Reduction of Toxic Cr⁶⁺ to Cr³⁺ in Presence of Non-Toxic Organic Substances

MERVETTE EL-BATOUTI[*] and ABDEL-MONEIM M. AHMED

Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt

*Corresponding author: Tel: +20 1285150304; E-mail: mervette_b@yahoo.com

Activated carbon was used for the removal of hexavalent chromium (Cr^{6+}) from wastewater. Different parameters affecting its removal from solution were investigated. These conditions include the concentration of organic acids, speed of rotating iron cylinder and the change in the physical properties of solution such as, density, viscosity and diffusion adsorption kinetics. Adsorption isotherms have been applied to study the kinetics of the adsorption behaviour and to determine the adsorption capacity of the absorbents. Regression analysis was investigated to study the mechanism of adsorption of the experiment and to identify the significance of the parameters used to enhance the adsorption capacity. The kinetics of the removal of toxic hexavalent chromium 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, sulphosalisylic acid, citric acid and phthalic acid) upon the reaction was also investigated. The applicability of the adsorption process to Langmuir, Freundlich and kinetic-thermodynamic isotherm was examined.

Keywords: Chromuim(VI), Removal, Diffusion controlled, Temperature, Non-toxic organic substances.

INTRODUCTION

Increasing in the use of heavy metals in last few years has resulted in increasing in reflux of metallic substances in aquatic environment. The presence of metallic substances in the aquatic environment in large amounts has harmful effects on both men and animals [1-3].

Wastewater pollution in industrial areas is one of the most important environmental problems. Heavy metal pollution especially chromium is a serious problem which affects all ecosystems and human health directly or indirectly as in food chain. The maximum limit value of chromium in wastewater is 0.05 mg/L as reported in World Health Organization (WHO) [4]. Trivalent chromium is present in nature, occurring in air, water, soil and biological materials. While, hexavalent chromium compounds are man-made and do not occur naturally in environment. Hexavalent chromium [Cr^{6+} is widely considered to have significantly greater toxicity than the trivalent form (Cr^{3+})]. This results in part from the recognition of hexavalent chromium (Cr^{6+}) as a known human carcinogen by the inhalation route of exposure, from the caustic properties of many of hexavalent compounds, the greater adsorption of hexavalent species following exposure by ingestion and inhalation and the ability of hexavalant chromium efficiently traverse cell membranes [5].

Although chromium is present in all plants, it has not been proved to be an essential element for plants. Chromium could be absorbed through roots or leaf surface. Several factors were found to affect the availability of chromium including pH of soil, carbon dioxide and oxygen concentration and interaction with other minerals [6-8].

The toxicity of chromium for soil bacterial isolated was studied by measuring the turbidity of liquid cultures supplemented with hexavalent chromium and trivalent chromium. Villaescusa *et al.* [9] proved that the toxicity of hexavalent chromium depends on the species formed in the solution, which change with pH value.

The object of the present work is to study the removal of toxic heavy metal (Cr^{6+}) from wastewater by adsorption. The kinetics of the removal of Cr^{6+} from aqueous potassium dichromate solution using activated carbon as adsorbent was studied. The parameters affecting the adsorption process such as initial concentration of Cr^{6+}, solution volume and addition of different adsorbent amounts were studied.

EXPERIMENTAL

Potassium dichromate produced by ADWIC, was used in the preparation of stock solutions. Powder activated carbon (PAC) produced from natural origin by ADWIC was used as adsorbent.

A definite volume of Cr^{6+} stock solution with a known initial concentration is stirred with a definite amount of adsorbent for certain time at fixed temperature and agitation rate using

magnetic stirrer to stir the potassium dichromate solution with adsorbent (activated carbon).

Kinetic measurements: Potassium dichromate and distilled water was used in the preparation of the stock solution. Several solutions with different initial concentrations of potassium dichromate (50, 100 and 150 ppm) were prepared. All experiments were carried out at 25 °C by adding different amounts of adsorbent (0.1, 0.3, 0.5, 0.7 and 1.0 g) to different volumes of potassium dichromate solutions (50, 100, 150 and 200 mL). The agitation rate for all experiments was of 150 rpm and the residence time was (1, 3, 5, 7, 10, 20, 30, 40, 50 and 60 min). In most of the reactions, equilibrium takes place after 10 min.

0.1 mL of sample was taken from the reaction solution and diluted to 10 mL by distilled water, the solution is then separated from the adsorbent by using filter paper and the residual heavy metal ions concentration in the solution is then determined using Shimadzu UV- 160A spectrophotometer at 365 nm.

RESULTS AND DISCUSSION

Adsorption kinetics: In a kinetic study of the adsorption of Cr^{6+} on different amounts of activated carbon at 25 °C using different solution volumes and different initial solution concentrations at the same contact time is covered out. A plot of log C against time was applied as shown in Fig. 1. It gave straight lines which indicated that the reaction was classified as a first order. In a first order reaction, the rate is directly proportional to the concentration of the reacting substance. According to the first order equation, the slope of the straight line is $-(k/2.303)$ and intercept is log C_0 as shown in the following equation:

$$\log C = -(k/2.303)t + \log C_0 \qquad (1)$$
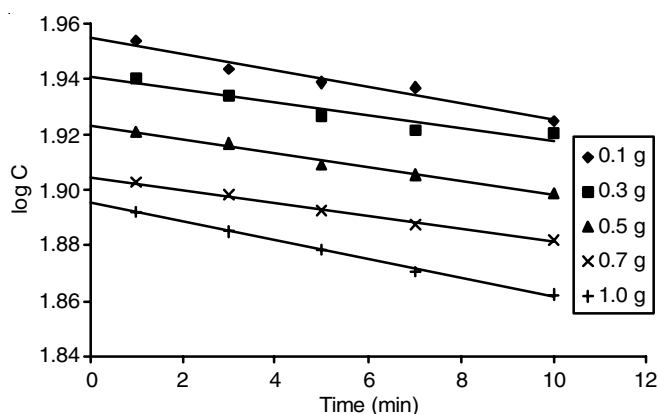
all parameters were mentioned above.

Fig. 1. Relation between log C and time for 200 mL of 100 mg L^{-1} Cr^{6+} solution (blank) in the presence of different amounts of activated carbon at 25 °C

Fig. 1 shows the reaction kinetics for the adsorption of Cr^{6+} on different amounts of activated carbon as well as different solution volumes using different initial concentrations at 25 °C. From the slopes of the straight lines obtained, the rate constants were calculated according to eqn. 1. It is clear that as the amount of adsorbent used increases, the rate constant directly increases; while increasing the initial concentration

as well as the volume of the solution the rate constant decreases. Figs. 2 and 3 show the relation between % removal which is given by eqn. 2 and contact time for the solutions in the presence of different amounts of adsorbent at 25 °C.

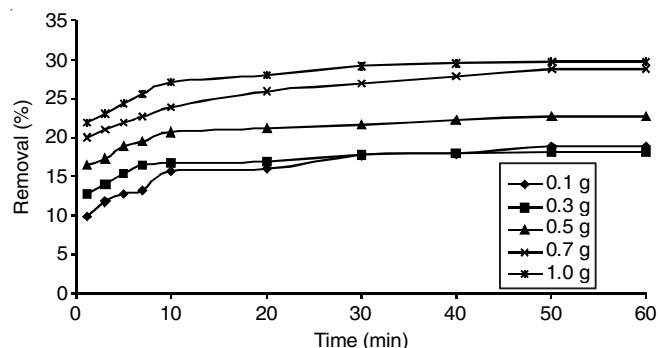$$\text{Removal (\%)} = (C_0-C)/C_0 \times 100 \qquad (2)$$

Fig. 2. Effect of time on % removal of Cr^{6+} ions in the presence of different amounts of activated carbon for (200 mL of 100 mg L^{-1} solution) at 25 °C
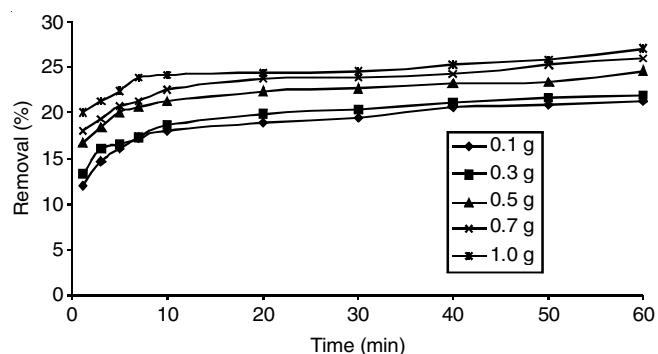

Fig. 3. Effect of time on % removal of Cr^{6+} ions in the presence of different amounts of activated carbon for (100 mL of 150 mg L^{-1} solution) at 25 °C

It is clear that at the beginning % removal increases rapidly in very few minutes. By increasing time of contact, % removal increases lightly and slowly till reaches maximum value and this can be explained on the basis that, at the beginning large surface area of adsorbent is available for the adsorption of metal and by time the surface adsorption sites become exhausted [10]. Increasing of time of contact not only increases % removal, but also increases the amount of Cr^{6+} adsorbed per gram of adsorbent used (q_e) which is given by the following eqn. 3:

$$q_e = (C_0-C_e) \, v/m \qquad (3)$$

where, C_0 is the initial concentration of Cr^{6+} solution (mg/L); C_e is the Cr^{6+} solution concentration at equilibrium (mg/L); m is the mass of adsorbent used (g); v is the Cr^{6+} solution volume (L).

Fig. 4 shows the relation between the amount of adsorbed ion per gram of adsorbent and contact time in the presence of different amounts of adsorbent at 25 °C. By increasing time of contact, (q_e) increases rapidly at first and by time slightly and slowly increases till reaches maximum value as explained above.

Fig. 5 shows the effect of time on adsorbed amount of Cr^{6+} in the presence of different amounts of activated carbon at 25 °C.
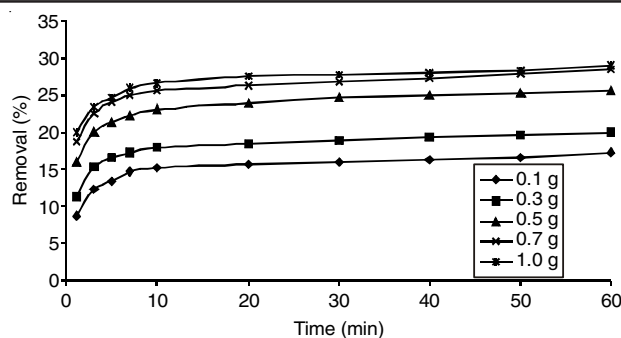
Fig. 4.   Effect of time on % removal of Cr^{6+} ions in the presence of different amounts of activated carbon for (50 mL of 150 mg L^{-1} solution) at 25 °C
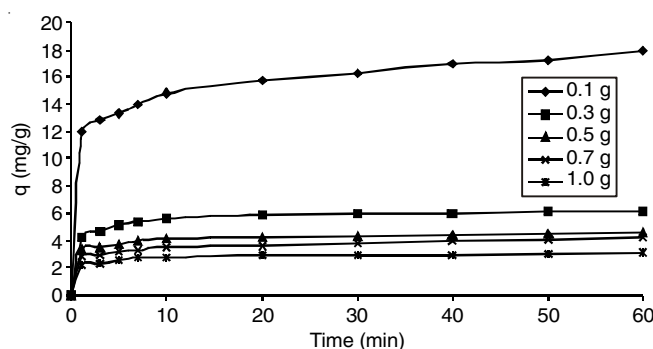

Fig. 5.   Effect of time on adsorbed amount of Cr^{6+} in the presence of different amounts of activated carbon for (100 mg L^{-1} of 100 mL solution) at 25 °C

Effect of variation of initial Cr^{6+} concentrations: The initial Cr^{6+} concentration is an important parameter in adsorption since a certain amount of adsorbent can adsorb a certain amount of Cr^{6+}. Fig. 6 shows the relation between % removal and Cr^{6+} initial concentrations. By increasing Cr^{6+} initial concentrations (C_0) from 50 to 150 ppm, % removal decreases and this may be due to the formation of aggregates as a result of flocculated particles for higher solid/liquid ratio. Dilution allows dispersing the particles and therefore increases the available adsorption sites [11]. Fig. 7 shows the relation between amount of Cr^{6+} adsorbed per gram adsorbent at equilibrium (q_e) and initial concentration of adsorbate (C_0). It is clear that (q_e) directly increases with increasing (C_0) from 50 to 150 ppm since increasing of initial concentration (C_0) increases the molecules build up on adsorbent surface [12].
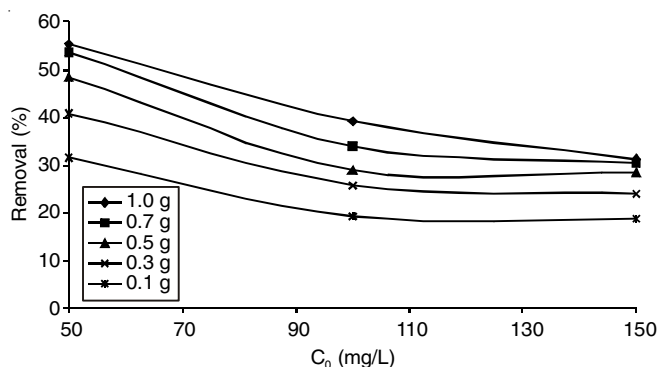

Fig. 6.   Effect of initial concentrations on % removal for 50 mL of Cr^{6+} solution in presence of different amounts of activated carbon at 25 °C
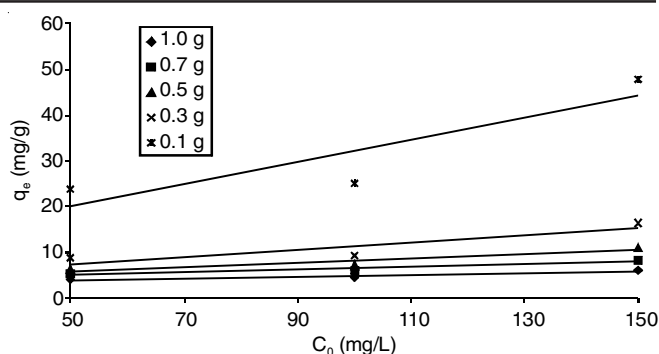

Fig. 7.   Effect of initial concentrations on quantity adsorbed for 150 mL of Cr^{6+} solution in presence of different amounts of activated carbon at 25 °C

Effect of variation of solution volume: Fig. 8 shows the relation between % removal and solution volumes. By increasing Cr^{6+} solution volume from 50 to 150 mL, % removal decreases. Fig. 9 show the relation between the amount of Cr^{6+} adsorbed per gram of adsorbent at equilibrium (q_e) and solution volume. It is clear that, (q_e) increases with increasing solution volume from 50 to 150 mL and this can be explained on the basis that there is a plenty of active sites on the surface of the adsorbent that can adsorb more Cr^{6+} by increasing its solution volume. Mathematically, (q_e) is directly proportional with the adsorbate volume as show in eqn. 2.
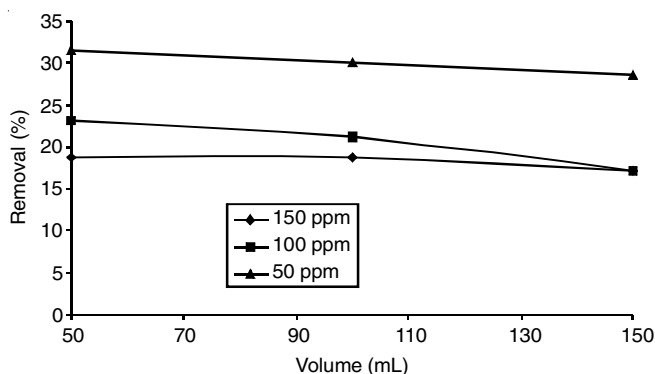

Fig. 8.   Effect of Cr^{6+} solution volume on % removal for different initial concentrations solution in presence of 0.1 g of activated carbon at 25 °C
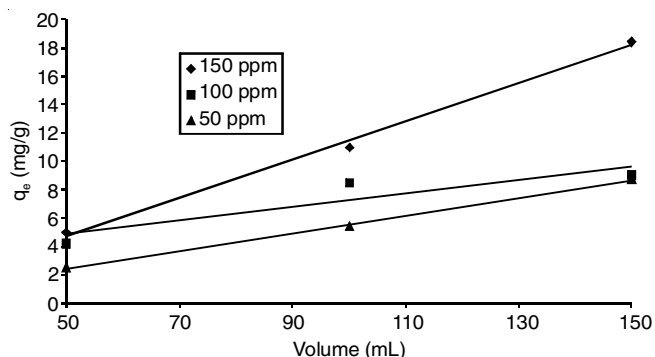

Fig. 9.   Effect of solution volume on Cr^{6+} adsorbed for different initial concentrations solution in presence of 0.3 g activated carbon at 25 °C

Effect of addition of different amounts of adsorbent: Fig. 10 shows the relation between % removal and amounts

of adsorbent used. By increasing the amount of adsorbent, % removal increases since more adsorption sites are available for adsorption process. Fig. 9 shows the relation between the amount of Cr^{6+} adsorbed per gram adsorbent at equilibrium (q_e) and amount of adsorbent used. It is obvious that, increasing amounts of adsorbent used decreases (q_e) and this is because the amount of adsorbate adsorbed is a function of surface area (external and intra particle). By increasing amount of adsorbent, the available surface increases and thus, amount of Cr^{6+} adsorbed per gram adsorbent at equilibrium (q_e) decreases and therefore; (q_e) is inversely proportional with the mass of adsorbent as shown in eqn. 2.
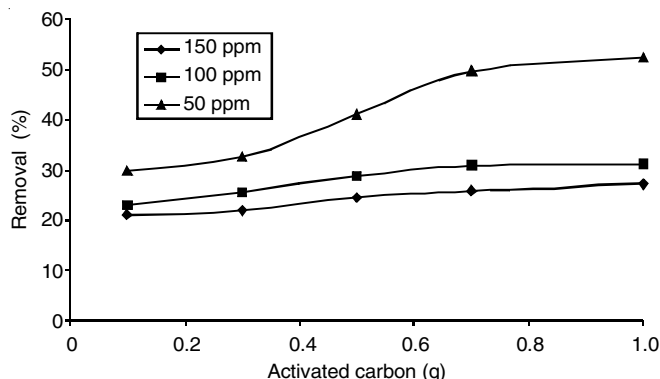

Fig. 10. Effect of the amount of activated carbon on % removal for 100 mL of different initial concentrations solution at 25 °C

Adsorption isotherm: Adsorption isotherm for adsorption of chromium ions on adsorbent (activated carbon) is shown in Fig. 11, plots of (q_e) against (C_e) are represented in all figures. (q_e) increases by increasing (C_e) with higher slope at the initial stages which indicates that initially, there are numerous readily accessible sites for adsorption process. Eventually (q_e) reaches maximum value at higher (C_e) indicating that the adsorption is saturated at this level. Analysis of isotherm data is important in order to develop an equation which accurately represents the results and could be used for design purposes. In this study, two models Langmuir and Freundlich isotherm have been selected.
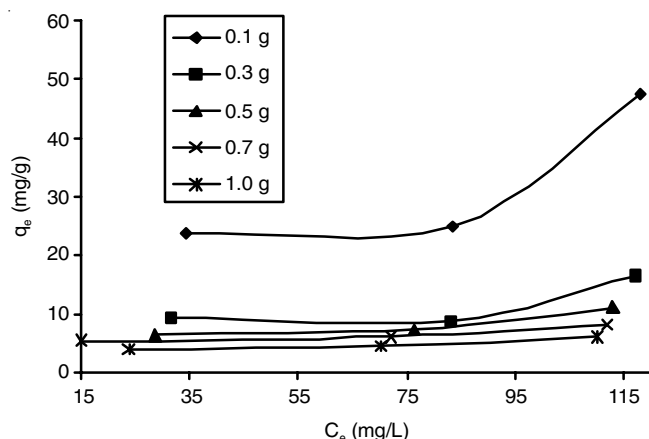

Fig. 11. Equilibrium adsorption isotherm using different amounts of activated carbon for 150 mL Cr^{6+} solution at 25 °C

Langmuir isotherm: Langmuir isotherm can be explained by the following equation:

$$q_e = (K_L C_e)/(1 + a_L C_e) \qquad (4)$$

where K_L, a_L are Langmuir constants while q_e, C_e were mentioned above.

This equation can be converted from convenient into a linear for plotting and determining Langmuir constants K_L, a_L as following:

$$C_e/q_e = 1/K_L + (a_L/K_L) C_e \qquad (5)$$

The plot of C_e/q_e against C_e using experimental data obtained at different masses leads to a linear relationship suggesting the applicability of Langmuir model. It demonstrates that monolayer coverage of the adsorbate occurs at outer surface of the adsorbent [13]. Values of K_L and a_L for different amounts of adsorbent (m) have been calculated (Table-1). The results obtained which indicates the existence of high correlation coefficients values r, the adsorption capacity of the adsorbent is decreasing with the mass of the adsorbent as a result of larger surface area attained. The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R, which is defined by the following equation [14].

$$R = 1/(1 + a_L C) \qquad (6)$$

where, C is the adsorbate concentration at q_{max} (mg/g), the separation factor indicates the shape of the isotherm as following:

Unfavourable:	R > 1
Linear:	R = 1
Favourable:	0 < R < 1
Irreversible:	R = 0

Values of R for Cr^{6+}/adsorbent system have been calculated R values indicated that activated carbon is favourable towards the adsorption of Cr^{6+}.

TABLE-1
LANGMUIR ADSORPTION PARAMETERS FOR
150 mL OF Cr^{6+} SOLUTION USING DIFFERENT
AMOUNT OF ACTIVATED CARBON AT 25 °C

Activated carbon (g)	K_L (dm³ mg⁻¹)	q_{max} (mg g⁻¹)	a_L	R_L	r
0.1	1.5250	52.35	0.0166	0.3435	0.9376
0.3	0.9095	18.45	0.0204	0.3023	0.9199
0.5	0.3311	11.61	0.0260	0.2568	0.8338
0.7	0.3208	8.95	0.0336	0.2157	0.8720
1.0	0.2824	6.55	0.0431	0.1791	0.9284

Freundlich isotherm: Freundlich isotherm model was also used to explain the observed phenomena. The experimental equilibrium data for the adsorption of Cr^{6+} on activated carbon is analyzed by using Freundlich isotherm as in the following equation:

$$q_e = K_F C_e \ 1/n \qquad (7)$$

where, K_F and n are Freundlich parameters, the equation may be linearized using a logarithmic plot which enables the exponent n and constant K_F to be determined as following equation:

$$\log q_e = \log K_F + 1/n \log C_e \qquad (8)$$

The linear plots of log q_e against log C_e obtained at different amounts of activated carbon indicating the applicability of Freundlich model. The parameters K_F and n obtained have been calculated from the experimental data and the results

obtained which show high correlation coefficients values r (Table-2). These results also show that the values of Freundlich exponent n are greater than unity indicating that Cr^{6+} is favourably adsorbed by activated carbon [15-17].

TABLE-2
FREUNDLICH ADSORPTION PARAMETERS
FOR 150 mL Cr^{6+} SOLUTION USING DIFFERENT
AMOUNTS OF ACTIVATED CARBON AT 25 °C

Activated carbon (g)	log K_F (dm^3 mg^{-1})	q_{max} (mg g^{-1})	1/n	r
0.1	0.458	52.35	0.573	0.9634
0.3	0.339	18.45	0.410	0.9395
0.5	0.314	11.61	0.341	0.9226
0.7	0.311	8.95	0.294	0.9490
1.0	0.232	6.55	0.257	0.9643

Mechanism of adsorption: All data indicate that activated carbon has an effective role in the removal of hexavalent chromium (Cr^{6+}) from wastewater and this is due to extensive porosity and very large available surface area. The mechanism suggested for the adsorption of Cr^{6+} on the studied activated carbon could be physisorption through weak van der Waals forces between ions and studied activated carbon [18-20], which based on the calculation of G_{ads} (Table-3).

TABLE-3
FREE ENERGY OF ADSORPTION (ΔG_{ads}) FOR
LANGMUIR ADSORPTION ISOTHERM FOR 150 mL
OF Cr^{6+} SOLUTION USING DIFFERENT AMOUNTS
OF ACTIVATED CARBON AT 25 °C

Activated carbon (g)	K_L (dm^3 mg^{-1})	$-\Delta G_{ads}$ (kJ mol^{-1})
0.1	1.5250	11.004
0.3	0.9095	9.722
0.5	0.3311	7.217
0.7	0.3208	7.139
1.0	0.2824	6.826

Conclusion

• In this work, we have investigated the effect of the presence of different organic acids (acetic acid, chloroacetic acid, dichloroacetic acid, trichloroacetic acid, sulphosalisylic acid, citric acid and phthalic acid) upon the reaction was investigated as a side chain on the rate of reduction of Cr(VI) to Cr(III) on iron sheet. Adsorption isotherms have been applied to study the kinetics of the adsorption behaviour and to determine the adsorption capacity of the absorbents.

• The % acceleration caused by organic acids depending on the type of substituting group attached and its concentration.

• Rate of the reaction increases by increasing the rotation speed which support that reaction diffusion controlled reaction.

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