Asian Journal of Chemistry; Vol. 27, No. 11 (2015), 3998-4006

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.19053

Reduction of Hexavalent Chromium by Ferrous Ions to Trivalent Chromium in Presence of Organic Acid Additives

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Received: 23 January 2015; *Accepted*: 13 April 2015; *Published online*: 16 July 2015; AJC-17390

The kinetics of the removal of toxic hexavalent chromium (Cr^{6+}) from acidified potassium dichromate solution using iron cylinder as reducing agent was studied. The effect of the presence of different organic acids (*e.g.*, acetic acid, chloroacetic acid, dichloroacetic acid, trichloroacetic acid, sulphosalicylic acid, citric acid and phthalic acid) upon the reaction was investigated. It is found that the presence of organic acids decreases or inhibits the rate of the reduction reaction. The percentage inhibition in the presence of organic acids was ranged between 62.33 and 79.82 % at 25 °C, indicate that, increasing of organic additives concentrations is followed by increasing in inhibition power and this could be due to decrease in the diffusion coefficient values of the solution containing organic acids. Also the rate of reduction was found to increase by increasing the temperatures. The factors studied were, the concentration of the organic acids and speed of rotating iron cylinder. The applicability of the adsorption process to the Langmuir, Florry-Huggins and kinetic-thermodynamic isotherm was delaminated.

Keywords: Chromium(VI) removal, Ferrous ions, Organic acids additives.

INTRODUCTION

The most important source of chromium pollution is due to different industries. Industries that use large amount of chromium as chromate or dichromate are the textile leather tanning and metal finishing for corrosior protection[1-3]. Hexacovalent chromium compounds cause dermatitis[4], perforation of nasal septum and inflammation of larynx and liver. Skin lesions and kidneys damage could be produced as a result of occupational exposure to hexavalent chromium compounds is probably carcinogen and lung is principle site of action[5].

Increasing the use of heavy metals in last few years has resulted in increasing in the reflux of metallic substances in the aquatic environment. The presence of metallic substances in the aquatic environment in large amounts has harmful effects on both man and animal. Therefore, it was important to develop new technologies to overcome this problem[6].

The reduction of Cr(VI) to Cr(III) decreases the toxicity and mobility of chromium contaminants in soils and water. In addition, the formation of a highly insoluble Cr(III)[7].

Trivalent chromium (Cr^{3+}) is essential in both man and animal since it plays an important role in glucose and lipids metabolism, its deficiency may cause problems in their rate of metabolism. The major environmental exposure to chromium occurs as consequence of its presence in food. Brown sugar and animal's fats, especially butter are chromium rich food[8].

Chromium exists in two common oxidation states as Cr(III) and Cr(VI). The hexavalent form is 500 times more toxic than the trivalent. It is toxic to microorganism plants, animals and humans. Human toxicity includes lung cancer, as well as kidney, liver and gastric damage[9,10]. Due to severe toxicity of Cr(VI), the USEPA (US environmental protection agency) has set the maximum contaminate level for Cr(VI) in domestic water supplies to be 0.05 ppm[11]. Trivalent form is an essential nutrient, but hexavalent form is toxic, carcinogenic and mutagenic in nature. It is highly mobile in soil and aquatic system and also is a strong oxidant capable of being adsorbed by the skin[12,13]. Consequently, the reduction of Cr(VI) to the Cr(III) is of environmental interest. Much work has been focused on the cleanup of Cr(VI)-contaminated waters by various reducing agents. Chemical reduction is known to remove hexavalent chromium rapidly and effectively, reduction using iron metal appears to be one of the most promising technologies[14]. The effect of iron metal type and pH value on rate of hexavalent chromium reduction by iron was evaluated[15].

Cementation is the recovery of an ionized metal from solution by spontaneous electrochemical reduction to its elemental metallic state, with consequent oxidation of a sacrificial metal. The process has been largely used in industry for a long time, not only in hydrometallurgy but also in the purification process of stream and wastewaters[16,17].

The cementation process has several advantages, such as recovery of metals is essentially pure metallic form, simple control requirements and low energy consumption. Nevertheless, the main disadvantage is excess sacrificial metal consumption, for example, when iron or zinc is used at low pH values[18]. The laboratory studies have been often carried out in small dimensions cells on a sacrificial metal under a massive form. In most of the cases the metal concerned in rotating disc[19]. The use of rotating disc has been justified by the advantage that the system presents a known and reproducible hydrodynamic. It is also established that the transposition of the obtained results to the industrial reactor using sacrificial metal under devised form is not possible.

The object of the present work is studying the removal of toxic heavy metals from wastewater by reduction. The kinetics of the removal of hexavalent chromium (Cr^{6+}) from aqueous potassium dichromate solution using organic acid on the rotating iron cylinder in the presence of organic acid was studied. The parameters affecting the adsorption process such as, Cr^{6+} initial concentration, solution volume and addition of different adsorbent amounts were studied. Adsorption isotherm was also studied, two models have been selected which are Langmuir and Freundlish isotherm.

EXPERIMENTAL

Potassium dichromate produced by ADWIC and sulfuric acid (98 % w/w) supplied by BDH Chemicals Ltd. were used in the preparation of experimental and stock solutions. Organic additives selected in the present work are (acetic acid, chloroacetic acid, dichloroacetic acid, trichloroacetic acid, sulphosalicylic acid, citric acid and phthalic acid) which are in the most possible pure forms.

The apparatus used in removal of Cr^{6+} from the solution permits the rotation of an immersed iron cylinder in a 250 mL glass beaker containing 250 mL of experimental solution. The iron cylinder used in each run is of 7 cm length and 1.2 cm diameter, only the peripheral surface of pure iron was exposed to the solution. The cylinder rotation recorded as revolution per minute was counted by optical tachometer.

Kinetic measurements: Potassium dichromate and distilled water containing 1 M sulfuric acid (98 % w/w) were used in the preparation of blank solution (100 ppm, pH = 2) as well as in the presence of eight different concentrations of organic acids (acetic acid, chloroacetic acid, dichloroacetic acid, trichloroacetic acid, sulphosalicylic acid, citric acid and phthalic acid). The rate of the reaction was determined at 25 °C and at different rotations 900, 700, 500, 300, 200 and 100 rpm.

Through the proceeding reaction, at different time intervals (10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110 and 120) min, 0.1 mL sample was taken from reaction solution and diluted to 10 mL by distilled water. The determination of hexavalent chromium (Cr^{6+}) concentrations was carried out at 365 nm using Shimadzu UV-160A spectrophotometer through the following equation[20]:

$$C = A/\varepsilon b \tag{1}$$

where, C: concentration in mol L^{-1}; A: absorbance; ε: molar absorpativity in l mol^{-1} cm^{-1}; b: path length in cm.

RESULTS AND DISCUSSION

Reaction kinetics: In the present work, oxidation-reduction reaction between potassium dichromate and iron takes place to produce Cr^{3+}. The kinetics of this reaction has been studied extensively[20,21] where, the rate controlling step was found to be the diffusion of Cr^{6+} to iron surface. In such case, the change in the rate of Cr^{6+} reduction in the solution is followed as in eqn. 2:

$$\log C_0/C = (A/v)\ kt \tag{2}$$

where, k is rate constant (s^{-1}), t is reaction time (s), C is concentration (mg/L) at time t (s), C_0 is initial concentration (mg/L), A is area of iron cylinder (cm^2) and v is solution volume (L).

The mechanism of the reaction was preceded as in the following steps:

(a) $Fe \rightarrow Fe^{2+} + 2e^-$ (dissolution of metal in acidic medium)
(b) $\underset{\text{bulk}}{Cr^{6+}} \rightarrow \underset{\text{interface}}{Cr^{6+}}$ (mass transfer step)
(c) $Fe^{2+} \rightarrow Fe^{3+} + e^-$ (charge transfer step)
$Cr^{6+} + 3e^- \rightarrow Cr^{3+}$

The reaction is diffusion controlled and its rate can be represented by eqn. 3:

$$\log C_0/C = (26.4/v)\ kt \tag{3}$$

This equation may be represented as a straight line where, 26.4 is the value of the area (A) which is constant and the other symbols have the definition mentioned before. Fig. 1 shows the relation between log C_0/C against time for the blank solution at 25 °C and different rpm and in the presence of different concentrations of acetic acid at 25 °C and 500 rpm. Fig. 1 indicates that the reaction is a first order reaction.

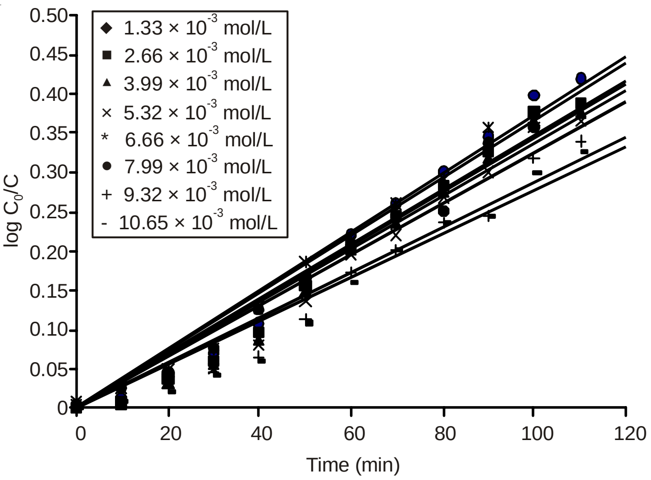

Fig. 1. Relation between log C_0/C and time for Cr^{6+} reduction in the presence of different concentrations of acetic acid at 25 °C and 500 rpm

Effect of stirring on the reaction: Fig. 2 gives the variation of log C_0/C with time at different speed of rotation (rpm) of iron cylinder at 25 °C for acidified 100 ppm Cr^{6+}solution as a blank solution. The effect of rotational speed on the rate constant (k) can also be used to determine whether the reaction

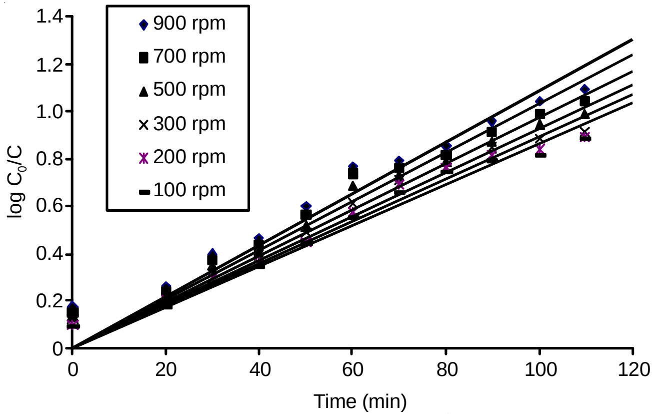

Fig. 2. Relation between log C_0/C and time for Cr^{6+} reduction at 25 °C and different rpm

is diffusion or chemically controlled. If the rate constant increase with increasing stirring speed, then the reaction is diffusion controlled. If the rate constant (k) is independent on stirring speed, then the reaction is chemically controlled. The data shown is Table-1 shows that the reaction is diffusion controlled[22].

TABLE-1
VALUES OF RATE CONSTANT (k) OF THE REACTION FOR SOLUTION AT DIFFERENT rpm AT 25 °C

rpm	$k \times 10^2$ (s^{-1})	rpm	$k \times 10^2$ (s^{-1})
100	7.19	500	8.23
200	7.48	700	8.61
300	7.76	900	9.00

Effect of diffusion coefficient on the reaction: Table-2 gives the values of diffusion coefficient (D) in the presence and absence of organic acids. (D) is calculated from conductance measurements[23]. It is obvious that the presence of organic additives decreases diffusion coefficient of the solution containing Cr^{6+} and this is due to increase in the interfacial viscosity in accordance with Stokes-Einstein equation[24] as shown in eqn. 4. Decreasing in diffusion coefficient values[25] lead to decreasing the rate constant (k). Table-2 show the effect of raising temperature on the diffusion coefficient of the solution according to Stokes-Einestein law:

$$\eta(D/T) = \text{constant} \tag{4}$$

where, η is viscosity, T is the absolute temperature.

Effect of organic compounds: In this study, the rate of reaction (k) values in the presence and absence of organic acids were estimated. It is found that the presence of organic acids decreases or inhibits the rate of the reduction reaction as shown in Fig. 3 and Table-2.

According to the obtained results from the reduction of Cr^{6+} on surface of iron cylinder, it can be concluded as follows:

- The degree of inhibition of used acids increases by increasing the concentration of the used acids. The presence of electron withdrawing group has increased the acidity. So, the degree of inhibition was found to be the following:

Trichloroacetic acid > dichloroacetic acid >
chloroacetic acid > acetic acid

TABLE-2
DIFFUSION COEFFICIENT (D) VALUES FOR THE SOLUTION IN PRESENCE OF DIFFERENT ORGANIC ADDITIVES ACID AT 25 °C

Acetic acid concentration × 10^3 (mol L^{-1})								
0.0	1.33	2.66	3.99	5.32	6.66	7.99	9.32	10.65
$D \times 10^6$ (cm^2 s^{-1})								
6.087	5.807	5.645	5.208	5.174	4.666	4.535	4.509	4.484
Chloroacetic acid concentration × 10^3 (mol L^{-1})								
0.0	0.84	1.69	2.53	3.38	4.23	5.07	5.92	6.77
$D \times 10^6$ (cm^2 s^{-1})								
6.087	5.828	5.872	5.328	5.314	4.745	4.610	4.535	4.480
Dichloroacetic acid concentration × 10^3 (mol L^{-1})								
0.0	2.0	4.0	7.0	9.0	12.0	14.0	17.0	19.0
$D \times 10^6$ (cm^2 s^{-1})								
6.087	5.525	5.231	4.851	4.634	4.384	4.316	4.248	4.204
Trichloroacetic acid concentration × 10^3 (mol L^{-1})								
0.0	1.22	2.44	3.67	4.89	6.12	7.34	8.56	9.79
$D \times 10^6$ (cm^2 s^{-1})								
6.087	5.472	5.363	5.077	4.748	4.363	4.204	4.161	4.139
Sulphosalicylic acid concentration × 10^3 (mol L^{-1})								
0.0	0.31	0.62	0.94	1.25	1.57	1.88	2.20	2.51
$D \times 10^6$ (cm^2 s^{-1})								
6.087	6.069	5.786	5.231	4.964	4.946	4.830	4.748	4.693
Citric acid concentration × 10^3 (mol L^{-1})								
0.0	0.41	0.83	1.24	1.66	2.08	2.49	2.91	3.32
$D \times 10^6$ (cm^2 s^{-1})								
6.087	6.046	6.010	5.979	5.935	5.926	5.870	5.824	5.766
Phthalic acid concentration × 10^3 (mol L^{-1})								
0.0	0.48	0.96	1.44	1.92	2.40	2.88	3.36	3.84
$D \times 10^6$ (cm^2 s^{-1})								
6.087	5.935	5.766	5.529	5.454	5.174	4.983	4.952	4.892

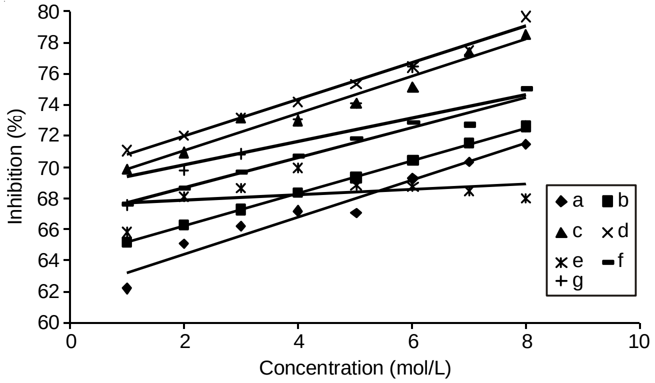

Fig. 3. Relation between % inhibition and concentration of different organic acids of Cr^{6+} reduction at 25 °C and 500 rpm; where, (a) acetic acid; (b) chloroacetic acid; (c) dichloroacetic acid; (d) trichloroacetic acid; (e) sulphosalicylic acid; (f) citric acid; (g) phthalic acid

- The presence of more than one acidic functional group has increases the degree of inhibition as the following:

Phthalic acid > citric acid > sulphosalicylic acid

The percentage of inhibition of different concentrations of the studied additives is estimated at 25 °C as shown in Fig. 3. The percentage of inhibition is represented as following:

$$\text{Inhibition (\%)} = (K_{\text{blank}} - K_{\text{organic}}) / K_{\text{blank}} \times 100 \qquad (5)$$

The percentage inhibition in the presence of organic acids was ranged between 62.33 and 79.82 % at 25 °C. Data represented in Fig. 3 indicate that increasing of organic additives concentrations is followed by increasing in inhibition power and this could be due to the a decrease in the diffusion coefficient values of the solution containing organic acids.

Adsorption isotherm: It is generally assumed that the adsorption of the inhibitor at the metal solution interface is the first step in the reaction mechanism of inhibitors in aggressive acid media. Four types of adsorption may take place in the inhibiting phenomena involving organic molecules at the (metal/solution) interface, namely:

- Electrostatic attraction between charged molecules and the charged metal.
- Interaction of uncharged electron pairs in the molecules with the metal.
- A combination of the above[26].

Adsorption isotherms are very important in determining the mechanism of organo-redox reactions. The most frequently used isotherms are those of Langmuir, Flory-Huggins and kinetic- thermodynamic isotherm. All these isotherms are of the general form:

$$f(\theta, x) \exp(-a\theta) = KC \qquad (6)$$

where $f(\theta, x)$ is the configuration factor depends essentially on the physical model and assumptions underlying the derivation of the isotherm. The mechanism of inhibition of reaction is generally believed to be due to the formation and maintenance of a protective film on the metal surface[27].

Langmuir isotherm: Inhibitor adsorption characteristics can be estimated by using the Langmuir isotherm given as[28]:

$$\theta/(1-\theta) = KC \qquad (7)$$

where K is the equilibrium constant of adsorption process, C is the concentration and θ is the surface coverage.

The degree of surface coverage (θ) at constant temperature was determined from[29]:

$$\theta = (K_{\text{blank}} - K_{\text{organic}})/K_{\text{blank}} \qquad (8)$$

From eqn. 7 a plot of [θ/(1-θ)] with (C) should yields straight line, as shown in Fig. 4 10-16 *i.e.* all the inhibitors verify Langmuir adsorption isotherm.

Flory-Huggins isotherm: Fig. 5 shows the Flory-Huggins adsorption isotherm plotted as log θ/C *vs.* log (1-θ) for Cr^{6+} reduction in presence of organic acids at 25 °C. Straight lines with slope x and intercept log xK are obtained. The experimental data fits the Flory-Huggins adsorption isotherm which represented by:

$$\log \theta/C = \log xK + x \log(1-\theta) \qquad (9)$$

Here x is the number of water molecules replaced by one molecule of the inhibitor. It is clear that the surface coverage data are useful for discussing adsorption characteristics. The adsorption of inhibitors at metal-solution interface may be due to the formation of electrostatic bonding between the organic acids and the metal surface atoms[30].

Kinetic-Thermodynamic isotherm: Plot of [log θ/(1-θ)] *vs.* (log C) should yield straight line relationships with slope Y and intercept log K. Fig. 6 shows straight line indicating that all the inhibitors verify kinetic-thermodynamic isotherm for Cr^{6+} reduction at 25 °C[31].

$$\log \theta/(1-\theta) = \log K + Y \log C \qquad (10)$$

where K is equilibrium constant, Y is a constant.

The free energy of adsorption (ΔG_{ads}) at different concentrations was calculated from the equation[32]:

$$\Delta G_{\text{ads}} = -RT \ln(55.5\,K) \qquad (11)$$

The value 55.5 is the concentration of water in solution, R is the gas constant and T is the absolute temperature.

The values of (ΔG_{ads}) are given in Table-3. In all cases except sulphosalicylic acid the (ΔG_{ads}) values are negative and lie in the range of -12.679 to -59.175 kJ/mol. The most efficient inhibitor shows the most negative (ΔG_{ads}) value. This suggests

TABLE-3
OVERALL PARAMETERS OF ADSORPTION ISOTHERMS FOR ALL ORGANIC ACIDS AT 25 °C

Organic acid	Langmuir isotherm		Florry-Huggins isotherm			Kinetic isotherm			
	K	$-\Delta G_{ads.}$ (KJ mol^{-1})	K	X	$-\Delta G_{ads.}$ (KJ mol^{-1})	K	Y	1/Y	$-\Delta G_{ads.}$ (KJ mol^{-1})
Acetic acid	0.112	45.301	46.137	5.504	36.584	5.550	0.185	5.379	14.207
Chloroacetic acid	0.116	46.171	99.153	6.918	38.481	5.973	0.222	4.486	14.389
Dichloroacetic acid	0.184	57.609	16.941	5.162	34.10	7.531	0.206	4.852	14.963
Trichloroacetic acid	0.196	59.175	37.063	6.273	41.750	14.67	0.206	4.849	16.617
Sulphosalicylic acid	0.130	49.110	40.917	5.302	36.287	5.678	0.134	7.440	15.680
Citric acid	0.119	46.804	57.844	6.628	42.854	6.980	0.160	6.215	14.775
Phthalic acid	0.222	62.264	63.418	5.506	37.373	11.73	0.231	4.317	16.062

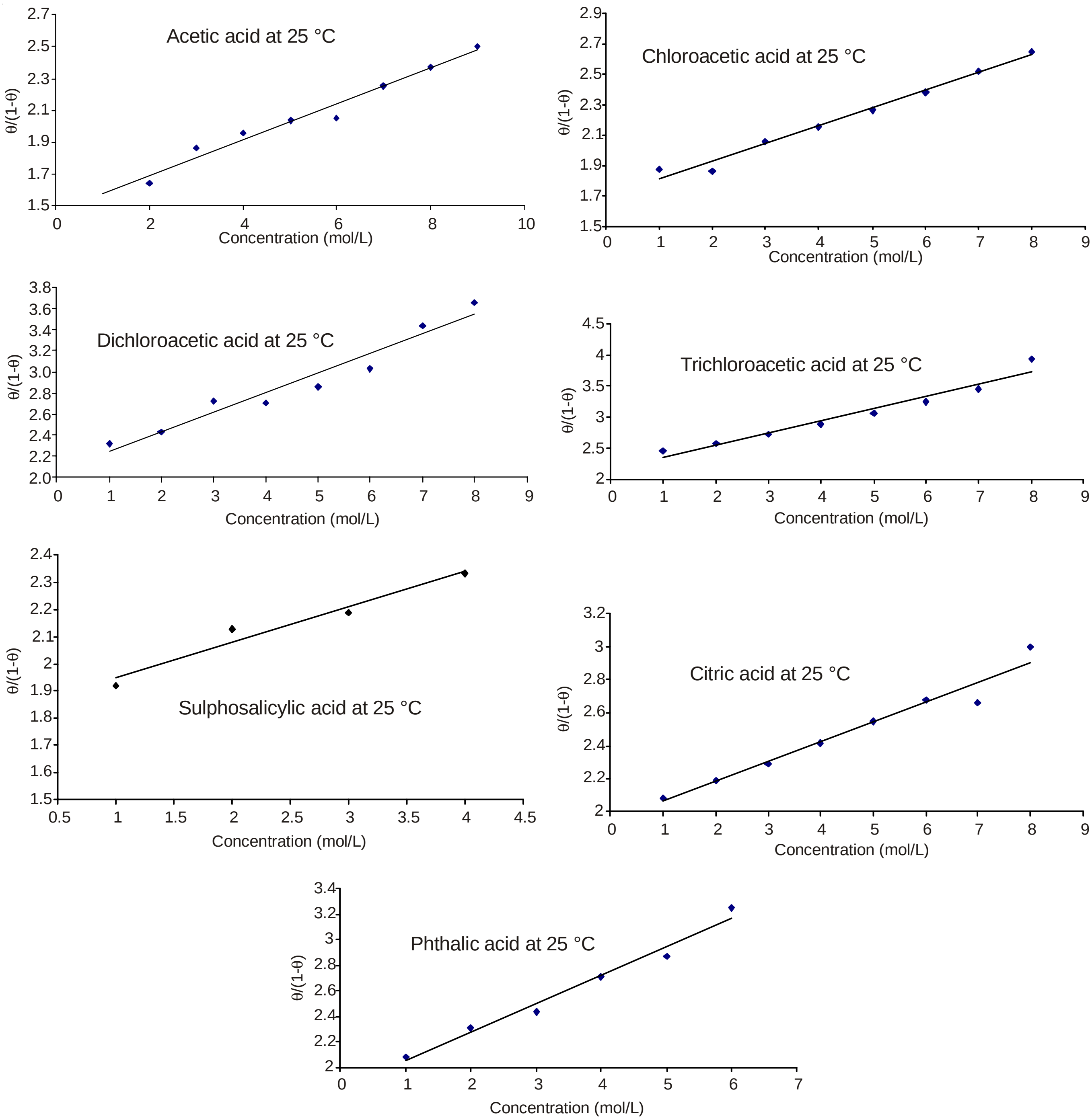

Fig. 4. Langmuir isotherm for the reduction of Cr^{6+} ions in presence of different organic acids at 25 °C

that they are strongly adsorbed on the metal surface. The negative values of (ΔG_{ads}) indicate the spontaneous adsorption of the organic acids. This usually characteristic of strong interaction with metal surface.

Data correlation: To obtain an overall data correlation under the present conditions, where a rotating cylinder is used, the method of dimensional analysis was used. To identify the variables, which affect the rate constant in the oxidation reduction reaction, the mechanism of forced convection mass transfer should be recalled first. Forced convection takes place as a result of cylinder rotation[33]. The thickness of this hydrodynamic boundary layer determines the thickness of the diffusion layer across which diffusion of Cr^{6+} from the solution bulk to surface of iron takes place the thickness of the hydrodynamic boundary layer at the rotating cylinder and the diffusion layer are determined by the physical properties of the solution, the geometry of the system (cylinder diameter) and rotating speed. This picture leads to the eqn. 12.

$$k = f(\eta, \rho, D, V, d) \qquad (12)$$

where, k = rate constant (s^{-1}); ρ = density of bulk ($g\ cm^{-3}$); η = viscosity of bulk ($cm^2\ s^{-1}$); D = diffusion coefficient, ($cm^2\ s^{-1}$); V = cylinder linear velocity ($V = \omega r$); ω = angular velocity ($\omega = 2\ \pi$ rpm/60); d = diameter of the cylinder (cm); r = radius of the cylinder (cm).

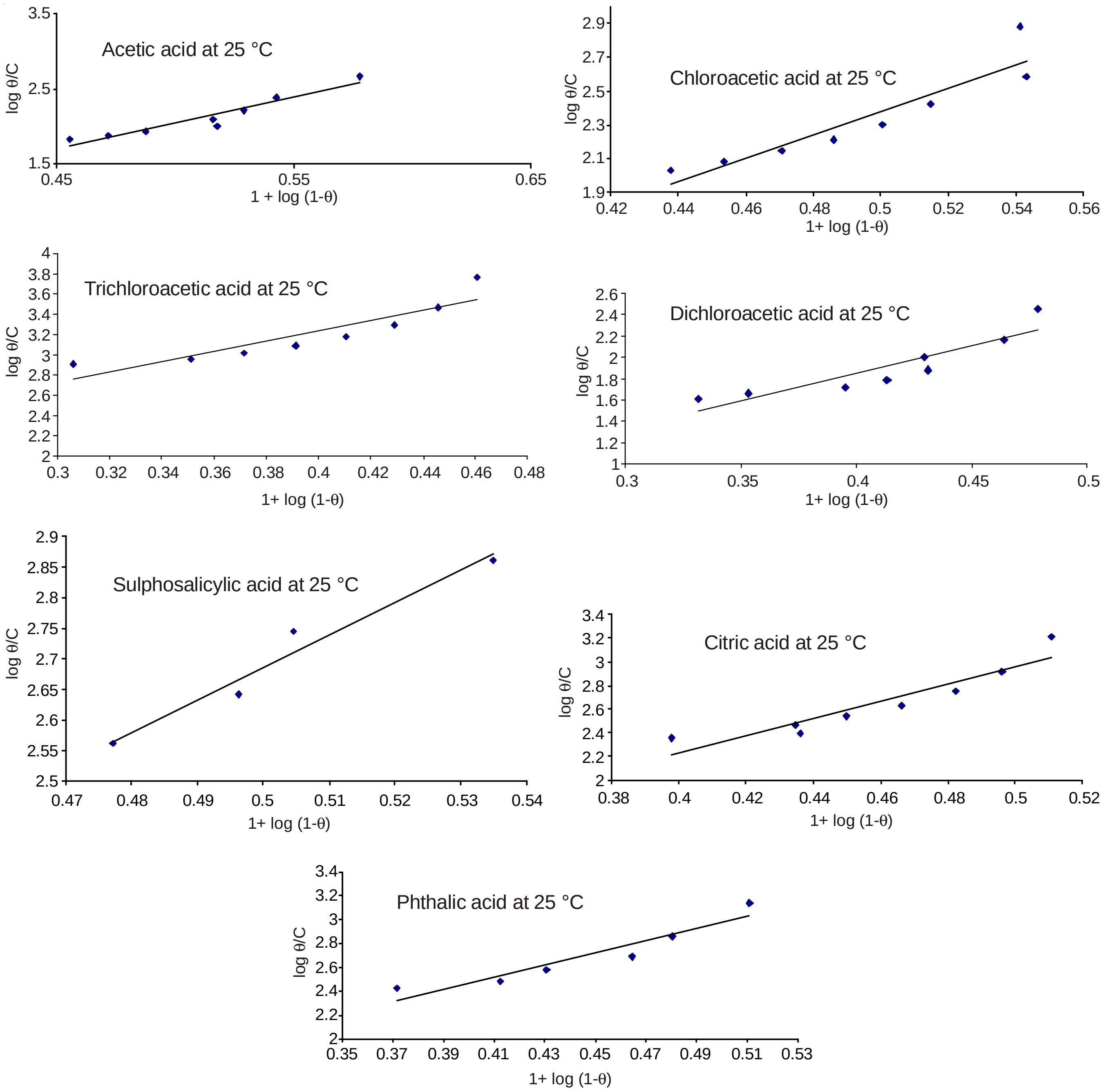

Fig. 5. Flory-Huggins isotherm for the reduction of Cr^{6+} ions in presence of different organic acid at 25 °C

By using the method of dimensional analysis, the above equation can be written as following:

$$Sh = a\, Sc^{b} Re^{c} \qquad (13)$$

where, Sh is Sherwood number, Sc is Schmidt number and Re is Reynolds number, a, b and c are constants, other equation was tested.

$$Sh = a\, Sc^{0.33} Re^{c} \qquad (14)$$

By plotting log $Sh/Sc^{0.33}$ against log Re straight lines were obtained in Fig. 7 where their slopes give the constant c and intercept give the constant a.

The data can be correlated by the following equations:

(1) For the solution in the presence of acetic acid.

$$Sh = 0.77\, (Sc)^{0.33}\, Re^{0.69}$$

(2) For the solution in the presence of chloroacetic acid.

$$Sh = 1.44\, (Sc)^{0.33}\, Re^{0.65}$$

(3) For the solution in the presence of dichloroacetic acid.

$$Sh = 1.24\, (Sc)^{0.33}\, Re^{0.80}$$

(4) For the solution in the presence of trichloroacetic acid.

$$Sh = 1.16\, (Sc)^{0.33}\, Re^{0.70}$$

(5) For the solution in the presence of sulphosalicylic acid.

$$Sh = 1.12\, (Sc)^{0.33}\, Re^{0.67}$$

(6) For the solution in the presence of citric acid.

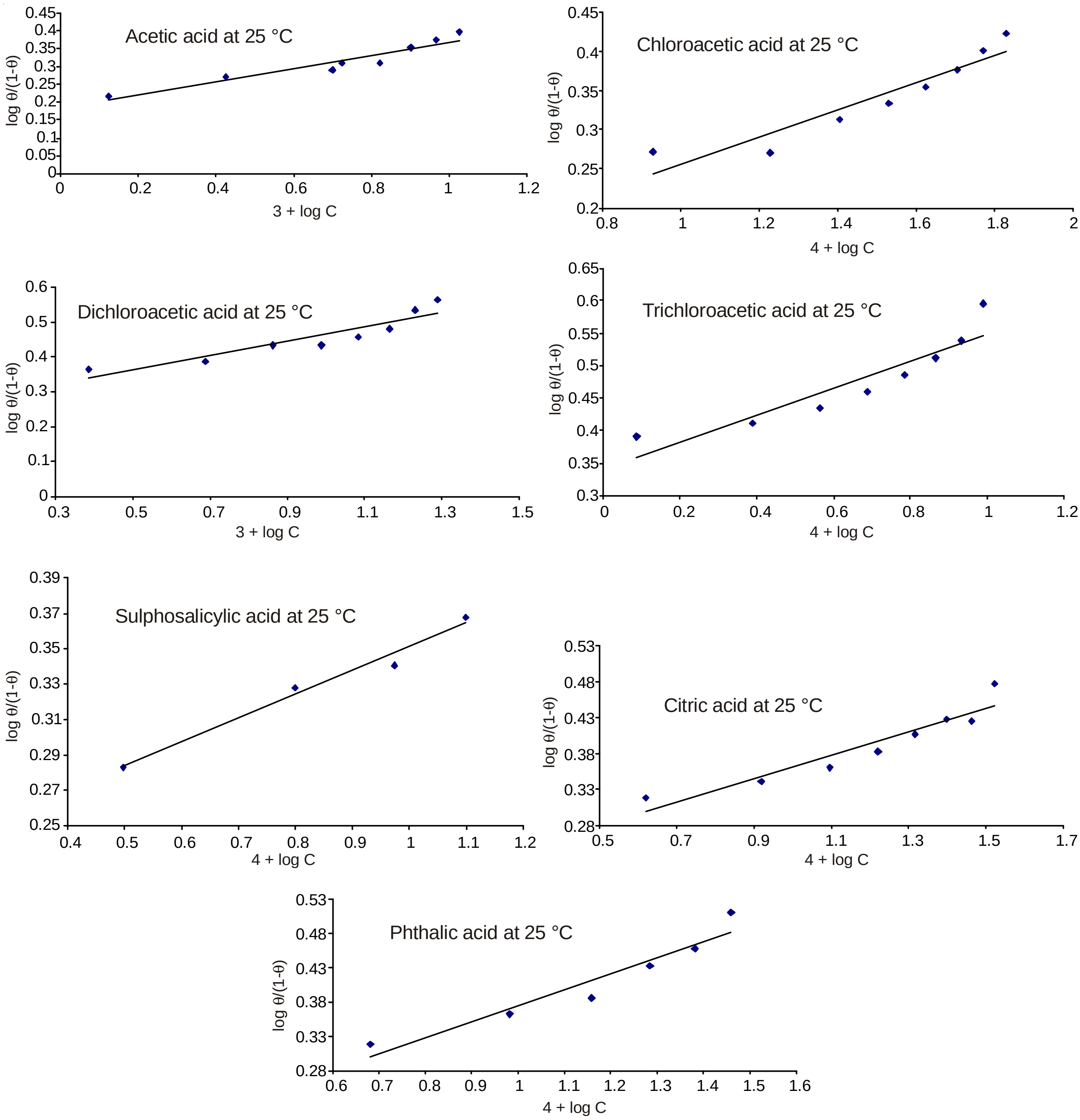

Fig. 6. Kinetic-thermodynamic isotherm for the reduction of Cr^{6+} ions in presence of different organic acids

$$Sh = 1.27\ (Sc)^{0.33}\ Re^{0.70}$$

(7) For the solution in the presence of phthalic acid.

$$Sh = 0.75\ (Sc)^{0.33}\ Re^{0.70}$$

Exponents in all equations denote a highly turbulent flow, which agree with the data studied in aqueous media. In this study, a forced convection mechanism is obtained which agrees very well with the relationship (eqn. 15) given by Eisenberg *et al.*[34]. for mass transfer of a rotating cylinder in turbulent flow system *i.e.* equation represents mass transfer by a convective diffusion mechanism without interference from electrical migration.

$$Sh = 0.079\ Sc^{0.326}\ Re^{0.7} \tag{15}$$

Also, the present results agree excellently with eqn. 16 given by Nassar *et al.*[35] for mass transfer of a rotating cylinder in an aqueous medium.

$$Sh = 1.58\ Sc^{0.33}\ Re^{0.725} \tag{16}$$

The present results also agree with eqn. 17 given by Ahmed *et al.*[36]. for mass transfer during copper cementation from alcoholic water mixtures using rotating cylinder in turbulent system.

$$Sh = 0.061\ Sc^{0.33}\ Re^{0.833} \tag{17}$$

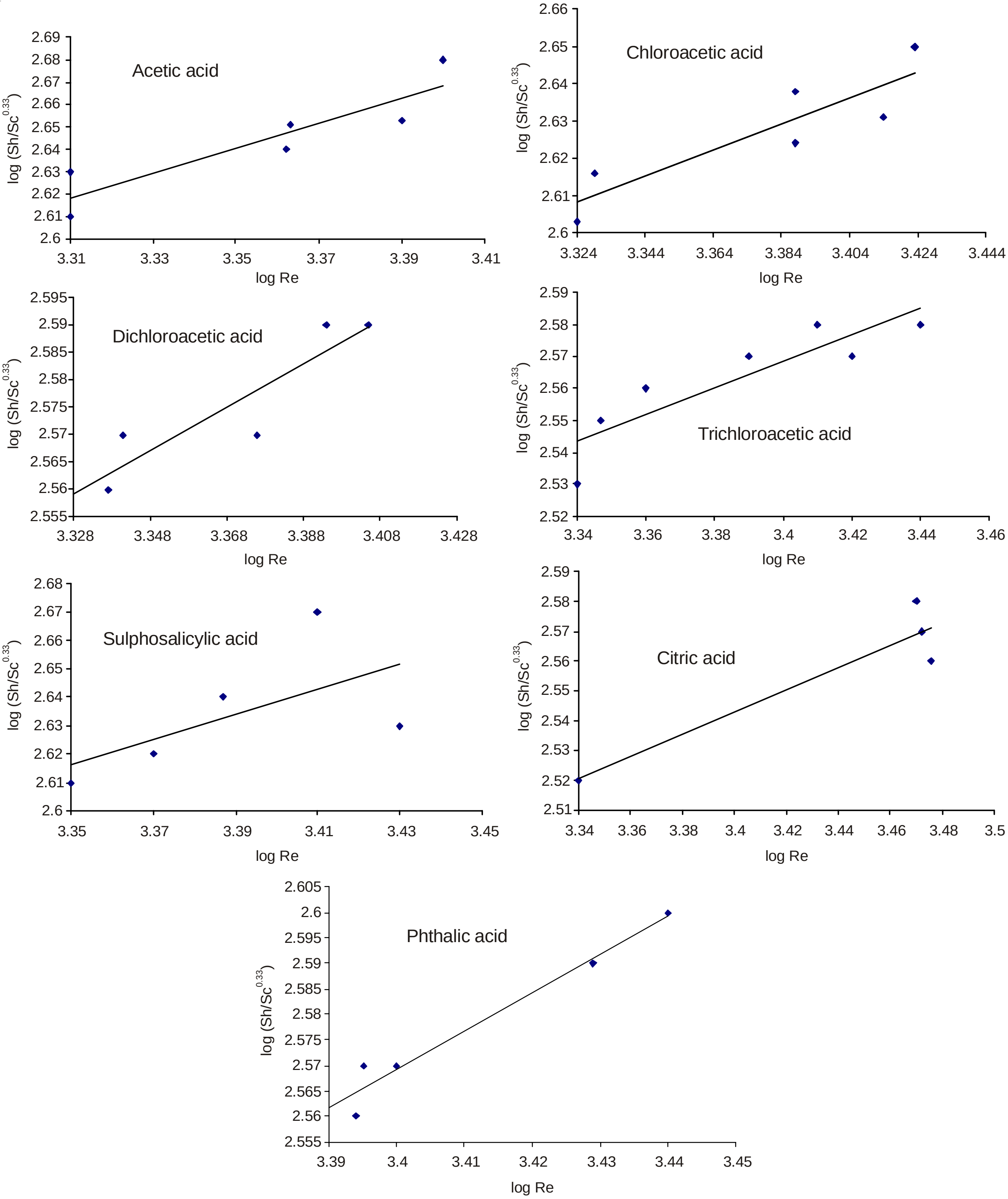

Fig. 7. Overall data correlation for the solution in the presence of organic acids

Conclusion

- The kinetics of the removal of toxic hexavalent chromium (Cr^{6+}) from acidified potassium dichromate solution using iron cylinder as reducing agent was studied.
- The rate of reduction was found to decrease by increasing the concentration of organic compounds and increased with the increasing of temperatures and the rate of rotation.

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