World Applied Sciences Journal 10 (3): 364-369, 2010
ISSN 1818-4952

Reaction Kinetics of Zinc as a Sacrificial Anode for Chathodic Protection of Copper Pipes Carrying Saline Water in Presence of Bacteria

Anees A. Khadom

Department of Chemical Engineering, College of Engineering,
Baghdad University, Aljaderia City 10071, Baghdad governorate, Iraq

Abstract: Rate of zinc consumption in saline water in absence and presence of bacteria was studied. Three rates equations were tested in present work. Zero, first and second order equations were used to represent the kinetic of zinc consumption. Gauss-Newton iteration method was used to select the best fitting of these equations. It was observed that rate of zinc consumption followed first order rate equation. Velocity of reaction increases with flow rate and presence of bacteria. Presence of bacteria did not change the kinetic of reaction. Other kinetics parameters such as half-life, fractional life times and fraction conversion were also obtained.

Key words: Reaction order · Sacrificial anode · Cathodic protection · Bacteria

INTRODUCTION

Many structures particularly in aggressive environments such as saline waters are protected by cathodic protection with sacrificial anodes, therefore, hundreds of researches were done in the subject of cathodic protection system with sacrificial anode, but few of them were deal with chemical kinetic of sacrificial anode. Chemical kinetics deals with the rates of chemical reactions, factors which influence the rates and the explanation of the rates in terms of the reaction mechanisms of chemical processes. In chemical kinetics, the time variable is introduced and rate of change of concentration of reactants or products with respect to time is followed. The chemical kinetics is thus, concerned with the quantitative determination of rate of chemical reactions and of the factors upon which the rates depend. With the knowledge of effect of various factors, such as concentration and temperature, medium, etc., on reaction rate, one can consider an interpretation of the empirical laws in terms of reaction mechanism [1]. The aim of this work is to study the reaction kinetics of zinc electrode in saline water in presence and absence of bacteria which named scientifically as (*pseudomonas flourescens*).

Experimental Data: The experimental data of Al-Jendeel [2] was used. He studied the cathodic protection of copper pipes carrying saline water in presence of aerobic bacteria (*pseudomonas flourescens*) without taking on to account the kinetics of zinc consumption. Table 1 shows the zinc consumption at various conditions [2].

RESULTS AND DISCUSSION

Table 1 show that the rate of zinc consumption in absence of bacteria increased with time and flow rate. Presence of bacteria increases this effect. The rate of reaction can be obtained by plotting concentration of zinc consumption against time and measuring the slope of the curve dW/dt (W is zinc consumption and t is time) at the required time. The rate of reaction obtained from such method is known as instantaneous rate. The concentration of the reactant varies exponentially or linearly with time as shown in Fig. 1 and 2. For determination of the instantaneous rate at any point, the slope of the curve is determined. It may also be noted from Fig. 1 and 2 that if the zinc consumption varies linearly with time, the slope of the curve or rate of the reaction will remain same throughout the course of reaction. However, if concentration of the reactant varies exponentially with time the slope of the curve or the rate of reaction will be different at different time intervals. Thus, it is not necessary that rate of reaction may always remain same throughout the course of reaction. The reaction may proceed with a different rate in the initial stage and may have different rate in the middle or near the end of the reaction.

Corresponding Author: Anees A. Khadom, Department of Chemical Engineering, College of Engineering, Baghdad University, Aljaderia City 10071, Baghdad governorate, Iraq, Email: aneesdr@gmail.com, mobile: 00964 790 2305786

Table 1: Zinc consumption in sacrificial anode in absence and presence of bacteria in 3.5 % NaCl and 20 °C [2]

		Zinc consumption (mg/cm^2)	
Flow rate (L/h)	Time (min)	Absence of bacteria	Presence of bacteria
300	50	0.0016	0.0021
	100	0.0095	0.0244
	150	0.064	0.0753
	180	0.0918	0.1289
400	50	0.0042	0.0058
	100	0.0265	0.0387
	150	0.0849	0.0769
	180	0.1172	0.1332
500	50	0.0122	0.0143
	100	0.0626	0.07215
	150	0.1332	0.1066
	180	0.1814	0.2101
600	50	0.0340	0.0389
	100	0.1008	0.1130
	150	0.1809	0.1931
	180	0.2515	0.2684

The rate of reaction can be expressed by following equation [3]:

$$\frac{dW}{dt} = kW^n \quad (1)$$

$$\ln\left(\frac{dW}{dt}\right) = \ln k + n \ln W \quad (2)$$

Where k is rate constant and n is order of reaction. Equation 2 can be drawn as shown in Figure 3 and the values of slope and intercept can be obtained. The values of rate constants were 0.0274 and 0.0301 min^{-1} in absence and presence of bacteria respectively. The velocity of reaction was higher in presence of bacteria. The orders of reaction were 0.75 and 0.7 in absence and presence of bacteria respectively, which indicates that the reaction mechanism did not changed and the reaction approximately first order. However, the average rates calculated by concentration versus time plots are not accurate. Even the values obtained as instantaneous rates by drawing tangents are subject to much error. Therefore, this method is not suitable for the determination of order of a reaction as well as the value of the rate constant. It is best to find a method where concentration and time can be substituted directly to determine the reaction orders. This could be achieved by integrating the differential rate equation as below [4]:

$$\int \frac{dW}{W^n} = k \int dt \quad (3)$$

Equation 3 can be integrated for different values of n. Equation 4, 5 and 6 represent the rate equation for zero, first and second order respectively:

$$k = \frac{W_t - W_i}{t} \quad (4)$$

$$W_t = W_i \exp(kt) \quad (5)$$

$$k = \frac{1}{t}\left(\frac{1}{W_t} - \frac{1}{W_i}\right) \quad (6)$$

Where W_t is zinc consumption at any time and W_i is the initial zinc consumption. Equation 4 through 6 can be tested in order to determine the accurate order of reaction. Nonlinear estimation regression based on Gauss-Newton iteration method has been used in order to select the more suitable rate equation. The results Gauss-Newton iteration method were listed in Table 2 at different conditions. It is clear from values of correlation coefficients (R^2) that the best fit was obtained by equation 5 (i.e. the first order reaction equation). Equation 5 was applicable in absence and presence of bacteria which agrees with above discussion. Also equation 5 state that the velocity of reaction increases with flow rate and with presence of bacteria. Figures 4 and 5 shows the relation between experimental zinc consumption and predicted by equations 4, 5 and 6. The best fitting was obtained by equation 5.

The reaction rates can also be expressed in terms of half-life or half-life period $t_{1/2}$. The half-life period is defined as the time required for the concentration of a reactant to decrease to half of its initial value. Half-life indicates the stability of reactants, the longer half-life the greater the stability of reactants. For first order reaction half-life period can be defined as [5]:

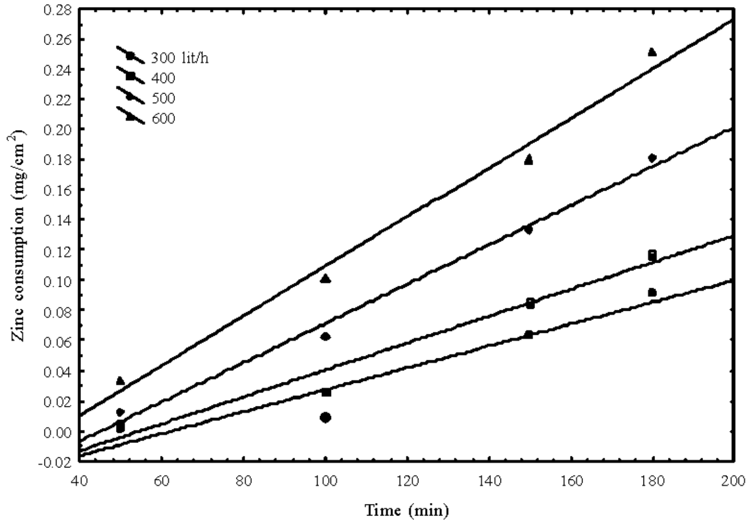

Fig. 1 Variation of zinc consumption with time at different flow rates.

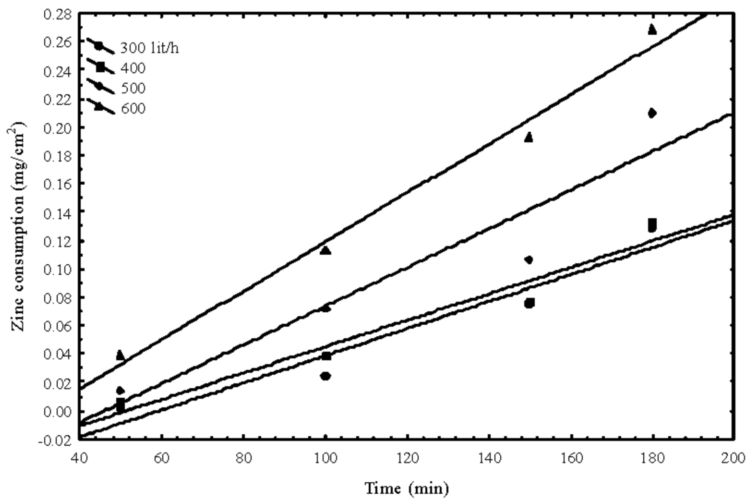

Fig. 2 Variation of zinc consumption with time at different flow rates in presence of bacteria.

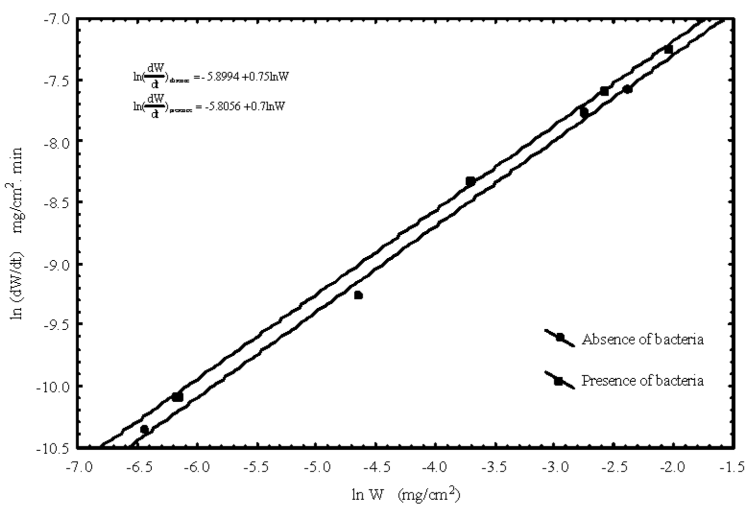

Fig. 3 Consumption rate of zinc against consumption of zinc in absence and presence of bacteria at 300 lit/h.

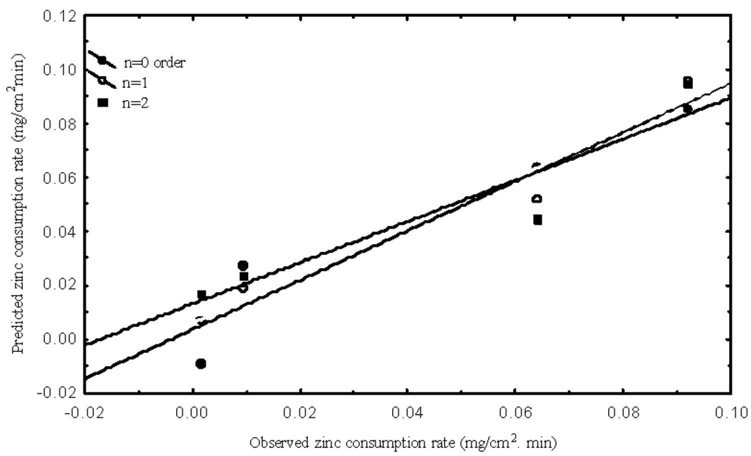

Fig. 4 Observed zinc consumption rate from experimental data against predicted zinc consumption rate from zero order rate equation in absence of bacteria at 300 lit/h.

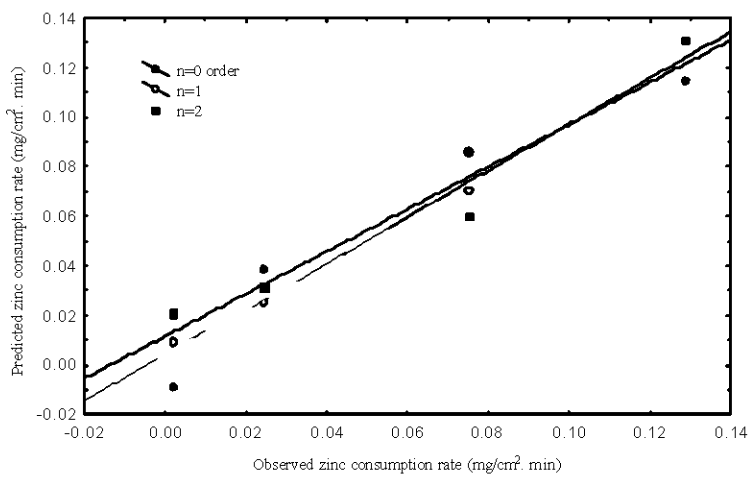

Fig. 5 Observed zinc consumption rate from experimental data against predicted zinc consumption rate from zero order rate equation in presence of bacteria at 300 lit/h.

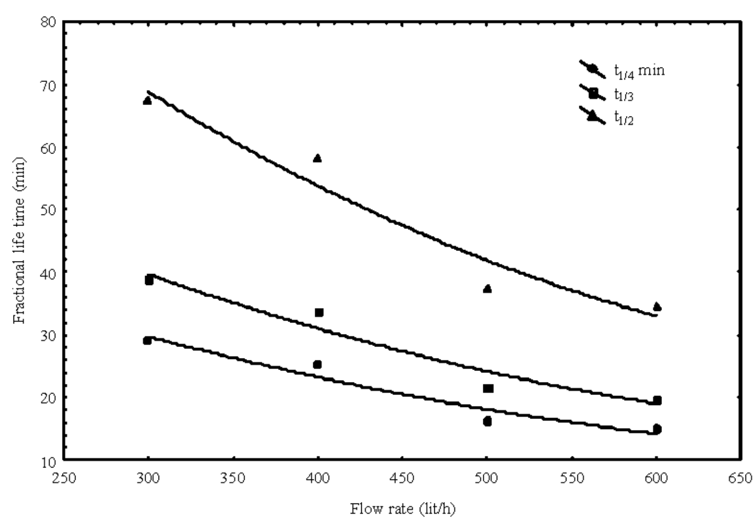

Fig. 6 Fractional life times of zinc consumption against flow rates in absence of bacteria.

Table 2: Reaction equations fitting and correlation coefficients of Zinc consumption in absence and presence of bacteria in 3.5 % NaCl and 20 °C

	Zero order		First order		Second order	
Flow rate (lit/h)	k (mg /cm^2.min)	R^2	k (min^{-1})	R^2	k (cm^2.mg)	R^2
$300_{absence}$	0.0007	0.9574	0.0103	0.9955	0.3172	0.9267
$400_{absence}$	0.0008	0.9817	0.0119	0.9913	0.3333	0.9112
$500_{absence}$	0.0011	0.9777	0.0185	0.9954	0.3712	0.9851
$600_{absence}$	0.0012	0.9613	0.0201	0.9932	0.3921	0.9129
$300_{presence}$	0.0008	0.9658	0.0211	0.9961	0.0741	0.9649
$400_{presence}$	0.0009	0.9719	0.0276	0.9944	0.1619	0.9731
$500_{presence}$	0.0013	0.9416	0.0280	0.9914	0.2503	0.9788
$600_{presence}$	0.0017	0.9841	0.0292	0.9927	0.3037	0.9644

Table 3: Half-life time, fractional life times and percent conversation at 180 minute for first order reaction of zinc consumption

Flow rate (lit/h)	$t_{1/4}$ (min)	$t_{1/3}$ (min)	$t_{1/2}$ (min)	f %
$300_{absence}$	29.1	38.8	67.3	0.8434
$400_{absence}$	25.2	33.6	58.2	0.8826
$500_{absence}$	16.2	21.6	37.5	0.9642
$600_{absence}$	14.9	19.9	34.5	0.9732
$300_{presence}$	14.2	18.9	32.9	0.9776
$400_{presence}$	10.9	14.5	25.1	0.9931
$500_{presence}$	10.7	14.3	24.8	0.9935
$600_{presence}$	10.3	13.7	23.7	0.9948

$$t_{1/2} = \frac{\ln 2}{k} \qquad 7$$

Also the time necessary to achieve reaction (t_f) and fractional life relations ($t_{1/4}$ and $t_{1/3}$) for first order reaction can be defined as:

$$t_f = -\frac{\ln(1-f)}{k} \qquad 8$$

$$t_{1/4} = \frac{\ln(4/3)}{k} \qquad 9$$

$$t_{1/3} = \frac{\ln(3/2)}{k} \qquad 10$$

Where f is fraction conversion of reactant, these kinetic parameters were listed in Table 3. It was observed that values of $t_{1/2}$ decreases with increases of flow rate, this mean that zinc consume to its half original weight as motion of saline water increased. Furthermore, the presence of bacteria reduces the values of $t_{1/2}$, i.e. the presence of bacteria increases the zinc consumption. The same behavior was obtained with $t_{1/4}$ and $t_{1/3}$. The relationship between fractional life times was shown in Figure 6. The ratios of fractional life times $t_{1/2}/t_{1/4} = 2.3$ and $t_{1/2}/t_{1/3} = 1.73$ were in a good agreement with the values of literature. These values are 2.409 and 1.709 respectively [6]. Equation 8 gives the relation between time required to achieve zinc consumption (t_f) and fraction of conversion (f). The maximum value of experimental time was 180 minutes; this value was taken in order to determine the values of f. The values of f increase with flow rates. Maximum value of f was at 600 lit/h and in presence of bacteria.

From above results, we can see that the physical effect of flow rate and bacteria on zinc consumption. The dissolution rate of zinc increases with increasing the flow rate. This may be attributed to the decrease in the thickness of hydrodynamic boundary layer and diffusion layer across which dissolved oxygen diffuses to the tube wall of copper with consequent increase in the rate of oxygen diffusion, then the surface film resistance almost vanishes, oxygen depolarization, the products of corrosion and protective film are continuously swept away and continuous corrosion occurs. The flow rate of saline water may also caused erosion which combined with electrochemical attack. In the presence of *pseudomonas flourescens* the effect of flow rate is important in bacterial corrosion process because it not only affects the transfer of species to the metal surface but also influences the overall bacterial adhesion process and the transfer of nutrients to the metal surface. Stagnant fluid offers the lowest mass transfer rates because convective mass transfer does not exist without fluid flow. However, cell adhesion and biofilm formation may benefit from the absence of shear. At the other end, a fast moving fluid generates turbulence that provides enhanced mass transfer, but the accompanying high shear stress may prove to be harmful to the cells and may lead to the prevention of cell adhesion and thus biofilm formation. A sufficiently high shear stress may even detach an established biofilm [7].

CONCLUSION

The results of Gauss-Newton iteration methods showed that the reaction of zinc consumption in saline water was first order reaction and the speed of reaction increases with flow rate of saline water. The presence of bacteria increases the rate of reaction without changing the mechanism of reaction. The fraction of zinc consumption increases with flow rate reaching a maximum value at 600 lit/h in presence of bacteria.

ACKNOWLEDGEMENT

This work was supported by Baghdad University, Chemical Engineering Department, which is gratefully acknowledged.

Nomenclature:

f	: fraction conversion	
k	: rate constant	
n	: order of reaction	
t	: time	(min)
$t_{1/4}$, $t_{1/3}$ and $t_{1/2}$	: fractional life times	(min)
t_f	: time required to achieve reaction	(min)
W	: weight loss per surface area	(mg/cm^2)

REFERENCES

1. Upadhyay, S.K., 2006. Chemical Kinetics and Reaction Dynamics," Anamaya Publishers, India.
2. Al-Jendeel, H.A., 2007. Cathodic protection of copper pipes carrying saline water in presence of aerobic bacteria. Ms.C thesis, Department of Chemical Engineering, College of Engineering, University of Baghdad, Baghdad, Iraq.
3. Musa, A.Y., A.A. Khadom, A.A.H. Kadhum, A.B. Mohamad and M.S. Takriff, 2010. Kinetic behavior of mild steel corrosion inhibition by 4-amino-5-phenyl-4H-1,2,4-trizole-3-thiol. J. Taiwan Institute of Chemical Engineers, 41(1): 126-128.
4. Missen, R.W., C.A. Mims and Bradley A. Saville, 1999. Introduction to Chemical Reaction Engineering and Kinetics," John Wiley and Sons, Inc., USA.
5. Eddy, N.O., S.A. Odoemelam2 and A.J. Mbaba, 2008. Inhibition of the corrosion of mild steel in HCl by Sparfloxacin. African J. Pure and Appl. Chem., 2: 132-138.
6. Hill, C.G., 1977. An introduction to chemical engineering kinetics and reactor design," John Wiley and sons, Canada.
7. Stoodley, Z. Lewandowski, J.D. Boyle and H.M. Lappin-Scott, 2000. Structural deformation of bacterial biofilms caused by short-term fluctuations in fluid shear: An *in situ* investigation of biofilm rheology. Biotechnol. Bioengineering, 65: 83-92.