTRACT

| Conc. (v/v %) | 1 M HCl | | | | | 0.5 M H$_2$SO$_4$ | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $E_{corr}$ (mV) | $I_{corr}$ (mA cm$^{-2}$) | $R_p$ ($\Omega$ cm$^2$) | IE (%) $I_{corr}$ | IE (%) $R_p$ | $E_{corr}$ (mV) | $I_{corr}$ (mA cm$^{-2}$) | $R_p$ ($\Omega$ cm$^2$) | IE (%) ($I_{corr}$) | IE (%) ($R_p$) |
| Blank HCl | 506.42 | 25.347 | 1.79 | – | – | 522.65 | 18.58 | 2.62 | – | – |
| 0.1 | 501.54 | 10.318 | 2.53 | 59.291 | 29.25 | 517.52 | 15.604 | 3.88 | 16.01 | 32.44 |
| 0.5 | 500.86 | 10.236 | 2.55 | 59.62 | 29.81 | 508.48 | 5.76 | 6.38 | 69.00 | 58.86 |
| 1 | 501.49 | 3.366 | 6.9 | 86.72 | 74.06 | 505.34 | 5.739 | 10.86 | 69.11 | 75.84 |
| 5 | 494.55 | 1.06 | 20.94 | 95.82 | 91.46 | 490.42 | 0.908 | 31.98 | 95.11 | 91.74 |
| 10 | 494.45 | 3.929 | 7.63 | 84.56 | 76.57 | 489 | 1.136 | 29.18 | 93.89 | 91.00 |

TABLE-2
ELECTROCHEMICAL IMPEDANCE PARAMETERS FOR MILD STEEL CORROSION IN 1 M HCl AND 0.5 M
SULPHURIC ACID SOLUTIONS WITHOUT AND WITH DIFFERENT CONCENTRATIONS OF ABI EXTRACT

| Conc. (% v/v) | 1 M HCl | | | | 0.5 M H$_2$SO$_4$ | | | |
|---|---|---|---|---|---|---|---|---|
| | $R_{ct}$ ($\Omega$ cm$^2$) | $C_{dl}$ ($\mu$ cm$^{-2}$) | IE (%) $R_{ct}$ | IE (%) $C_{dl}$ | $R_{ct}$ | $C_{dl}$ | IE (%) $R_{ct}$ | IE (%) $C_{dl}$ |
| Blank | 3.117 | 343.64 | – | – | 3.181 | 348.32 | – | – |
| 0.1 | 4.911 | 293 | 36.53 | 14.7 | 7.96 | 289 | 29.31 | 17.03 |
| 0.5 | 20.792 | 199.7 | 85.01 | 41.9 | 10.529 | 249.15 | 69.79 | 28.47 |
| 1 | 28.603 | 167.41 | 89.1 | 51.3 | 14.477 | 222.46 | 78.03 | 36.13 |
| 5 | 149.49 | 97.773 | 97.91 | 71.5 | 82.248 | 75.134 | 96.13 | 78.43 |
| 10 | 62.896 | 96.229 | 95.04 | 72 | 33.55 | 109.83 | 90.52 | 68.47 |

**Mechanism:** The literature survey on phytochemical constituents revealed the presence of organic compounds such as amino acids, fatty acid, flavones, glucosides and phenol in leaves of *Abutilon indicum* and some of the major phytochemical constituents are given below.
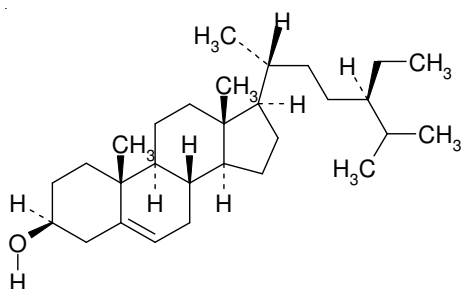
$$(CH_3)_2CHCH_2CH(NH_2)COOH$$

Valine (amino acid)

$$H_3C(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$$

Linoleic acid
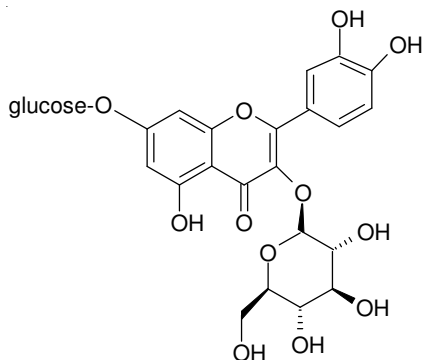


Quercetin-3-*o*-β-glucopyranoside



β-sistosterol

The inhibition of mild steel corrosion in HCl and H$_2$SO$_4$ is associated to adsorption of phytochemical constituents on to the metal surface. The functional groups such as -NH, C=O, -COOH and O-H and unsaturated C=C bond present in the structures might have involved in the formation of bonding between the constituents and the metal atom, leading to adsorption on active metal surface. The reaction between constituents Org$_{(sol)}$ and the adsorbed water molecule on the metal surface Fe(H$_2$O)$_s$ leading to the formation of Fe-Org complex (**Scheme-I**).

$$\text{Org}_{(sol)} + \text{Fe(H}_2\text{O)}_s \longrightarrow \text{Fe-Org Complex} + \text{H}_2\text{O}_{(sol)}$$
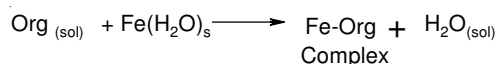
**Scheme-I**

Adsorption, for example, could also occur through quercetin derivative with multiple -OH groups. The coordination bond formed between Fe atom and one of the oxygen atoms of hydroxyl group of quercetin-3-*o*-β-gluco pyranoside is given in **Scheme-II**. **Scheme-II** shows formation of only one bond between quercetin-3-*o*-β-glucopyranoside and metal atom. With several OH groups in this single molecule, the same or different metal atoms can bind through available active centers, leading to chelation and cross linked structure with enhanced stability. There is a possibility of inter molecular hydrogen bonding results in larger molecular size promoting larger surface coverage and thereby improving corrosion inhibition ability.

Amino acids are reported to be effective mild steel corrosion inhibitors in acid solutions[24-26]. Regarding amino acids present in *Abutilon indicum* extract, existing as cations as -RNH$_3^+$ in acid solutions, may get adsorbed through already adsorbed Cl$^-$ anions in HCl or SO$_4^{2-}$ ion in H$_2$SO$_4$ or by loosing H$^+$ ions followed by interaction with the ferrous atom through lone pair of electrons on the hetero atoms, may get adsorbed directly on to the metal surface and thus enhance inhibition.
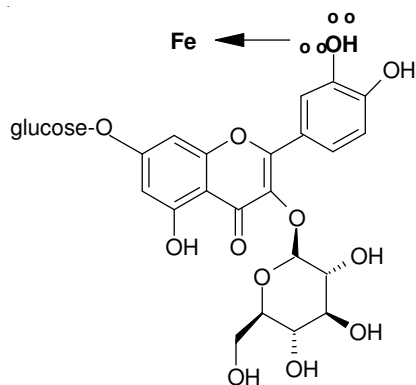
**Scheme-II:** Interaction between quercetin derivative and iron atom

Otherwise the protonated amino acids may compete with cathodic reaction of $H^+$ ion reduction and have control over cathodic reaction. The other constituents like fatty acids and flavones present in the extract may exist as neutral species may bind through active centers like oxygen or double bond or aromatic ring and contribute to adsorption, leading to formation of protective coating. Hence, the overall inhibition action of *Abutilon indicum* extract can be attributed to synergistic effect of all the constituents present in the acid extract.

### Conclusion

Potentiodynamic results revealed corrosion inhibitive nature of *Abutilon indicum* extract in both the acid solutions as mixed type. The inhibitory action of *Abutilon indicum* extract was due to the synergistic effect of all the constituents present in the acid extract.

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