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Inhibition of corrosion of mild steel in hydrochloric acid by the leaf juice of chanca piedra (*Phyllanthus niruri)* plant

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Abstract

The inhibition of corrosion of mild steel in 0.5M, 1.0M and 2.0M hydrochloric acid solutions by chanca piedra's juice obtained from squeezed fresh leaves and added to the acid solutions at 15ml and 20ml per litre has been studied using coupons. Corrosion inhibition was obtained. The inhibition rate appears to attenuate from about the fourth hour upwards with a transition to a constant corrosion rate presentation. This indicates a possible depletion of the corrosion inhibiting constituents following the apparent completion of the reactions that produce corrosion products that adhere to the surface of the mild steel. A maximum corrosion efficiency of 70 percent was attained. It is proposed that a higher corrosion inhibition efficiency level could be attained by concentrating the leaf juice by water evaporation from it. The mechanisms of corrosion inhibition are proposed to be by adsorption through coordinate type of linkage facilitated by dipoles presented by elements like nitrogen and oxygen found in chanca piedra's constituents like the alkaloids. Alternatively adsorption can be provided by organic compounds containing unsaturated bonds that are prevalent in many of the chanca piedra's constituents for example, rutin, or by organic compounds containing very large molecules like the tannins also found in chanca piedra.

Keywords: Corrosion inhibition; Chanca piedra; Mild steel

1. Introduction

Corrosion inhibitors are added to a corrosion system to decrease or eliminate anodic dissolution. A good example of their application is in acid pickling operations that are employed to remove oxide scales formed during metal working operations. An effective acid inhibitor minimizes acid attack on the base metal once the scale has been removed, protecting the surface, optimizes acid utilization and even proves effective in removing scales more quickly than the uninhibited acid (Riggs and Hurd, 1968; Nguyen et al., 1999). Furthermore many current corrosion control methods use coatings and conversion layers that contain toxic and environmentally hazardous materials, for example, chromates. These are very good inhibitors that are added as dissolved Cr^{+4} ions into an aqueous environment, or are added to paints as a pigment or are applied to a surface as a chromate conversion coating (CCC). These chromates possess an important inhibition propensity of promoting self-healing of corroding exposed areas of metal substrate (Zhao et al., 2001). Hydrazine is another important inhibitor that is also toxic. Their carcinogenic and toxic properties are currently beginning to limit their applications. There is therefore a need to find non-toxic and environmentally friendly replacements that are compatible with current industrial technologies. A possible replacement could be offered by juice extracts of plants that have an array of constituents with known corrosion inhibition qualities. Chanca piedra, *phyllantus niruri* popularly called stonebreaker because of its use to dissolve calcium oxalate crystals (gall stones and kidney stones), (Campus et al., 1999; freitas, 2002), is a possible candidate. Chanca piedra is a weed that grows extensively in the tropics.

The main phytochemicals in chanca piedra are: alkaloids, astragalin, brevifolin, carboxylic acids, corilagin, cymene, ellagic acid, ellagitannins, gallocatechins, geranin, hypophyllanthin, lignans, lintetralins, lupeols,methyl salicylate, niranthin, nirtetralin, niruretin,nirurin, nirurine, niruriside, norsecurinines, phyltetralin, repandusinic acids, quercetin, quercetol, quercitrin, rutin, saponins, triacontanal, and tricontanol (Taylor, 2003). These constituents of *phyllanthus niruri* (chanca piedra) are placed in three primary groups: lignans (phyllanthine and hypophyllanthine), alkaloids and flavonoids (http://www.arjunanatural.com). These are essentially organic compounds and they are expected to exhibit the characteristics of adsorption on the local anodic and /or cathodic sites to provide barriers between the metal surface and the environment. The mechanism of corrosion inhibition may be by coordinate type of linkage via the availability of lone pairs of electrons as are provided by elements like nitrogen, oxygen and sulphur for example. These elements are found in alkaloids etc. These elements enable the formation of the positive (nitrogen) and negative (oxygen and sulphur) of the dipole. Alternatively adsorption can be provided by organic compounds containing unsaturated bonds that are prevalent in many of the chanca piedra's constituents, rutin, for instance. Another adsorption mechanism can be by organic compounds containing very large molecules like the tannins also found in chanca piedra.

It is pertinent therefore to highlight a brief representative overview of some of the constituents of chanca piedra that may play corrosion inhibition roles.

Alkaloids: Strictly speaking an alkaloid is a naturally occurring amine produced by a plant (Carey, 2006.). They are usually derivatives of amino acids, were originally used to describe any nitrogen-containing base and most of them have a very bitter taste (nicotine is an exception). They are basic and form water-soluble salts with acids. Amines are known to generally exhibit corrosion inhibition properties (Davis, 2001). It is known that historically, the first proprietary inhibitors were fatty imidazolines made from by-product of fatty acids and polyethylene amines (Davis, 2001). Phyllanthine, hypophyllanthine, saponin and other alkaloids would therefore be expected to exert corrosion inhibition influence on mild steel.

Flavonoids: They are polyphenolic compounds possessing fifteen carbon atoms; two benzene rings joined by a linear three carbon chains. They have six major classifications: chalcones, flavones, flavanols, flavanone, anthocyanin, isoflavonoids. They are more commonly known for their antioxidant activity. Quercetin, rutin, astralagin and gallocatechin that are constituents of chanca piedra are flavonoids.

Rutin: Rutin is an antioxidant that has a high affinity for Fe^{2+} ions (http://en.wikipedia.org/wiki/Rutin). Quercetin is the most active of the flavonoids exerting a portent antioxidant activity (http://en.wikipedia.org/wiki/Queretin).

Lignans: Plant lignans are polyphenolic substances derived from Phenylalanine via dimerization of substituted cinnamic alcohols to a dibenzylbutane skeleton 2 (http://en.wikipedia.org/wiki/Lignan). Bonding with the OH- ions to form an insoluble metal substrate adherent compound could be a relevant cathodic reaction inhibition mechanism.

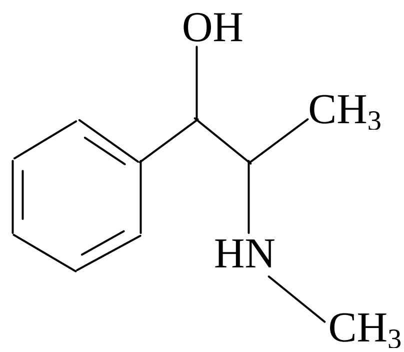

Fig.1. Ephedrine.

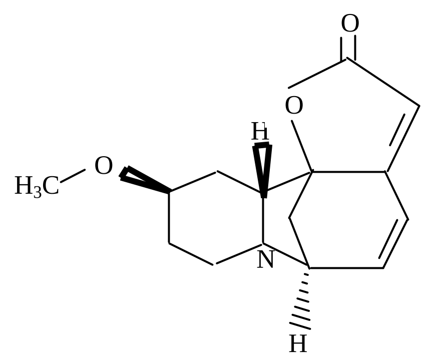

Fig. 2. Phyllanthine, an alkaloid.

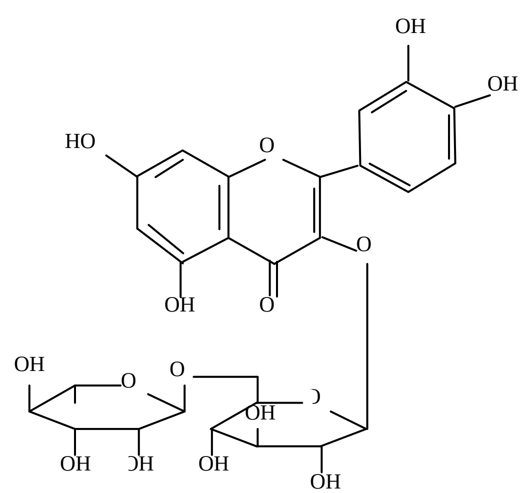

Fig. 3. Rutin, a flavonoid.

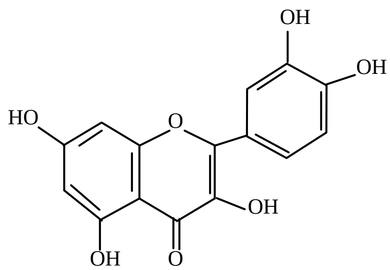

Fig. 4. Quercetin, a flavonoid.

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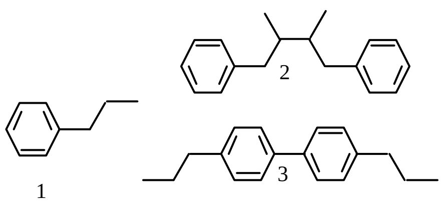


Fig. 5. Dimerization of substituted cinnamic alcohol to dibenzylbutane skeleton, (2).

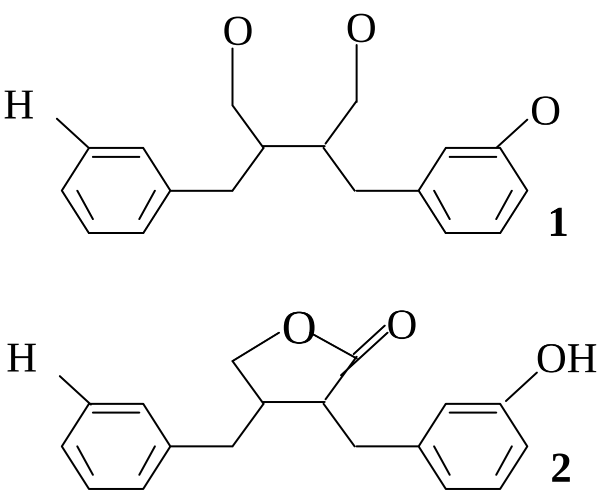


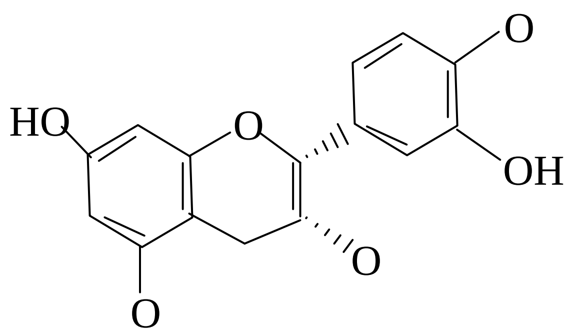
Fig. 6. 1, enterodiol and 2, enterolactone.

Other polyphenolic constituents of chanca piedra that may be relevant in corrosion inhibition reactions are ellagic acid catechin and tannins.

Cathechins: are powerful polyphenolic antioxidant plant metabolites, specifically flavonoids called flavan-3-ols. Epigallocatechin contains an additional phenolic hydroxyl group when compared to epicatechin.

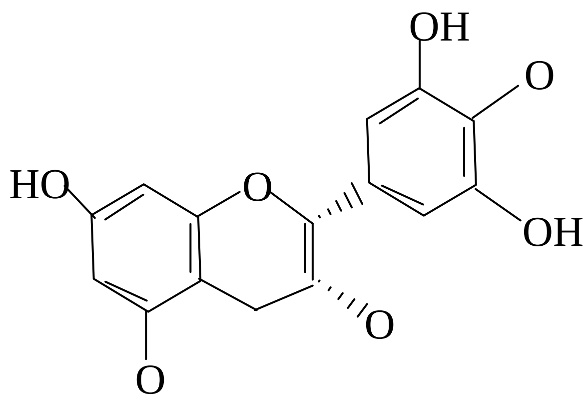
Ellagic acid: is another polyphenolic antioxidant found in chanca piedra (http://en.wikipedia.org/wiki/ellagic_aicd).

Tannins: Tannins are polyphenolic compounds containing sufficient hydroxyl and other groups (such as carboxyls) to form strong complexes with proteins and other macromolecules. They are bitter tasting and have molecular weights ranging from 500 to over 20,000 (http://en.wikipedia.org). While hydrolysable tannis and most condensed tannins are water soluble, some very large condensed tannins are insoluble. Geraniin, with the chemical formula, $C_{41}H_{28}O_{27}.7H_2O$ (Luger et al. 1998), and therefore a molecular weight of 1078, is a tannin contained in chanca piedra.



(1)

Fig. 7. (1). Epicatechin (EC).



(2)

Fig. 7. (2) Epigallocatechin (EGC).

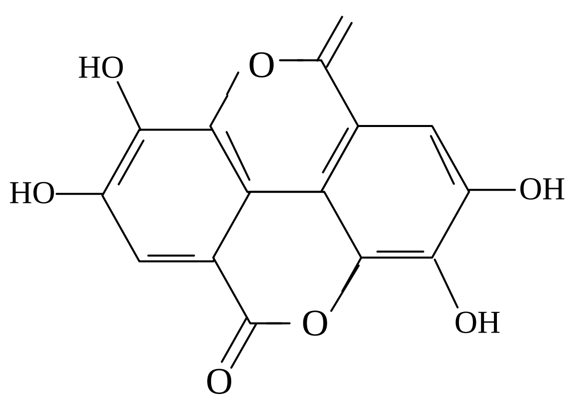


Fig. 8. Ellagic acid.

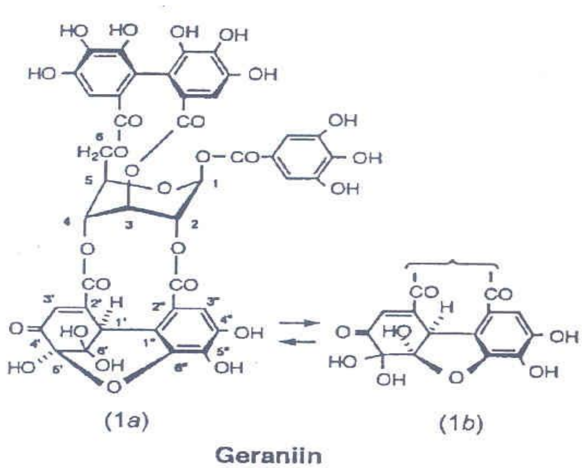
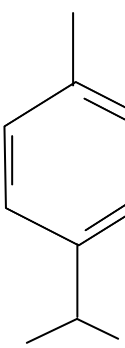


Fig. 9. Geraniin.

Most of the other constituents may more or less belong to any of any of the groups highlighted above. For instance, phyllanthin, hypophyllanthin niranthin, nirtetralin, and lintetralin are lignans (Elfahmi, et al., 2006). Other compounds of commensurate significance vis-a- vis their high concentrations in chanca piedra (Table 1) are cymene and methyl salicylate.
Cymene: Cymene is a naturally occurring aromatic organic compound, an essential oil that is insoluble in water but mixes with ethanol. Its structure consists of a benzene ring para-substituted with a methyl group and an isopropyl group.



Cymene

Fig. 10. Cymene.

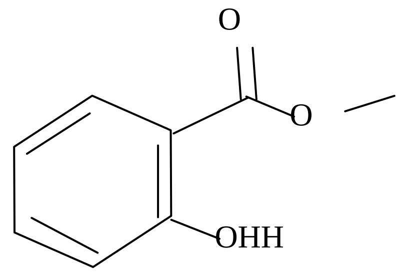


Fig. 11. Methyl salicylate.

Methyl salicylate: Methyl salicylate also known as salicylic acid methyl ester, oil of wintergreen, betula oil, methyl-2-hydroxybenzoate, is a natural product of many species of plants. It is therefore seen that chanca piedra has a variety of corrosion inhibition constituents that could synergistically contribute to corrosion inhibition.

2. Materials and methods

Uniform coupon size of 40mm x 30mm x1.5mm was cut. The coupons were then pickled with dilute hydrochloric acid and were copiously cleaned and washed in acetone before storage in desiccators. The chanca piedra leaves were obtained from the surrounding vegetation and were squeezed to extract their juice. For the experimental set up, some of the coupons were immersed in 0.5M, 1.0M, 1.5M and 2.0M HCl to which chanca piedra leaf juice had been added at 15ml/litre or 20ml/litre as the case may be. In each of these cases similar setups, which had no chanca piedra's leaf juice additions were made to provide comparison for results. Another arrangement was provided where no leaf juice was added to the acid but the coupons themselves were coated with the leaf juice and allowed to dry before their immersion in the acid media. The experimental duration was seven hours.

The mild steel used has the following composition.

%C	%Si	%S	%P	%Mn	%Ni	%Cr	%Mo	%Cu	%As	%Sn	%Co	%Al	%Zn
0.030	0.006	0.015	0.010	0.253	0.026	0.013	0.005	0.087	0.007	0.010	0.003	0.0007	0.005

3. Results and discussions

3.1 Effect of addition of chanca piedra's leaf juice extract on the corrosion of mild steel immersed in different concentrations of hcl

The results are presented in Figs. 1 to 4. Figure 1 shows the effect of chanca piedra leaf juice extract on the corrosion inhibition of mild steel. The inhibition rate appears to attenuate from about the fourth hour upwards with a transition to a constant corrosion rate presentation. This indicates a possible depletion of the corrosion inhibiting constituents following the apparent completion of the reactions that produce corrosion products that adhere to the surface of the mild steel. The same trend is approximated for Fig. 2 for acid concentration of 1.0M. Here the onset of inhibition attenuation rate is at about three hours signalling the depletion of the corrosion inhibition constituents and maintenance of an essentially constant corrosion rate as in Fig. 1.

For 2.0M HCl, Fig. 3, that trend of corrosion rate attenuation to constant corrosion rate transition appears to be approached in about six hours for 20ml per litre of inhibitor.

Table 1
Brief resume of some compounds in chanca piedra

Alkaloids	Flavonoids	Tannins	Carboxylic acids
(i) They contain Nitrogen & are usually derived from amino acids. (ii) They are bitter tasting & are generally white solids (except nicotine that is a brown liquid. (iii) They (caffeine excepted) give precipitates with heavy metal iodides. (iv) They are basic and form water-soluble salts with acids. Examples in Cp Phyllanthine, hypophyllanthine, saponin	(i) They are polyphenolic compounds possessing 15 carbon atoms; two benzene rings joined by a linear three carbon chains. (ii) They have six major classifications: (chalcones, flavones, flavanols, flavanone, anthocyanin, isoflavonoids). (iii) They are more commonly known for their antioxidant activity Examples in Cp astragalin (flavonol glucoside) astragaline gallocatechin	(i)They are polyphenolic compounds containing sufficient hydroxyl and other groups (such as carboxyls) to form strong complexes with proteins and other macromolecules. (ii)They are bitter tasting and have molecular weights ranging from 500 to over 20,000 [16,]. (iii) While hydrolysable tannins and most condensed tannins are water soluble, some very large condensed tannins are insoluble. Examples in Cp Corilagin Geranin Ellagitannins Lignans Lintetralin Niranthin Nirtetralins	(i)They are organic acids characterized by the presence of the carboxyl group. (ii) In water they form the equilibrium: $RCOOH=RCOO^- + H^+$ Examples Cp Brevifolin

The characterization of some constituent compounds in chanca piedra with their percentage concentrations is given in Table 2 below.

Table 2
Characterization of Some Compounds in Chanca Piedra *(Phyllanthus niruri)* [6]

S/no.	Compound	Chemical type	Plant part	Quantity
1	Astragalin	Flavonone	Leaf	-
2	Brevifolin	Coumarin (carboxylic acid)	Entire plant	00.00067%
3	Corilagin	Tannin	Entire plant	00.0007%
4	Cymene	Monoterpene	Essential oil	11.0%
5	Ellagic acid	Coumarin	Entire plant	00.01081%; 0.09729%
6	Gallocatechin	Flavonoid	-	-
7	Geraniin	Tannin	Entire plant	00.23243%
8	Hypophyllanthin	Lignan	Leaf	00.05%; 00.14%; 00.167%
9	Lintetralins	Lignan	Leaf/ entire plant	00.0002%; 00.00025%;; 00.000335%; 00.0005%; 00.0015%; 00.002%; 00.02%
10	Lupeols	Triterpene	-	-
11	Methyl salicylate	Benzenoid	Essential oil	0.5% - 7.2%
12	Niranthin	Lignan	Leaf	00.0009% ; 00.043%
13	Nirtetralin	Lignan	Leaf	00.0009%; 00.093%
14	Nirurin	Flavanone	Entire plant	00.04%
15	Nirurine	Indolizidine alkaloid	Aerial parts	00.00398%

16	Niruriside	Phenylpropanoid	Flower + leaf + stem	00.016%
17	Norsecurinines	Pyrrolizidine alkaloid	Entire plant	-
18	Phyllanthin	Lignan	Leaf, aerial parts	00.04%; 00.11%; 00.18%; 00.2%; 00.325%
19	Phyllanthine	Indolizidine alkaloid	-	-
20	Phyllanthenol	Triterpene	Aerial parts	00.002%
21	Phyllochrysine	Indolizidine alkaloid	Leaf + stem	-
22	Phyltetralin	Lignan	Leaf	00.14%
23	Repandusinic acids	tannin	Entire plant	00.11709%
24	quercetin	flavanol	Entire plant	-
25	quercetrin	flavanol	Entire plant	-
26	Rutin	flavanol	Entire plant	-
27	Triacontanal	Alkanal C5 or more	Aerial parts	00.006%
28	triacontanol	Alkanol C5 or more	Aerial parts	00.056%

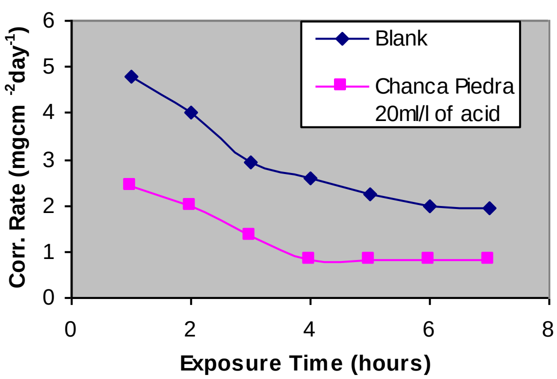


Fig.1. Effect of addition of chanca piedra's leaf juice on corrosion of mild steel coupons immersed in 0.5m HCl.

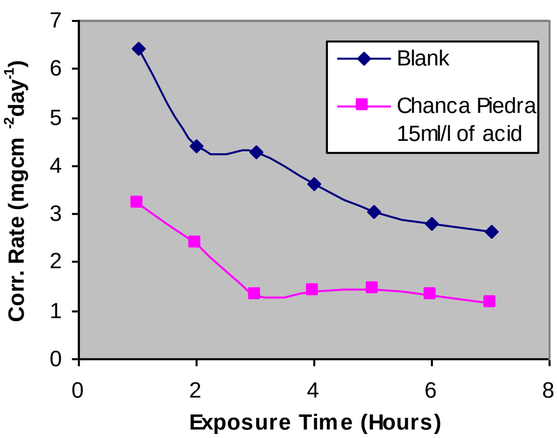


Fig.2. Effect of addition of chanca piedra's leaf juice on corrosion of mild steel coupons immersed in 1.0m HCl.

Fig. 4 shows the comparative effect of chanca piedra's leaf juice on the corrosion inhibition of mild steel immersed in 0.5M. 1.0M and 2M HCl is shown in fig. 4. . It is seen that the lowest corrosion rate of about $0.75 mgcm^{-2}d^{-1}$ was attained for the case of addition of 20ml/l of acid to 0.5M HCl. It is clear as has been pointed out that this is most probably consistent with the quantitative availability of the corrosion inhibiting constituents of chanca piedra.

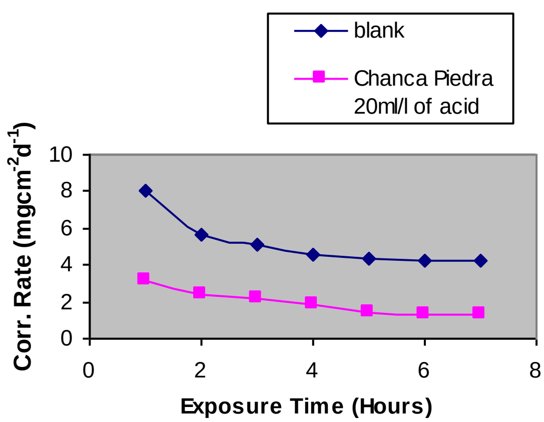


Fig.3. Effect of addition of chanca piedra's leaf juice on corrosion of mild steel coupons immersed in 2.0m HCl.

The near parallel presentation of the 0.5M HCl corrosion curve in contrast to those of the 1.0M HCl and 2.0M HCl curves lends credence to the formation of a more uniform and more extensively adherent corrosion products courtesy the more quantitative availability of the corrosion inhibiting constituents of the leaf juice of chanca piedra.

Fig.5 shows that maximum inhibition efficiency of about 70 percent was attained for the 0.5M HCl and 1.0M HCl curves containing 15ml/l and 20ml/l respectively of chanca piedra's leaf juice. The 2.0M HCl curve trailed this maximum efficiency level slightly. Table 2 shows that the concentrations of the possible corrosion inhibiting compounds in chaca piedra are very small. Therefore a higher corrosion inhibition efficiency level could be attained by concentration of the leaf juice as obtained from from its squeezed fresh leaves by water evaporation from the juice.

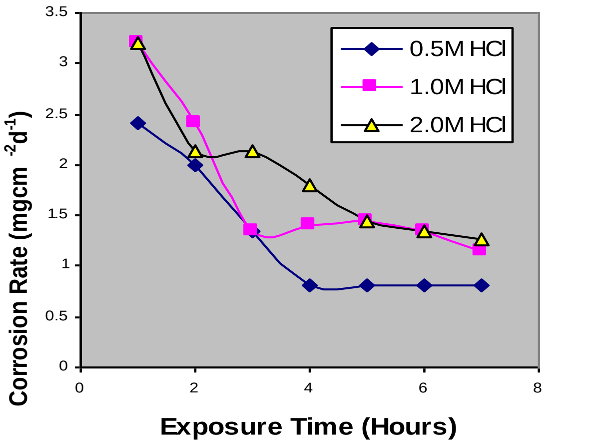


Fig.4. The comparative effect of chanca piedra's leaf juice on corrosion inhibition of mild steel immersed in 0.5m, 1.0m and 2.0m HCl.

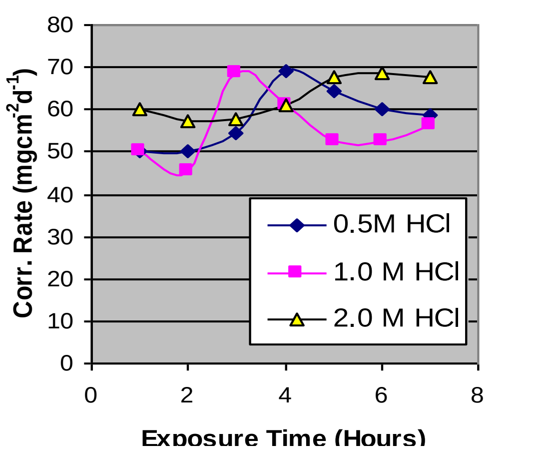


Fig.5. Chanca piedra's corrosion inhibition efficiency for mild steel immersed in 0.5m, 1.0m and 2.0m HCl.

4. Conclusion

Chanca piedra leaf juice as obtained from its squeezed fresh leaves therefore provides appreciable corrosion inhibition of mild steel in hydrochloric acid. The maximum corrosion inhibition efficiency was 70 per cent. The mechanism could essentially be by adsorption provided by coordinate type of linkage via the availability of lone pairs of electrons provided by nitrogen and oxygen in the alkaloids of chanca piedra for example etc. These elements enable the formation of the positive (nitrogen) and negative (oxygen) of the dipole. Alternatively adsorption mechanism could be provided by organic compounds containing unsaturated bonds that are prevalent in many of the chanca piedra's constituents. Another adsorption mechanism can be by organic compounds containing very large molecules like the tannins also found in chanca piedra. A higher corrosion inhibition efficiency level could be attained by concentrating the leaf juice by water evaporation from it.

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