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Corrosion Behavior of Ti-6Al-4V Alloy in Different Media

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Abstract

In this work the corrosion behavior of Ti-6Al-4V alloy was studied by using galvanostatic measurements at room temperature in different media which includ sodium chloride (food salt), sodium tartrate (presence in jellies, margarine, and sausage casings,etc.), sodium oxalate (presence in fruits, vegetables,etc.), acetic acid (presence in vinegar), phosphoric acid (presence in drink), sodium carbonate (presence in 7up drink,etc.), and sodium hydroxide in order to compare.

Corrosion parameters were interpreted in these media which involve corrosion potential(E_{corr}) and corrosion current density (i_{corr}), since the results of (E_{corr}) indicate that Oxalate ions are more corrosive than other materials while the results of (i_{corr}) indicate that NaCl is more corrosive than other materials. Cathodic and Anodic Tafel slopes that were used to calculate the polarization resistance (Rp) to know which materials effect on Ti-6Al-4V alloy uses in dental materials and the results of (Rp) were: Na_2CO_3 >Oxalate >H_3PO_4 >CH3COOH >NaOH >Tartrate >NaCl.

The change in free energy (ΔG) and rate of corrosion in (mpy) were calculated, and the results of rate indicate that increasing in the following sequences: NaCl>Tartrate >NaOH >Oxalate> CH_3COOH> H_3PO_4> Na_2CO_3.

Keywords: *Corrosion, titanium alloy, free energy, tafel method.*

1. Introduction

Titanium and its alloy provide excellent resistance to general and localized attack under most oxidizing, neutral and inhibited reducing conditions in aqueous environments and remain passive under mildly reducing conditions, although they may be attacked by strongly reducing or complexing media . Titanium is especially known for its outstanding resistance to chlorides and other halides generally present in most process streams. [1]

A study of the corrosion resistance of titanium is basically a study of the properties of the oxide film. The oxide film on titanium is very stable and is attacked only by a few substances including hot concentration reducing acids, most notably, hydrofluoric acid. Titanium is capable of healing this film almost instantaneously in every environment where a trace of moisture or oxygen is present because of titanium's strong affinity for oxygen.

Anhydrous conditions in the absence of a source of oxygen should be avoided since the protective film may not be regenerated if damaged. Figure (1) shows the pourbaix diagram of Ti/H_2O system.

There are many studies about corrosion of Ti-alloy from many authors, Smith BJ and co-workers studies of fretting corrosion experiments were performed on Ti-6Al-4V similar metal, pin-on-flat fretting couple, relative displacement amplitudes between the fretting specimens were directly measured using LVDT`s. [2]

Latifa Kinani, Abdelilah Chtani and co-workers studies the effect of eugenol on the titanium corrosion in artificial saliva enriched with eugenol at different concentration. The corrosion behavior and titanium surface characterization were investigated by electrochemical measurements. [3]

M.Nakagaw and co-workers studies titanium which is used as a metal for biocompatible materials such as dental implants or restorations because of its excellent chemical stability [4].

Chohayeb A.A. and co-workers studies the corrosion behavior of couples consisting of titanium and one of the dental casting alloys, Ni-Cr, Co-Cr, Au-Pd-Ag or Pd-Ag. Alloys and Ti were studied using materials in the cast condition. Potentiodynamic polarization techniques were used for making electrochemical measurements on the alloys and couples in artificial saliva at 37°C. Corrosion potentials, corrosion rates and general corrosion behavior, including passivation range and breakdown potentials, were determined for all materials and couples. [5]

In this study we choose some media which have an effect on the titanium alloy in the field of dentistry such as NaCl, Oxalate, Tartrate, Carbonate, Acetic acid, Phosphoric acid and NaOH.

2. Experimental Part

2.1. Materials and Chemicals

Ti-6Al-4V alloy was cut into square shape with (1cm^2) area and (1cm) thickness, and made into electrode by pressing a copper wire into a hole on one side and then insulating all but one side with an epoxy resin (Fig. 1).

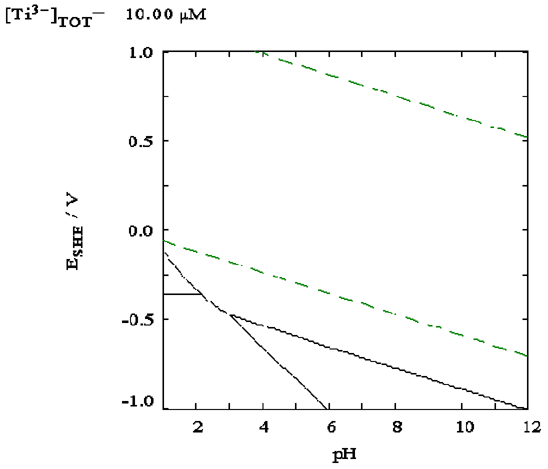
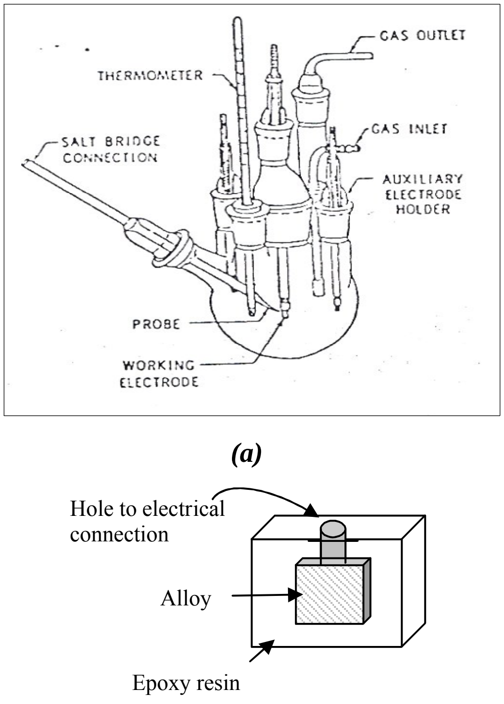


Fig.1. Pourbaix Diagram of Ti/H_2O System.

The exposed area was grinding on emery papers 400,600 and 1000-mesh grit. A braiding was done by power-driven wheels. The electrochemical cell was of the usual type (Fig. 2) with provision for working electrode (Ti-alloy), auxiliary electrode (Pt electrode), and a Luggin capillary for connection with an SCE reference electrode.



(a)

(b)

Fig.2. (a)-The Standard Corrosion Cell (ASTM) [7]. (b)- Working Electrode.

Many materials were used in this work such as materials that have effects on Ti-alloy in dentistry field and some of them have general effect. These materials are shown in table (1).

Table 1,
The Molecular Weight and Purity of Materials.

Materials	M. wt (g.mol^{-1})	Concentration
Sodium hydroxide	40.00	0.1M
Sodium chloride	58.44	0.1M
Potassium hydrogen Tartrate	188.18	0.1M
Acetic acid	60.0	10%M
Phosphoric acid	68	4%M
Sodium carbonate	106	0.1M
Sodium oxalate	134	0.1M

2.2. Galvanostatic Measurement

The galvanostatic was measured using WENKING M Lab. from BANK ELEKTRONIK (Germany). The galvanostatic scan started about ¼ hour after the electrode immersion in the test solution, the range of voltage depending on OCP value versus the saturated calomel electrode.

Both the cathodic and anodic curves were obtained with decreasing and increasing polarization, and this was repeated several times.

The polarization curve obtained involved the cathodic and anodic regions. Extensive data could be derived from the detailed analysis of each polarization region using extrapolated method to determine both the corrosion current density (i_{corr}) and corrosion potential (E_{corr}) .

3. Results and Discussion

3.1. Corrosion Behavior

The study of polarization behavior of Ti-6Al-4V alloy in different media involves the active region which consists of cathodic and anodic region to calculate the corrosion potentials and corrosion current densities by using linear Tafel method.

Figs. (3) to (9) show the polarization curves of Ti-6Al-4V in different media. The corrosion parameters of Ti-6Al-4V in different media were listed in table (2).

The cathodic region represents the reduction reaction which occurs on the surface of alloy according to the medium of corrosion.

$$2H^+ + 2e \rightarrow H_2 \quad \text{(in the acidic medium)} \quad \ldots(1)$$

$$\tfrac{1}{2} O_2 + H_2O + 2e \rightarrow 2OH^- \quad \text{(in the neutral and basic solution)} \quad \ldots(2)$$

While the anodic region represent the dissolution of metal or metals in alloy to ions according to the following reactions:

$$Ti \rightarrow Ti^{2+} + 2e \quad \ldots(3)$$

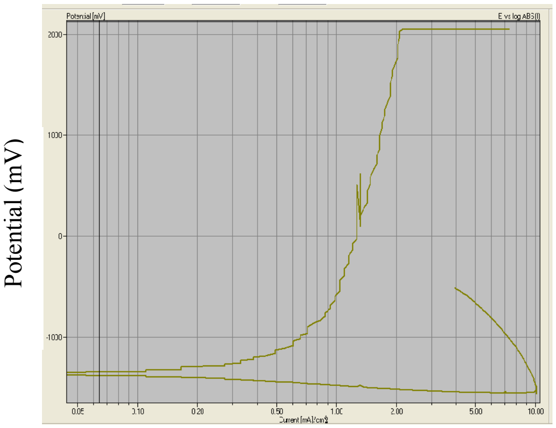


Fig.3. Polarization Curve of Ti-6Al-4V Alloy in NaCl Solution at Room Temperature.

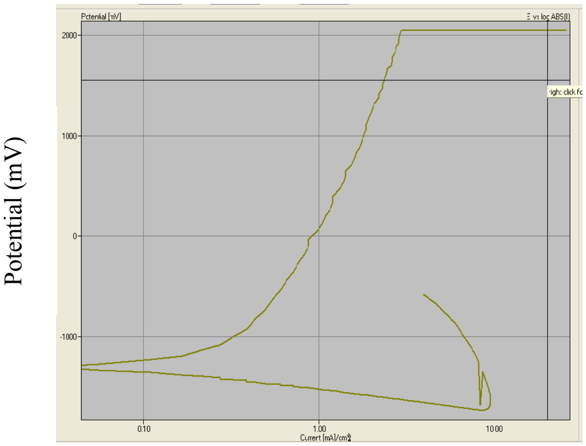


Fig.4. Polarization Curve of Ti-6Al-4V Alloy in Sodium Tartrate Solution at Room Temperature.

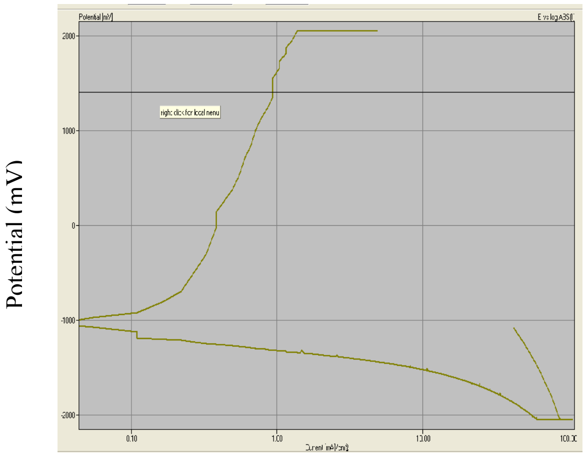


Fig.5. Polarization Curve of Ti-6Al-4V Alloy in Sodium Hydroxide Solution at Room Temperature.

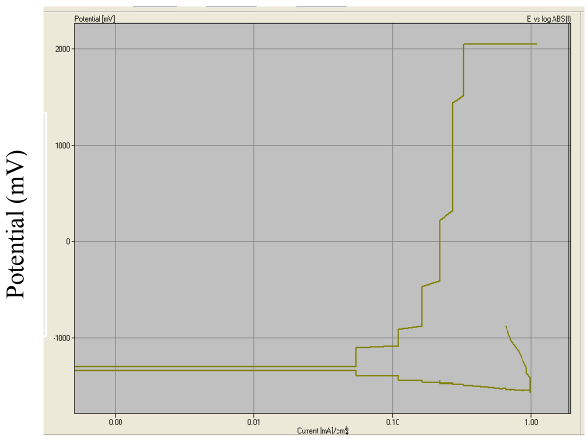


Fig.6. Polarization Curve of Ti-6Al-4V Alloy in Sodium Oxalate Solution at Room Temperature.

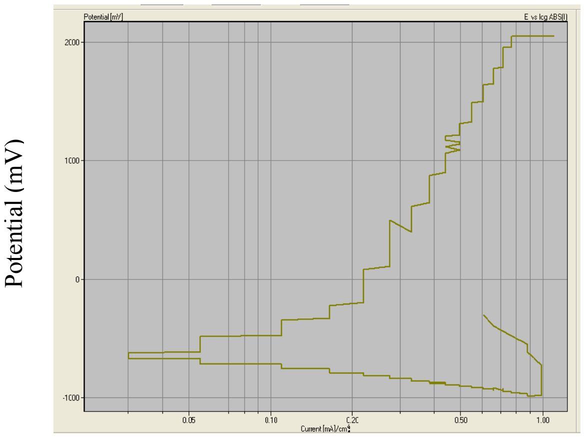


Fig.8. Polarization curve of Ti-6Al-4V Alloy in H_3PO_4 Solution at Room Temperature.

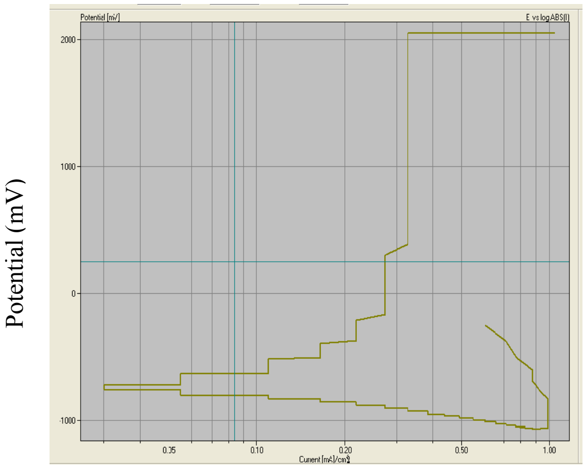


Fig.7. Polarization Curve of Ti-6Al-4V Alloy in CH_3COOH Solution at Room Temperature.

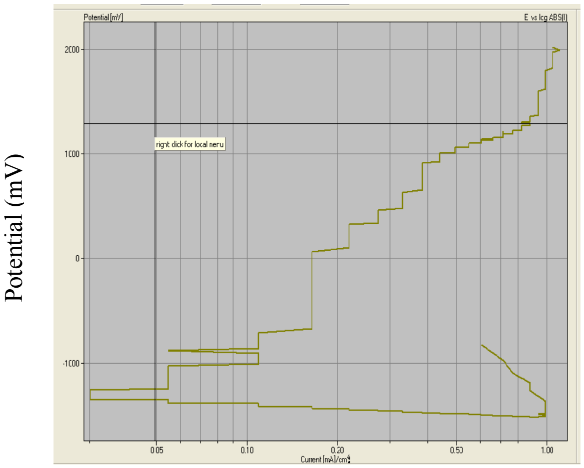


Fig.9. Polarization Curve of Ti-6Al-4V Alloy in Na_2CO_3 Solution at Room Temperature.

Table 2,
The Corrosion Parameters of Ti-6Al-4V in Different Media.

Medium	Corrosion Potential $-E_{corr}$(mV) (SCE)	Corrosion Current Density i_{corr} ($\mu A.cm^{-2}$) $*10^{-3}$	-bc ($mV.dec^{-1}$)	+ba ($mV.dec^{-1}$)	$R_p x10^{-7}$ ($\Omega.cm^{-2}$)
NaCl	148.26	1357.6	113.0	206.6	0.2330
Sodium tartarate	1317.3	160.68	199.3	666.5	4.1460
NaOH	1029.2	114.83	221.7	741.3	6.4530
Sodium Oxalate	1324.2	75.48	261.7	678.9	10.866
Acetic acid	736.8	63.95	171.5	333.5	7.6900
Phosphoric acid	639.9	63.91	216.3	452.5	9.9420
Na_2CO_3	1319.9	61.43	225.9	862.0	12.652

3.2. Corrosion Parameters

The corrosion potential (E_{corr}) of material in a certain medium at a constant temperature is a thermodynamic parameter which is a criterion for the extent of the corrosion feasibility under the equilibrium potential (in opposite sign) of the cell consisting of the working electrode and the auxiliary electrode when the rate of anodic dissolution of working electrode material becomes equal to the rate of the cathodic process that take place on the same electrode surface. From the results of (E_{corr}) in Table (2), it can be shown that:

$-E_{corr}$ (mV) Oxalate>Na_2CO_3>Tartrate>NaOH> CH3COOH>H_3PO_4>NaCl

It is shown that (E_{corr}) value is a measure for the extent of the feasibility of the corrosion reaction on purely thermodynamic basis.

The corrosion current density (i_{corr}) is a kinetic parameter and represents the rate of corrosion under specified equilibrium condition. At constant temperature for Ti-6Al-4V alloy, (i_{corr}) values vary with variation of ions present in medium and take the following sequences:

i_{corr} (µA/cm2) NaCl> Tartrate >NaOH>Oxalate> CH3COOH> H_3PO_4>Na_2CO_3

From deep analysis of the cathodic and anodic regions of the polarization curves for Ti-6Al-4V alloy in different media, it was possible to derive data concerning the cathodic and anodic Tafel slopes. From the results which shown in table (2), values of Tafel slopes (bc & ba) for both cathodic and anodic reactions were generally close to or higher than 120 mV/decade.

A cathodic Tafel slope of -120 mV/decade in general diagnostic of a discharge – chemical desorption mechanism for hydrogen evolution reaction of the cathode in which the proton discharge is the rate – determining step.

Where the two basic reactions paths for hydrogen evolution reaction are:

$$H_3O^+_{\text{(Bulk solution)}} \xrightarrow{\text{Diffusion}} H_3O^+_{\text{(Metal/solution interface)}} \quad \ldots(4)$$

This is followed by the discharge step:

$$H_3O^+ + M + e \rightarrow M\text{–}H + H_2O \quad \ldots(5)$$

Another parameter can be calculated from corrosion measurement is the polarization resistance (R_p) which represent the measure of the resistance of the metal to corrosion in the solution in which the metal is immersed.

The polarization resistance (R_p) can be determined from Stern- Geary equation [6]:

$$R_p = \left(\frac{dE}{di}\right)_{i=0} = \frac{b_a b_c}{2.303(b_a + b_c)i_{corr}} \quad \ldots(6)$$

Where E is the applied potential (Volt) , i is the current density (A.cm^{-2}) and b_c, b_a are cathodic and anodic Tafel slops respectively.

The values of R_p are presented in table (2) which indicates that the corrosion in the sodium carbonate (Na_2CO_3) solution resists more than the other solutions. The values of polarization resistance in the other solution take the following sequence:

R_p (Ω.cm^{-2}) Na_2CO_3 >Oxalate >H_3PO_4> CH3COOH >NaOH >Tartrate >NaCl

3.3. The Free-Energy Change (ΔG)

The free-energy change accompanying an electrochemical reaction can be calculated by the following equation [7]:

$$\Delta G = -nFE \quad \ldots(7)$$

Where ΔG is the free-energy change, n is the number of electrons involved in the reaction, F is the faraday constant, and E equals the cell potential.

Under standard conditions, the standard free energy of the cell reaction ΔG is directly related to the standard potential difference across the cell, E^0

$$\Delta G^0 = -nFE^0 \quad \ldots(8)$$

Electrode potential can be combined algebraically to give cell potential.

For a galvanic cell, which operates spontaneously, a positive cell voltage will be obtained if the difference is taken in the usual way, as

$$E_{cell} = E_{cathode} - E_{anode} \quad \ldots(9)$$

The free energy change in a galvanic cell, or in a spontaneous cell reaction, is negative and the cell voltage is positive. In electrolytic cell, the reaction is driven in the non spontaneous direction by an external electrical force. The free energy change in an electrolytic cell, or in a non spontaneous cell reaction, is therefore positive and the cell voltage is negative.

When the measured value of (E_{corr}) becomes less negative, the potential of the corresponding Galvanic cell becomes less positive, hence the (ΔG) value for the corrosion process becomes less negative, and the process is thus less spontaneous.

The results of ΔG shown in table (3) indicate that the change in free – energy takes the following sequence:

ΔG (J/mol) Oxalate > Na_2CO_3> Tartarate >NaOH> CH_3COOH >H_3PO_4>NaCl

Table 3,
Thermodynamic and Kinetic Function Values for Corrosion of Ti-6Al-4V Alloy in Different Media.

Medium	Free-energy values $-\Delta G$(J/mol)	Rate of corrosion R_{mpy}
NaCl	57228.36	938.9
Sodium tartarate	508477.8	110.6
NaOH	397271.2	79.4
Sodium Oxalate	511141.2	52.2
Acetic acid	284404.8	44.227
Phosphoric acid	247001.4	44.2
Na_2CO_3	509211.2	42.48

The negative sign of ΔG value refer to spontaneous of the corrosion reaction and the corrosion in (Oxalate solution) in most spontaneous compared with other media.

3.4. Rate of Corrosion (R_{mpy})

Any factor that enhances the value of (i_{corr}) results in enhanced value of the corrosion rate on pure kinetic ground. The kinetic parameters were obtained from the corrosion current densities and their dependencies on temperature using the following relationship [8, 9]:

$$\text{Rate}_{(mpy)} = 0.13 \ i_{corr} \ (e/p) \qquad \ldots(10)$$

Where:

R_{mpy}: is the rate of corrosion in (mil/year).

i_{corr} : is corrosion current density ($\mu A/cm^2$).

e: equivalent weight of metal or alloy (gm).

p: density of metal or alloy (gm/cm^3).

The results of rate of corrosion were listed in the Table (3) which takes the following sequence:

$R_{(mpy)}$ NaCl > tartrate > NaOH > oxalate > CH3COOH >H_3PO_4 > Na_2CO_3

4. Conclusion

From the results of studing the corrosion of Ti-6Al-4V alloy in different media by using electrochemical process at room temperature it can be concluded:

1. The corrosion of Ti-6Al-4V alloy in sodium oxalate solution has highest negative value of corrosion potential which was thermodynamic parameter.
2. The corrosion of Ti-6Al-4V alloy in NaCl solution has highest value of corrosion current density which was kinetic parameter.
3. The corrosion of Ti-6Al-4V alloy in NaCl solution has lowest value of polarization resistance.
4. The corrosion process of Ti-6Al-4V alloy in sodium oxalate solution more spontaneous than other media accordance with ΔG calculation (thermodynamic function).
5. The corrosion rate of Ti-6Al-4V alloy in NaCl solution is the highest among the other media (kinetic function).

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سلوك التآكل لسبيكة Ti-6Al-4V في اوساط مختلفة

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الخلاصة

في هذا البحث تم دراسة سلوك التآكل لسبيكة (Ti-6Al-4V) باستخدام القياسات الكلفانية الساكنة في درجة حرارة الغرفة وفي اوساط مختلفة تضمنت كلوريد الصوديوم (ملح الطعام) وترترات الصوديوم (المستخدم في الهلام، الزبد النباتي، وأغلفة السجق، الخ.) واوكزالات الصوديوم (الموجود في الفواكه و الخضروات ،الخ.) وحامض الخليك (الموجود في الخل) وحامض الفسفوريك (الموجود في مشروب الببسي) وكاربونات الصوديوم (الموجودة في مشروب السفن اب) وهيدروكسيد الصوديوم لغرض المقارنة.

تم تفسير متغيرات التآكل المحسوبة للأوساط والتي تتضمن جهد التآكل وكثافة تيار التآكل، حيث بينت نتائج جهد التاكل ان مادة الاوكسالات هي الاكثر تأكلاً في حين اظهرت نتائج كثافة تيار التاكل بان كلوريد الصوديوم هو الاكثر تأكلاً من بقية المواد. تم استخدام نتائج ميول تافل الكاثودية والانودية لحساب مقاومة الاستقطاب لمعرفة المواد الاكثر تأثيراً على سبيكة Ti-6Al-4V المستخدمة في مجال طب الاسنان وكانت النتائج كما يلي:

Na_2CO_3 >Oxalate >H_3PO_4 >CH3COOH >NaOH >Tartrate >NaCl

كما تم حساب التغير في الطاقة الحره وسرعة التآكل في الاوساط المختلفة. بينت نتائج حساب معدل سرعة التآكل بوحدة (ملم لكل سنة) بأنها تأخذ التسلسل التالي: NaCl>Tartrate>NaOH>Oxalate>CH_3COOH>H_3PO_4 >Na_2CO_3 .
