

Equilibrium and kinetic studies of Cr(VI) removal from aqueous solution using DiaionSA20A exchange resin.

F.H.G.Mesbah*, T.M.Zewail, H.A.Farag

Abstract— The removal of Cr(VI) from aqueous solutions by the use of ion exchange (Diaion SA20A) resin has been investigated. Batch sorption processes were carried out to investigate various physicochemical parameters such as pH, equilibrium contact time, initial metal ion concentration, rpm, resin dosage, and temperature. The optimum pH for Cr(VI) removal was found at 4.28. The equilibrium data were tested using three isotherm models namely, Langmuir, Freundlich and Temkin. The present equilibrium data was found to be best described by Langmuir isotherm model with a high correlation coefficient. The maximum adsorption capacity of the resin was found to be 166.6 mg/g. The present kinetic data are well described by the pseudo second-order reaction to a great extent. The results revealed that both film diffusion and intraparticle diffusion contribute to the rate-determining steps.

Index Terms— Cr(VI) removal, Equilibrium, Freundlich, ion exchange, kinetic, Langmuir, waste water treatment.

1 INTRODUCTION

Recently most of scientists become more interested in industrial effluent wastewater treatment specially the removal of heavy metals contaminants as Chromium, Copper, Manganese, Mercury and Cadmium which are significantly toxic to living creatures, ecological environments and increase the water pollution due to their disposal from different industrial sectors.

Chromium is extensively used in many chemical processes such as pigments and paints, leather tanning, fungicides, electroplating, cement, steel, ceramic and glass industries. Chromium plating was once widely used to give steel a polished silvery mirror coating. Chromium is used in metallurgy to impart corrosion resistance and a shiny finish; Chromium (IV) oxide (CrO_2) is used to manufacture magnetic tape. The presence of Cr(VI) ion in the wastewater generated from these industries has become a major concern today due to its deleterious effects on health and environment[1],[2].

Chromium is unique among regulated toxic elements in the environment in that, chromium exists in nature in three oxidation states namely : Cr(II), Cr(III) and Cr(VI), only the latter two are stable[3]. The most common Cr(VI) forms are chromate (CrO_4^{2-}), hydrogen chromate (HCrO_4^-) also called bichromate, and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) can also occur. The relative amount of these species depends on pH, and concentration.

Hexavalent chromium is known to be toxic to human,

animals, plants and microorganisms. In contrast trivalent chromium is essential for human and less toxic than hexavalent chromium and easily to be removed by simple chemical precipitation by lime as $\text{Cr}(\text{OH})_3$ [4].

Various physicochemical methods have been developed for removal of Cr(VI), including reduction, and chemical precipitation, electrochemical deposition, ion exchange, membrane separation and adsorption. However, in chemical reduction chemical costs are high and the system must include filtration or sedimentation. Moreover, these systems are not cost-effective for low concentrations of Cr(VI) in the wastewater.

Adsorption is relatively new practice for the removal of chromium. It has been a useful tool for controlling the extent of metal pollution. Activated carbons are expensive and can remove a few milligrams of metal ions per gram of activated carbon, and there are still some problems encountered in the regeneration process.

Membranes can treat inorganic effluent with a high Cr(VI) concentration. Depending on membrane characteristics, membrane filtration system can remove chromium at a wide range of operational conditions. Another technique for removal of Cr(VI) was electrochemical treatment with the advantage of low-cost and high selectivity, many simultaneous processes could take place on the electrode surface or in the aqueous solution. Selection of a suitable technique depends on initial Cr(VI) concentration, plant flexibility and reliability, environmental impacts and economic consideration and operational cost.[5]

The main advantages of ion exchange are recovery of metal value, selectivity, less sludge volume produced and

- Fatma H. G. Mesbah is currently pursuing Doctorate degree program in chemical engineering in Alexandria university, Egypt. E-mail: elmshkat@gmail.com
- Hasan A. Farag is professor in chemical engineering Alexandria University, Egypt. E-mail: abulfarag111@yahoo.com
- Taghreed M.Zewail is Associate professor in chemical engineering Alexandria University, Egypt. E-mail: tageng2009@gmail.com

the meeting of strict discharge specifications. Ion exchange using synthetic resins is the method of choice for removing toxic metal contaminants in wastewater [6].

Ion exchange materials are insoluble substances containing loosely held ions which are able to be exchanged with other ions in solutions which come in contact with them. These exchanges take place without any physical alteration to the ion exchange material. [7]

Ion exchange process depends on the mechanism by which mobile ions from an external solution are exchanged in the opposite direction for an equivalent number of ions that are electrostatically bound to the functional groups contained within a solid matrix of the ion exchange material. Kinetics of the ion exchange reaction represents the speed with which reaction takes place. Upon designing an ion exchange process system, the rate of exchange, which is subjected to mass-transfer resistances in both liquid and solid phases, is highly significant in the design and operation of the ion exchange process. Adsorption isotherm is an invaluable curve describing the phenomenon governing the retention (or release) or mobility of a substance from the aqueous porous media or aquatic environments to a solid-phase at a constant temperature and pH. [8]

The main objective of the present study is to investigate the equilibrium and kinetic studies of Diaion SA20A strong anion exchange resin for the removal of Cr(VI) from synthetic wastewater. To this end the following parameters are studied: initial Cr(VI) ion concentration, temperature, contact time, rpm, resin amount, and initial pH values.

2 MATERIAL AND METHOD

2.1 Material

The resin used in this study was Diaion SA20A (Mitsubishi Chemical, Japan) which was supplied by Alex. Petroleum Company. Table [1] shows the main physicochemical properties of the resin investigated. All the chemicals used were of analytical grade. Distilled water was used to prepare all solutions throughout the experiments. Cr(VI) stock solution of 1000 ppm was prepared by dissolving 2.829 g $K_2Cr_2O_7$ salt in distilled water.

TABLE 1
 THE PHYSICAL AND CHEMICAL SPECIFICATION OF DIAION SA20A

Particle size range	0.3 – 1.18 mm
Uniformity coefficient	1.6 max
Ionic form as shipped	Cl^-
Volume change	15 max % $Cl^- \rightarrow OH^-$ form
Total exchange capacity	>1.3 meq/ml (Cl^- form)
Moisture holding capacity	45 to 52% (Cl^- form)
pH stability range	0 – 14
Operating pH range	0 – 12
Operating temperature	40°C max. (OH^-) : 60°C max. (Cl^-)

2.2 Methods

A series of standard Cr(VI) solution were prepared by dilution of the stock solution(100 -500 ppm). The resin was conditioned by soaking in conc. HCl for 15 min, washed with distilled water, and then soaked in 2M NaOH for 24 hours to change the ion-exchanger from Cl^- to OH^- form. The resin was washed with distilled water until the pH reached 8 to 9. The resin was air dried and stored for batch studies. [9]

For Cr(VI) ion kinetics and equilibrium studies, 5g dried ion-exchange resin was brought in contact with 2L of Cr(VI) solution at constant speed using 45° pitched impeller at 25°C. Samples were withdrawn every five min., for analysis. The concentrations of Cr(VI) ions in initial and final solutions were determined spectrophotometrically at 540nm by UV-vis spectrophotometer (MODEL 4401/20, Bargain) using 1,5-diphenyl carbazide as a complexing agent.[10]

The % Cr(VI) removal was calculated using the following equation:

$$\% \text{ removal} = \left(\frac{C_0 - C_t}{C_0} \right) * 100 \quad (1)$$

Where C_0 is the initial Cr(VI) concentration, C_t is the Cr(VI) concentration at time t. The effect of pH on Cr(VI) ion adsorption was evaluated by adjusting the initial pH of the initial solution within the range of 2–6. The pH solution was adjusted to the desired value with 2M NaOH or 2M HCl.

3 RESULTS AND DISCUSSION

3.1 Effect of solution pH

Fig. (1) Represents the effect of initial pH on the removal of the Cr(VI) by Diaion SA20A resin. It is well seen that the sorption of Cr(VI) increases with the increase of pH from 2 to 4.28 . Beyond pH=4.28 there is a decrease in %Cr(VI) removal with further increase in pH to 6.

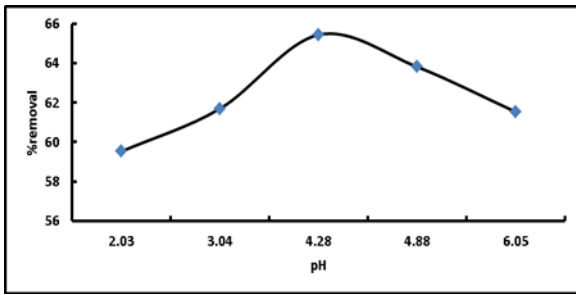


Fig. 1 Effect of pH on the % removal of Cr(VI) by Diaion SA20A (conditions: C_o , 200ppm; amount of resin, 5 g; temperature, 25 ± 2 °C; stirring rate 350 rpm; t, 40 min)

At very low pH values, the surface of the resin would be surrounded by the H^+ ions which enhance Cr(VI) interaction with binding sites of the resin by greater attractive force. [11]

Fig. (2) represents the relative distribution of Cr(VI) species in water as a function of pH and Cr(VI) concentration.

It can be noted that the hexavalent species exists primarily as chromic acid (H_2CrO_4) and its salts, hydrogen chromate ion ($HCrO_4^-$) and chromate ion (CrO_4^{2-}), depending on the pH within the range of Cr(VI) concentration used in the present study. The predominant species present, are H_2CrO_4 at pHs less than about 1, $HCrO_4^-$ at pHs between 1 and 6, and CrO_4^{2-} at pHs above about 6. [12]

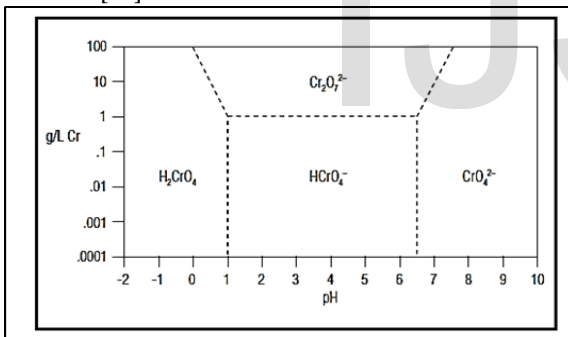


Fig. 2 Relative distribution of Cr(VI) species in water as a function of pH and Cr(VI) concentration.

At $pH > 4.28$, the decrease of %Cr(VI) removal can likely be ascribed to the decrease of $HCrO_4^-$ ion concentration and the effect of competitive binding between CrO_4^{2-} and OH^- for the binding sites on the surface of the resin. [13]

The present result is in agreement with previous studies. [25], [27]

3.2 Effect of contact time

Fig. (3) shows the effect of contact time on the % removal of Cr(VI). The % removal of Cr(VI) increased with increasing contact time and attained equilibrium at about 40 min.

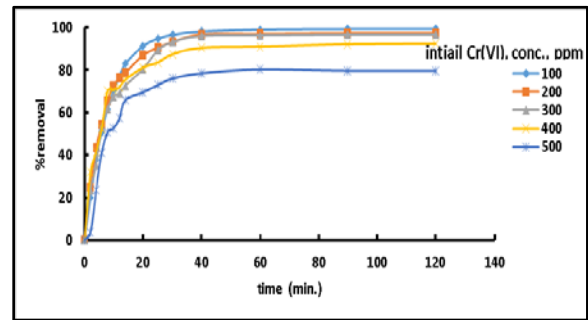


Fig.3 Effect of contact time on the % removal of Cr(VI) Diaion SA20A resin (amount of resin 5 g; temperature, 25 ± 2 °C; stirring rate 350 rpm; initial pH 4.28)

3.3 Effect of Initial Cr⁺⁶ Concentration

Fig. (4) shows the effect of initial Cr(VI) concentrations on % removal. It is well seen that % removal of Cr(VI) decreases as the initial Cr(VI) increases. It should be indicated that as the initial concentration of Cr(VI) ions increases for a constant resin weight the ratio of the exchange sites available to Cr(VI) ions decreases.

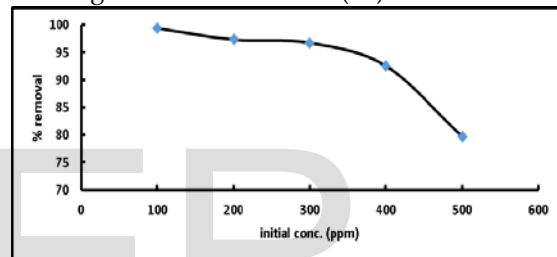


Fig. 4 Effect of initial concentration on % removal of Cr(VI). (Initial pH of 4.28; Contact time of 120 min; amount of resin 5 g; and Temperature of 25 ± 2 °C & 350 rpm.)

3.4 Effect of rpm

Fig. (5) Shows the effect of rpm on % Cr(VI) removal. It is well obvious that the increase of rpm increases %Cr(VI) removal. As the rpm increases, the degree of mixing and turbulence increase, with a consequence decrease of both the hydrodynamic and the concentration boundary layer thicknesses. The film resistance around each resin particle decreases and mass transfer rate increases. The present trend is in agreement with previous study. [9]

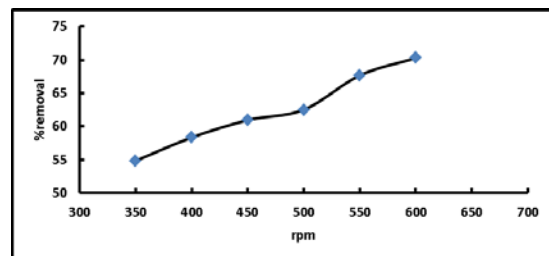


Fig. 5 Effect of rpm on % Cr(VI) removal. (pH of 4.28; Contact time of 40 min; amount of resin 5 g; and Temp. 25 ± 2 °C; C_o = 500ppm.)

3.5 Effect of resin amount

The effect of the amount of resin on % removal of Cr(VI) ions was investigated. Fig. (6) shows the effect of the amount of resin on % Cr(VI) removal. It is well clear that as the amount of resin increases % Cr(VI) removal increases considerably. It is well known that the ratio of the number of available exchange sites to the number of Cr(VI) ions at fixed Cr(VI) concentration increases with the increase of the amount of resin and this results in an increase in %Cr(VI) removal.

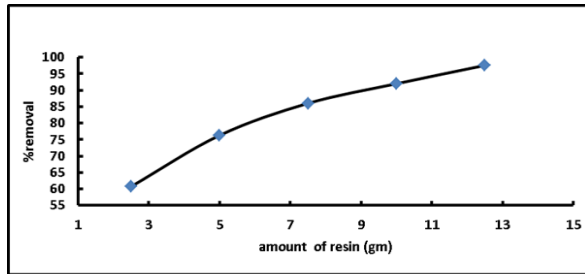


Fig. 6 Effect of resin amount on % removal of Cr(VI). (Initial pH of 4.28; contact time 120 min; temperature of 25±2 °C; C_o = 200ppm & 350 rpm.)

3.6 Effect of Temperature

The effect of temperature on the % removal of Cr(VI) by Diaion SA20A is shown in Fig. (7). It can be noticed that as temperature increases, % Cr(VI) removal increases. The increase of % Cr(VI) removal with temperature may be attributed to that as temperature increases, the viscosity of the solution decreases with a consequence increase of chromate diffusivity according to Stokes-Einstein equation.[14]

$$D\mu/T = \text{constant} \quad (2)$$

The present results are in agreement with other investigators. [1], [27], [30]

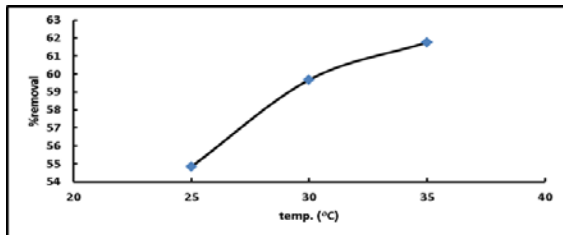


Fig. 7 Effect of temperature on % Cr(VI) removal . pH 4.28; Contact time 40 min; amount of resin 5 g;350 rpm & C_o = 500ppm

3.7 Determination of the ion exchange Capacity

The ion exchange capacity at any time t, was calculated according to the following equation:

$$qt = \frac{(C_o - C_t)V}{W} \quad (3)$$

Where: q_t = ion exchange capacity at time (t), C_o = initial concentration of Cr(VI) in the solution, C_t = concentration of Cr(VI) at time (t), V = volume of the solution and W = weight of the resin.

Fig. (8) Shows a plot of ion exchange capacity versus time at different initial Cr(VI) concentrations.

It can be seen that as time increases the ion exchange capacity increases until a plateau is reached at about 40 minutes, It may be concluded that at 40 minutes, equilibrium has been established between solute concentration in solid and its concentration in solution.

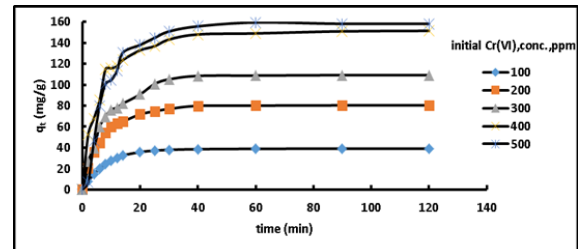


Fig. 8 Ion exchange capacity versus time at different initial Cr(VI) conc. (pH of 4.28; Contact time of 120 min; amount of resin of 5 g; 350 rpm and Temp. 25±2 °C.)

3.8 Equilibrium Studies

The sorption of Cr(VI) ions was carried out at different initial chromium concentrations at optimum pH . Sorption isotherms can be used to describe how solutes interact with the resin at equilibrium. Three kinds of known isotherm equations, Langmuir, Freundlich and Temkin isotherms, have been applied for present study. These isotherms relate metal uptake per unit weight of resin q_e at equilibrium to the equilibrium metal ion concentration in the bulk fluid phase C_e. The three isotherms will be described in the following sections.

Langmuir Isotherm can be described by the following equation:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (4)$$

which in linearized form can be represented by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (5)$$

Where C_e = the equilibrium concentration of adsorbate, q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium, q_m = maximum monolayer coverage capacity, K_L = Langmuir isotherm constant. The values of q_{max} and K_L were computed from the slope and intercept of the Langmuir plot of C_e/q_e versus C_e .

Fig. (9) represents the relation between C_e/q_e versus C_e using the present equilibrium data.

It is well seen that the present equilibrium data well fit the Langmuir isotherm with a high correlation coefficient (0.9987). This may indicate that sorption of Cr(VI) ions form mono adsorption layer on the resin. The present results are in agreement with other investigators [23], [25].

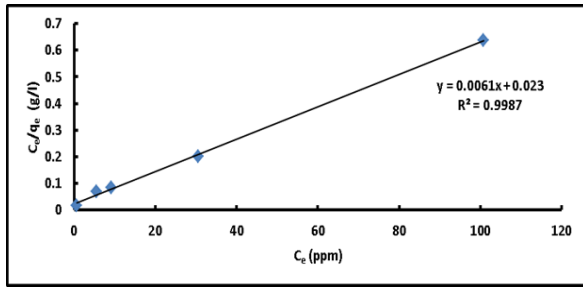


Fig. 9 Langmuir isotherm of Cr(VI) sorption on Diaion SA20A (conditions: $C_o = 100 - 500$ ppm ; amount of resin, 5 g; temperature, 25 ± 2 °C; stirring rate 350 rpm; stirring time: 120 min)

A separation factor (R_L) is a dimensionless constant, which can be represented by the following equation:

$$R_L = \frac{1}{1 + K_L C_o} \quad (6)$$

Where K_L is the Langmuir constant and C_o is initial concentration. In a deeper explanation, R_L value indicates the adsorption nature to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$) [15].

Fig. (10) depicts the relation of R_L versus initial Cr^{6+} conc. It is well obvious that values of R_L lay between 0 and 1 which indicate favorable sorption.

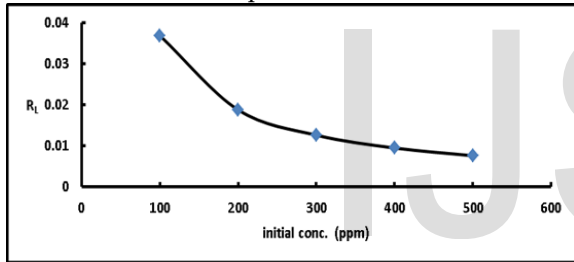


Fig. 10 Separation factor of Cr(VI) sorption by ion exchange resin (DiaionAS20A).

Table [2] shows the values of maximum adsorption capacity of Cr(VI) at different types of ion exchange resins ($q_{max} = 166.66$). The table shows also that the present resin is relatively competitive with other resin types in its ability to remove Cr(VI)

Freundlich Isotherm can be described by the following equation:

$$q_e = K_f C_e^n \quad (7)$$

Linearization of the Eq. (7) would yield the following equation:

$$\ln q_e = \ln K_f + n \ln C_e \quad (8)$$

Where K_f is Freundlich isotherm constant, n = adsorption intensity; C_e = the equilibrium concentration of adsorbate. q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium.

Fig. (11) represents the relation between $\ln q_e$ versus $\ln C_e$ using the present equilibrium data. It is well noticed that the present data fit the Freundlich isotherm to a relatively high correlation coefficient (0.9406). The values of n (0 - 1)

where its values represent adsorption intensity or surface heterogeneity, as the value of (n approaches zero) the surface becomes more heterogeneous. [16]

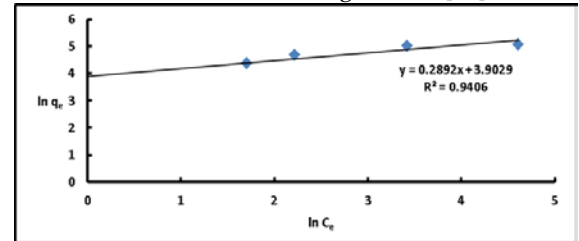


Fig. 11 Freundlich isotherm of Cr(VI) sorption on Diaion SA20A ($C_o = 100 - 500$ ppm ; amount of resin, 5 g; temp., 25 ± 2 °C; stirring rate 350 rpm; stirring time, 120 min; pH, 4.28)

TABLE 2
THE MAXIMUM ADSORPTION CAPACITY OF CR(VI) AT DIFFERENT TYPES OF ION EXCHANGE RESINS

Ion exchanger' name	q_{max} (mg/g)	pH	Reference number
Amberlite IRA96	135.332	3	[1]
Dowex 1X8	158.868	4	[1]
Lewatit MP 62	117.68	5	[5]
Lewatit M 610	120.622	5	[5]
Cell - AE	122.45	3.5	[21]
Duolite A7	34.01	3.5	[21]
Amberlite IRA 743	29.25	3-5	[22]
KIP210	100	3	[23]
magnetic PS-EDTA	250	4	[24]
Spectra/Gel IE 1x8	169.49	3.5	[25]
AmberliteIRA900	116	4.64	[26]
A- 400	120.55	4-5.3	[27]
A - 850	95.82	4-5.3	[27]
Chitosan(amido-grafted)	935	4	[28]
Chitosan grafted - polyacrylonitrile	218.82	4-5.5	[29]
DiaionSA20A	166.66	4.28	Current study

Temkin Isotherm: [16]

The model could be represented by the following equations:

$$q_e = B \ln A_T + B \ln C_e \quad (9)$$

$$\text{Where } B = \frac{RT}{b_T} \quad (10)$$

A_T = Temkin isotherm equilibrium binding constant, b_T = Temkin isotherm constant, R = universal gas constant, T = Temperature, B = Constant related to heat of sorption.

Fig. (12) Shows the liner plots of q_e versus $\ln C_e$ of the present equilibrium data. The present data fit Temkin Isotherm to a relatively high extend.

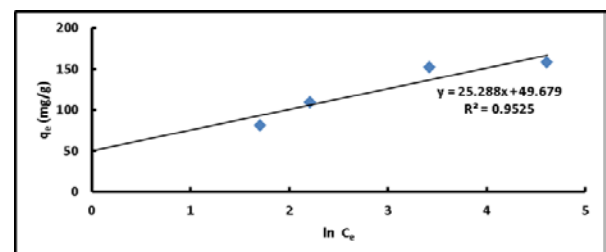


Fig. 12 Temkin isotherm of Cr(VI) on Diaion SA20A ($C_o = 100 - 500$ ppm ; amount of resin, 5 g; temp., 25 ± 2 °C; stirring rate 350 rpm; stirring time, 120 min; initial pH, 4.28).

Table [3] gives the values of all constants of each isotherm with their correlation coefficient (R^2).

TABLE 3
VALUES OF ALL CONSTANTS OF THE INVESTIGATED ISOTHERMS AND THEIR CORRELATION COEFFICIENTS.

Langmuir Model	Freundlich Model	Temkin-isotherm-model
$q_m=166.6 \text{ mg/g}$	$K_F = 49.501 \text{ (l g}^{-1}\text{)}$	$B=25.28 \text{ (J/mol)}$
$K_L = 0.261 \text{ (l g}^{-1}\text{)}$	$1/n = 3.460$	$b_T = 98.005$
$R^2 = 0.9987$	$n = 0.289$	$A_T=7.133 \text{ (lg}^{-1}\text{)}$
	$R^2 = 0.9406$	$R^2 = 0.9525$
Error analysis	Error analysis	Error analysis
$\chi^2 = 15.368$	$\chi^2 = 10.069$	$\chi^2 = 3.991$
HYBRID= 11.400	HYBRID = 10.317	HYBRID = 4.085

3.9 Kinetic studies

In order to investigate the mechanism of sorption and potential rate controlling steps such as mass transport and chemical reaction processes, kinetic models have been used to test the present experimental data. These kinetic models include the pseudo-first order model, the pseudo-second order model, Elovich kinetic model and intra-particle diffusion model.

The Pseudo-first Order Model: [17]

Lagergren (1898) presented a first-order rate equation to describe the kinetic process of liquid-solid phase adsorption of oxalic acid and malonic acid onto charcoal; it can be presented as

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (11)$$

The integrated form of Eq. (11) becomes:

$$\log (q_e - q_t) = \log (q_e) - \left(\frac{k_1}{2.303}\right) t \quad (12)$$

Where q_e and q_t are the adsorption capacities at equilibrium and time t , respectively. k_1 is the pseudo-first-order rate constant for the kinetic model.

Fig.(13) shows the relation between $\log (q_e - q_t)$ versus time at different initial Cr(VI) concentrations. The present data fit the pseudo-first order model with a high correlation coefficient. The driving force, $(q_e - q_t)$, is proportional to the available fraction of active sites [18].

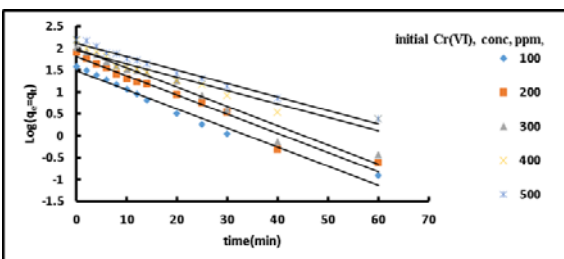


Fig. 13 Pseudo-first order model for the adsorption of Cr(VI) onto (DiaionSA20A), (amount of resin 5 g, pH 4.28, at 25 ± 2 °C; time = 120 min. & 350 rpm)

The pseudo-first order model proposed fits the experimental data well for an initial period of the first reaction step only. [19]

The Pseudo-second Order Model: [20]

If the rate of sorption is a second order mechanism, the pseudo second order chemisorption kinetic rate equation is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \quad (13)$$

Where q_e and q_t are the sorption capacity at equilibrium and at time t , respectively and k_2 is the rate constant of pseudo-second order sorption.

$$h = k_2 q_e^2 \quad (14)$$

Where h can be regarded as the initial sorption rate as $q_t = 0, t = 0$.

Eq. (13) can be written as:

$$\frac{t}{q_t} = \frac{1}{h} + \left(\frac{1}{q_e}\right) t \quad (15)$$

Fig. (14) shows a plot of t/q_t versus t at different initial Cr(VI) concentrations. The present data fit to a great extent the pseudo-second order model with high correlation coefficient (0.99).

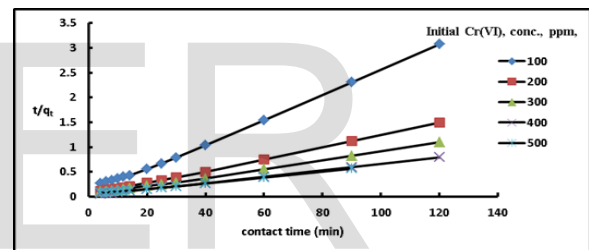


Fig.14 Pseudo-second-order kinetic plot for the adsorption of Cr(VI) onto (DiaionSA20A), (amount of resin 5 g ,pH 4.28, at 25 ± 2 °C; time = 120 min. & 350 rpm)

This suggests that the rate-limiting step may be chemisorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate. [19]

The present trend is in agreement with previous studies [21], [25].

Elovich Kinetic Model: [17]

The linear form of Elovich Equation is given by the following equation:

$$q_t = \frac{\ln a_e b_e}{b_e} + \frac{1}{b_e} \ln t \quad (16)$$

Where (a_e) is the initial adsorption rate, and the parameter (b_e) is related to the extent of surface coverage and activation energy for chemisorption. The values of a_e , and the desorption constant, (b_e) , were calculated from the intercept and slope of the straight-line plots of q_t against $\ln t$.

Fig. (15) represents a plot of q_t versus $\ln t$ at various initial Cr⁺⁶ conc. It is well seen that the Elovich kinetic model fits the present kinetic data to a relatively good extent,

particularly at low initial Cr⁶⁺ conc., however the model does not fit the kinetic data at initial conc. greater than 300 ppm.

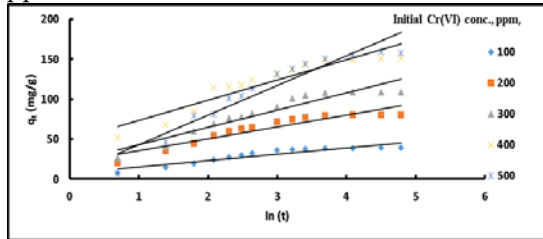


Fig. 15 Elovich kinetic plot for ion exchange of Cr (VI) onto (DiaionSA20A), (resin dose = 5 g, pH 4.28, at 25±2 °C; time =120 min. & 350 rpm)

Intra-particle Diffusion Model:

The intra-particle diffusion model is represented by the following equation:

$$q_t = k_i t^{1/2} + c \quad (17)$$

Fig. (16) shows the relation between q_t versus $t^{0.5}$ at different initial Cr(VI)conc. and Fig. (17) represents intra-particle diffusion model. The results revealed that both film diffusion and intraparticle diffusion contribute to the rate-determining steps. It is obvious that at conc. = 500ppm, the contribution of external film diffusion is negligible i.e. the reaction is mainly controlled by intraparticle diffusion.

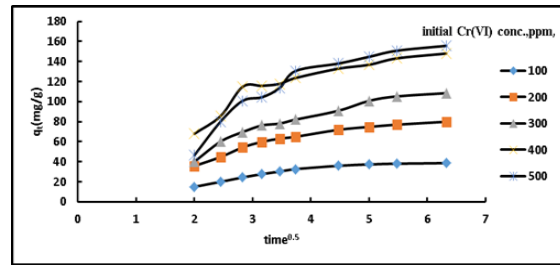


Fig.16 q_t versus $t^{0.5}$ at different initial Cr(VI)conc. for ion exchange of Cr (VI) onto (DiaionSA20A), (resin dose 5 g, pH 4.28, at 25±2°C, time =120min. & 350 rpm)

The present results are in agreement with other investigators [22], [24].

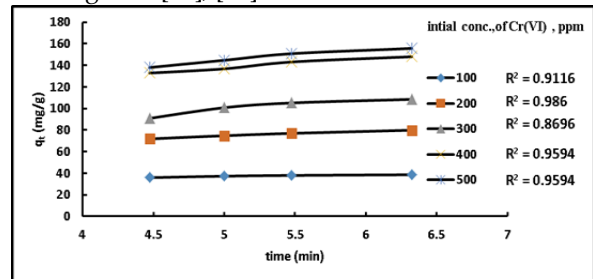


Fig. 17 intra-particle diffusion model plot for the sorption of Cr (VI) onto (DiaionSA20A), (resin dose 5 g, pH 4.28, at 25±2°C time =120min. & 350 rpm)

Table [4] gives a summary of the values of parameters of all investigated models and their correlation coefficients.

TABLE 4
 KINETIC MODEL PARAMETERS FOR CR (VI) SORPTION ON DIAION SA20A

Pseudo –first order				Pseudo-second order			
C_0 (ppm)	k_1 (min^{-1})	R^2		C_0 (ppm)	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	h ($\text{mg}/(\text{g} \cdot \text{min})$)	R^2
100	0.1004108	0.9809		100	0.0048	8.474	0.997
200	0.1011017	0.9718		200	0.0024	20.408	0.998
300	0.101332	0.9694		300	0.0014	22.222	0.998
400	0.0700112	0.9316		400	0.0015	41.666	0.999
500	0.0709324	0.9841		500	0.0004	14.492	0.918
%SSE = 5.090				%SSE = 1.901			
Intra-particle diffusion model				Elovich kinetics model			
C_0 (ppm)	k_i ($\text{mg g}^{-1} \text{min}^{-1/2}$)	C	R^2	C_0 (ppm)	b_s	a_s	R^2
100	1.4038	29.957	0.9116	100	0.126	20.506	0.86
200	4.3061	52.922	0.986	200	0.067	60.382	0.878
300	9.06	53.097	0.8696	300	0.046	58.443	0.904
400	8.4179	95.4	0.9737	400	0.039	173.835	0.879
500	9.5458	96.514	0.9594	500	0.027	43.848	0.912
%SSE = 12.3055				%SSE = 2.6492			

4 CONCLUSIONS

This study identified that [the gel type strong base Diaion SA20A resin] can be utilized for the removal of Cr(VI) ions from aqueous solution.

The effect of process variables, such as pH, resin amount, concentration of Cr (VI), temperature and phases contact time, on the sorption of Cr (VI) was investigated. The Cr (VI) removal efficiency is highest in solutions of initial pH at 4.28 and decrease with increasing Cr(VI) concentration and increases with the rise of resin dose, solution

temperature and phases contact time. The equilibrium data were better correlated with the Langmuir isotherm indicating chemisorption process in a monolayer on homogeneous active sites of the resin particles (ionic exchange). Kinetic calculations of the experimental data shows that sorption of Cr (VI) on the studied resin follows the pseudo-second order equation and is controlled by film diffusion in the initial stage of the sorption and by intra particle diffusion in the later stage.

REFERENCES:

- [1] S. Edeballi and E. Pehlivan, "Evaluation of Amberlite IRA96 and Dowex 1× 8 ion-exchange resins for the removal of Cr (VI) from aqueous solution", *Chemical Engineering Journal*, vol.161, no. 1, pp. 161-166, 2010.
- [2] Chromium – Cr, water treatment solution, <http://www.lenntech.com/periodic/elements/cr.htm>
- [3] S. Chen, Q. Yue, B. Gao, Q. Li, X. Xu, and K. Fu, "Adsorption of hexavalent chromium from aqueous solution by modified corn stalk: A fixed-bed column study", *Bioresource technology*, vol. 113, pp. 114-120, 2012.
- [4] L. E. Hawley, A. R. Deeb, C. M. Kavanaugh and R. G. J. Jacobs, *Treatment technologies for chromium (VI). Chromium (VI) handbook*, CRC Press, Boca Raton, pp. 275-310, 2004.
- [5] M. Owlad, M. K. Aroua, W. A. W. Daud, and S. Baroutian, "Removal of hexavalent chromium-contaminated water and wastewater: a review", *Water, air, and soil pollution*, vol. 200, no. 1-4, pp.59-77, 2009.
- [6] F. Gode and E. Pehlivan, "Removal of Cr (VI) from aqueous solution by two Lewatit-anion exchange resins", *Journal of Hazardous Materials*, vol. 119, no. 1, pp. 175-182, 2005.
- [7] Alchin David, Ion exchange resins, Service chemist: pp.1-7. also available at:
 - a. (<http://nzic.org.nz/ChemProcesses/water/13D.pdf>)
- [8] M. Luqman, *Ion Exchange Technology I, Theory and Materials*, Springer, vol. 1, 2012.
- [9] T. Shi, Z. Wang, Y. Liu, S. Jia, and D. Changming, "Removal of hexavalent chromium from aqueous solutions by D301, D314 and D354 anion-exchange resins", *Journal of hazardous materials*, vol. 161,no. 2, pp. 900-906, 2009.
- [10] U.S.Environmental protection agency,"Wastes Hazardous test Methods, Method 7196A", http://www.epa.gov/osw/hazard/testmethods/sw846/online/7_series.htm.
- [11] Malkoc E and Nuhoglu Y, "Potential of tea factory waste for chromium (VI) removal from aqueous solutions: thermodynamic and kinetic studies", *Separation and Purification Technology*, vol. 54, no. 3, pp. 291-298, 2007.
- [12] Dionex Technical Note, no. 26, May 1990.
- [13] A. H. Tuama, and A. A. Mohammed, "Removal of heavy metal ions from aqueous solutions using tobacco leaves as a sorbent", *European Journal of Applied Engineering and Scientific Research*, vol. 3,no. 2,pp. 19-32.
- [14] W. L. McCabe, J. C. Smith, and P. Harriott, *Unit operations of chemical engineering, 5th edition*, McGraw –Hill, Inc., New York, 1993.
- [15] K. Y. Foo and B. H. Hameed, "Insights into the modeling of adsorption isotherm systems", *Chemical Engineering Journal*, vol. 156, no. 1, pp. 2-10, 2010.
- [16] A. O. Dada, A. P. Olalekan, A. M. Olatunya and O. Dada, "Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms studies of equilibrium sorption of Zn²⁺ unto phosphoric acid modified rice husk", *J Appl Chem*, vol. 3, pp. 38-45, 2012.
- [17] H. Qiu, L. Lv, B. C. Pan, Q. J. Zhang, W. M. Zhang, and Q. X. Zhang, "Critical review in adsorption kinetic models", *Journal of Zhejiang University Science A*, vol.10,no. 5, pp. 716-724, (2009).
- [18] V. Sarin, T. S. Singh and K. K. Pant, "Thermodynamic and breakthrough column studies for the selective sorption of chromium from industrial effluent on activated eucalyptus bark", *Bioresource technology*, vol. 97,no. 16, pp. 1986-1993, 2006.

- [19] Y. S. Ho, and G. McKay, "Pseudo-second order model for sorption processes", *Process Biochemistry*, vol. 34, no. 5, pp. 451-465, 1999
- [20] X. J. Hu, J. S. Wang, Y. G. Liu, X. Li, G. M. Zeng, Z. L. Bao, ... and F Long, "Adsorption of chromium (VI) by ethylenediamine-modified cross-linked magnetic chitosan resin: isotherms, kinetics and thermodynamics", *Journal of hazardous materials*, vol. 185, no. 1, pp. 306-314, 2011.
- [21] T. S. Anirudhan, S. Jalajamony, and P. S. Suchithra, "Improved performance of a cellulose-based anion exchanger with tertiary amine functionality for the adsorption of chromium (VI) from aqueous solutions", *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 335, no. 1, pp. 107-113, 2009.
- [22] M. R. Gandhi, N Viswanathan, and S. Meenakshi, "Adsorption mechanism of hexavalent chromium removal using Amberlite IRA 743 resin", *Ion Exchange Letters*, vol. 3, pp. 25-35, 2010.
- [23] J. Yang, M. Yu, and T. Qiu, "Adsorption thermodynamics and kinetics of Cr (VI) on KIP210 resin", *Journal of Industrial and Engineering Chemistry*, vol. 20, no. 2, pp. 480-486, 2014.
- [24] N. Mao, L. Yang, G. Zhao, X. Li, and Y. Li, "Adsorption performance and mechanism of Cr (VI) using magnetic PS-EDTA resin from micro-polluted waters", *Chemical Engineering Journal*, vol. 200, pp. 480-490, 2012.
- [25] M. A. Barakat, J. Rashid, and M. A. Alghamdi, "Removal of chromium (VI) from synthetic wastewater using spectra/gel ion-exchange resin", *Seventeenth International Water Technology Conference*, 2013.
- [26] L. Alvarado, I. R. Torres, and A. Chen, "Integration of ion exchange and electrodeionization as a new approach for the continuous treatment of hexavalent chromium wastewater", *Separation and Purification Technology*, vol. 105, pp. 55-62, 2013.
- [27] C. Balan, I. Volf, and D. Bilba, "Chromium (VI) removal from aqueous solutions by purolite base anion-exchange resins with gel structure", *Chemical Industry and Chemical Engineering Quarterly*, vol. 19, no. 4, pp. 615-628, 2013.
- [28] G. Z. Kyzas, M. Kostoglou and N. K. Lazaridis, "Copper and chromium (VI) removal by chitosan derivatives—Equilibrium and kinetic studies", *Chemical Engineering Journal*, vol. 152, no. 2, pp. 440-448, 2009.
- [29] A. Shanmugapriya, R. Ramya, S. Ramasubramaniam, and P. N. Sudha, "Studies on removal of Cr (VI) and Cu (II) ions using Chitosan-grafted-polyacrylonitrile", *Archives of Applied Science Research*, vol. 3, no. 3, pp. 424-435, 2011.
- [30] Z. N. Shu, and C. H. Xiong, "Adsorption and desorption properties of D318 resin for Cr (VI)", *Journal of Central South University of Technology*, vol. 16, pp. 405-409, 2009.