



Kinetic Studies on Adsorption of Hexavalent Chromium using Blue Green Algae

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ABSTRACT: Adsorption of hexavalent chromium from synthetic solution is investigated using blue green algae as adsorbent. Its removal efficiency is investigated kinetically. The kinetic data were tested with Pseudo first order, Pseudo second order, Weber and Morris Intra Particle diffusion model, Boyd model, Homogeneous diffusion model, shrinking core model and Elovich model for different initial Cr (VI) concentration. The Cr (VI) ions may probably be transported from the aqueous bulk solution into the solid surface by intra-particle diffusion process. If the intra-particle diffusion is the sole rate limiting step, the linear lines would pass through the origin. Since this was also not the case in the range of initial Cr (VI) ion concentration investigated in this study, it has to be concluded that surface adsorption and intra-particle were concurrently operating during the adsorption of adsorption of Cr (VI) on to blue green algae. It is clearly seen that when compared to Weber and Morris Intra-Particle Diffusion Model, the Shrinking core model, Elovich model and Boyd model does not fit the experimental data over the total time range employed in this investigation.

Keywords: Hexavalent Chromium, Blue green algae, Pseudo first order, Pseudo second order, Weber and Morris, Intra Particle diffusion model, Boyd model, Homogeneous diffusion model, shrinking core model, Elovich model.

I. INTRODUCTION

Utilization of heavy metals is inevitable in process industries such as metal plating facilities, mining operations and tanneries [1]. Effluent emanating from these industries contains certainly heavy metal ions. While they are discharged directly into water body, this can lead into contamination of freshwater and marine environment [2]. Heavy metals are non-biodegradable which results the accumulation in living organisms, causing various diseases and disorders. Antimony, Chromium, Copper, Lead, Manganese, Mercury, Cadmium, etc., are off some heavy metals are harmful to life, they are significantly toxic to human beings and ecological environments [3]. Hexavalent Chromium Cr (VI) is considered in this study. Chrome tanning, as done in modern industry, is done by the use of trivalent chromium salts [4, 5]. The use of a significant amount of chrome during tanning is also characteristic, under conditions which lead to little depletion. This system still produces sludge that has an excessive chrome concentration. The chrome concentration in the effluents is higher the regulation ceiling of 1 mg/l set by the authorities [6]. Industrial operations including chrome plating, petroleum refining, leather, tanning, wood preserving, textile manufacturing and pulp processing are the main sources for chromium pollution consequences [7]. It exists in both hexavalent and trivalent forms. Cr (III) is environmental contaminant of major importance because of their toxic effect to man, animal and plant life. The Harmful effects of chromium are the irritant, nausea and vomiting, carcinogen (Oxidation state of +6), Low level exposure can irritate the skin and cause ulceration. Long-term exposure would spoil the function of kidney and liver damage, and damage of circulatory and nerve tissue. The present study is aimed to focus the contamination by chromium [8]. Tanning and leather industries, electroplating industries, catalyst and pigments manufacturing

industries, fungicides, ceramics, crafts, glass, photography and corrosion control application are main sources for Chromium. These industrial effluents can contain Cr (VI) from 10 to 100 mg/L which is higher than the standard limit of 0.1 mg/L in industrial waste water. Chromium is a transition metal. It transpires in nine different forms of its oxidation states [9]. The range is found to be Cr (-II) up to Cr (+VI). The oxidized states of Cr (III) and Cr (VI) are the most commonly observed in chromium compounds. In aqueous systems, the chromium contamination is mainly found as Cr (III) and Cr (VI). The remaining forms are rare states [10]. Cr (III) is considered as a bio element since it plays an important role in the metabolic activity of plants and animals at its low concentrations. But Cr (VI) is highly toxic. Precipitation, ion exchange, adsorption, filtration, electrode position, reverse osmosis etc., are the conventional technologies employed in these process industries. Though it has several advantages, most of them are failed to achieve the zero-liquid discharge [11]. Precipitation method is mostly consistent but huge settling tanks for the precipitation of voluminous alkaline sludges and a subsequent treatment is needed. Ion exchange is the favourable one for allowing the recovery of metallic ions, but it is costly. Adsorption on solid-solution interface is preferable means for controlling the extent of pollution due to heavy metal ions. The usage of activated carbon and ion exchange resins is not appropriate for developing countries owing to their high capital and operational costs. This has encouraged research into discovering materials that are both efficient and cheap [4]. Natural materials with high sorption capacity for removal of heavy metals is often advisable in order to avoid generation of secondary pollutant. Investigation on identification of low-cost adsorbents has been increased to a great extent to replace the conventional costly one. Cheaper in cost, availability in abundant, simple in employability and

easy to disposal are the prime factors in identifying them to overcome the conventional one in heavy metal sorption. Bark, tannin-rich materials, lignin, chitin, chitosan, peat moss, moss, modified wool and cotton are reported by many investigators as low-cost adsorbent. Also, the insoluble starch xanthates, agricultural waste materials such as spent grain, polymerized onion skin, rice husks, bark and sawdust, maize cobs, wheat bran have been investigated widely and reported their effectiveness in binding heavy metal ions. The report indicates that presence of proteins, carbohydrates, and phenolic compounds which have carboxyl, hydroxyl, sulfate, phosphate, and amino groups are the responsible to increase the sorption capacity. This can bind metal ions on their active sites. This article reported the efficiency of marine algae for the removal of hexavalent chromium from synthetic aqueous solutions [7]. The present study is the thriving effort to utilize the blue green algae biomass as adsorbent. The significance of this study is to discuss the mechanism of the adsorption processes. Kinetic data were tested with Pseudo first order, Pseudo second order, Weber and Morris Intra Particle diffusion model, Boyd model, Homogeneous diffusion model, shrinking core model and Elovich model for different initial concentration.

II. MATERIALS AND METHODS

Blue Green Algae (BGA) is used as an adsorbent in this investigation for adsorption of the hexavalent chromium from its respective synthetic solution under equilibrium condition. Preparation of adsorbent, synthetic stock solution and determination optimum experimental parameters viz., pH, temperature and adsorbent dosage under batch condition are provided here along with the effect initial metal ion concentration on equilibrium metal uptake. Analysis of effluent concentration to calculate the equilibrium metal uptake experimentally and theoretically with kinetic models are discussed [4].

Adsorbent – BGA: Blue Green Algae (BGA) is used in this study for the biosorption of Cr (VI) ions from its synthetic stock solution. The algae are collected from ponds in and around Chidambaram town and Veeranam Lake. The algae are washed with distilled water and dried at room temperature (above 30°C) then it is powdered with a uniform size of 150-200 microns. The dried and powdered algae is immobilized on silica gel using standard methods for continuous adsorption which involves wetting a mixture of silica gel and biomass with ultra-pure water followed by drying at 150°C for 20 mins [1-4].

Adsorbate – Cr (VI): Analytical grade salt Potassium Dichromate $K_2Cr_2O_7$ is used to prepare the synthetic hexavalent chromium Cr (VI) solution. The stock solution of Cr (VI) is prepared by dissolving a pre calculated quantity of respective salt in double distilled water. This stock solutions are further diluted to obtain desired concentration in the range of 25 -200 ppm. The pH of each solution is adjusted 2 to 6. The pH adjustments are done by using 0.1N nitric acid (HNO_3) and 0.1N sodium hydroxide (NaOH) solutions.

III. ANALYSIS

The batch bio sorption study is carried out in a 500 ml conical flask. The initial metal ion concentrations are varied to 25, 50, 100, 125, 150, 175, 200 and 250 ppm. The pH adjustments are done by using 0.1N nitric acid (HNO_3) and 0.1N sodium hydroxide (NaOH) solutions.

The biomass to be added to the conical flask is varied from 0.5, 1.0, 1.5, 2.0 and 2.5 g. All the experiments are performed at the room temperature. The flasks are kept in a rotary shaker at rpm of 120 for 24 hours. This is more than sufficient for adsorption equilibrium. The samples are taken regularly with predetermined time intervals. The percentage removal and specific uptake of metal is then calculated [1, 2]. The adsorption of Cr(VI) metal ions from its respective synthetic solutions by the BGA is performed under shaking conditions in rotary shaker (REMI-12, India). The experiments are performed under batch operation mode. To each 400 ml of metal solution a desired quantity of the blue green microalgae is added in 500 ml conical flasks. The mixture is agitated in the rotary shaker at the room temperature and at 120 rpm for predetermined time intervals. The initial and final concentrations of metal solutions are predicted by double beam Atomic Adsorption Spectrophotometer (AAS SL176-Elico Limited India). The percentage removal of metal ions is calculated from the initial concentration (C_i) and the analysed final concentration (C_{eq}) of the metal ion solution according to the following Eqn. 1.

$$\% \text{ Removal} = \frac{C_i - C_{eq}}{C_i} \times 100 \quad (1)$$

The equilibrium metal uptake is calculated from the initial concentration (C_i) and the analysed final concentration (C_{eq}) of the metal ion solution according to the following Eqn. 2

$$q = \frac{V}{M} (C_i - C_{eq}) \quad (2)$$

Where V is the volume of liquid sample in litre and M is the weight of bio sorbent. The same procedure is repeated for another initial metal ion concentration of 50 ppm, 75 ppm, 100 ppm, 125 ppm, 150 ppm, 175 ppm, 200 ppm and 250 ppm of all the metals. The experimental variables namely pH and biomass loading are optimized and at these optimized conditions the effect of Initial metal ion concentration on percentage removal and specific uptake of metal ions are studied [3, 4].

IV. RESULTS AND DISCUSSION

The mechanism of adsorption depends on the physical and chemical characteristics of the adsorbent. Algae powder is characterized by a higher adsorption capacity of Cr (VI). Kinetics of chromium adsorption was modelled by Pseudo first order, Pseudo second order, Weber and Morris Intra Particle diffusion model, Boyd model, Homogeneous diffusion model, shrinking core model and Elovich model for different initial concentration.

Pseudo First Order Model: The Eqn. 3 represents the linear form of pseudo first order model.

$$\log(q_{eq} - q_t) = \log q_{eq} - \frac{k_1}{2.303} t \quad (3)$$

where k_1 (min^{-1}) is the pseudo first order model kinetic parameter; q_t is the amount of Cr (VI) adsorbed (mg/g) at time t(min) and q_{eq} represents the amount of Cr (VI) adsorbed at equilibrium (mg/g).

The plot of the $\log(q_{eq} - q_t)$ verses t provides the k_1 and q_{eq} values. The results of first order kinetics at various initial Cr (VI) ion concentrations is given in Table 1. Two different trends were noticed. The pseudo first order rate constant increases with an increase in initial Cr (VI) ion concentration from 25 ppm to 125 ppm. There after the rate constant decreased drastically from the initial Cr

(VI) ion concentration of 150 ppm. Further it is increased gradually as in the case of first one up to 250 ppm. The adsorption first order rate constants ranged between 0.0074 – 0.0355 min⁻¹ and 0.0028 – 0.0032 min⁻¹ for the initial Cr (VI) ion concentration range 25 – 125 ppm and 150 – 250 ppm respectively (Table 1). The dissimilarity in rate should be relative to the first power of concentration for strict surface adsorption. However, the association between initial solute concentration and rate of adsorption will not be linear when pore diffusion limits the adsorption process. The calculated q_{eq} values from the intercept of 25 ppm to 250 ppm were compared with Experimental q_{eq} values. It is found that except 200 ppm of initial Cr (VI) metal ion concentration, the fit is very poor. This model infers that rapid adsorption occurs well only for the 200-ppm initial Cr (VI) ion concentration but cannot be applied for the other initial

Cr (VI) ion concentrations. This is ensured by the subsequent R^2 values. An irregular trend is observed while increasing the initial Cr (VI) ion concentration, may be due to poor fit of the data with the pseudo first order kinetic model. Large deviation is noticed between the experimental q_{eq} and calculated q_{eq} values indicates that the adsorption of Cr (VI) by Blue green algae does not obeys the Lagergren first order model except the initial Cr (VI) ion concentration of 200 ppm. This confirms that it is not appropriate to use the Lagergren first order kinetic model to predict the adsorption kinetics for Cr (VI) onto blue green algae for the range of initial Cr (VI) ion concentrations except 200 ppm. Fig. 1 and 2 represents the pseudo first order kinetic model for the initial concentration from 25 ppm to 125 ppm and from 150 ppm to 250 ppm respectively.

Table 1: Pseudo First Order kinetics for the initial Concentration of Cr (VI) from 25 ppm to 250 ppm

C_{in}	slope	K_1	Intercept	q_{eqCal}	R_2	q_{eqExp}
25	-0.0032	0.0074	3.5353	3.43×10^3	0.7812	4.4
50	-0.0065	0.0150	6.8628	7.29×10^3	0.7248	9.0
75	-0.009	0.0207	9.3709	2.39×10^3	0.6611	13.6
100	-0.0124	0.0286	12.931	8.53×10^{12}	0.6703	18.4
125	-0.0154	0.0355	16.201	1.59×10^{16}	0.6490	23.2
150	-0.0012	0.0028	1.2979	19.86	0.8094	27.8
175	-0.0013	0.0030	1.3342	21.59	0.7417	32.6
200	-0.0012	0.0028	1.5406	34.72	0.9667	37.4
225	-0.0012	0.0028	1.3132	20.57	0.7329	37.2
250	-0.0014	0.0032	1.2159	16.44	0.5907	37.0

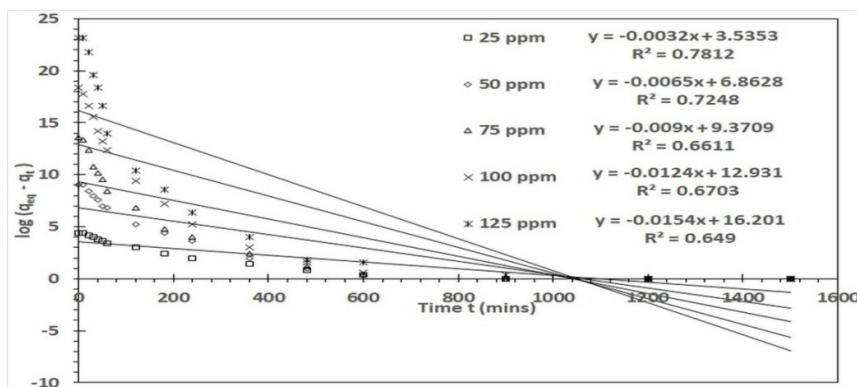


Fig. 1. Pseudo first order kinetics for the initial concentration of 25 ppm to 125 ppm.

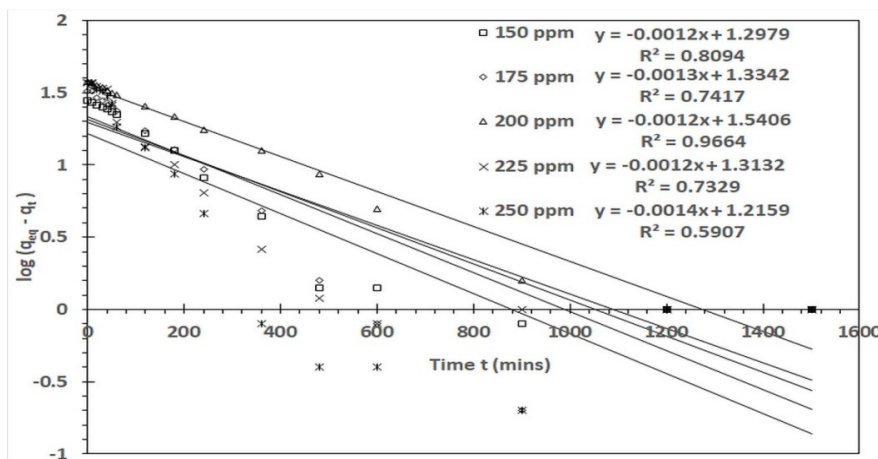


Fig. 2. Pseudo first order kinetics for the initial concentration of 150 ppm to 250 ppm

Pseudo Second Order Model: Due to Unfit of experimental data with pseudo first order kinetic model, the adsorption kinetics was tested with pseudo second order model. Eqn. 4 represents the linear form of pseudo second order model.

$$\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{t}{q_{eq}} \quad (4)$$

Where k_2 ($g\ mg^{-1}\ min^{-1}$) is the pseudo second order adsorption kinetic parameter. From the slope and intercept of the plot (t/q_t) versus t , k_2 and q_{eq} can be obtained. The second order rate constant k_2 , the calculated q_{eq} values and correlation coefficients were reported in Table 2 for the initial Cr (VI) ion concentrations from 25 ppm to 250 ppm.

It was observed that the pseudo second order constant k_2 decreased linearly with an increase in initial Cr (VI) ion concentration up to 200 ppm. Thereafter for 225 ppm and 250 ppm linear decreasing trend has been found to be deviated. The calculated q_{eq} values were

compared with experimental q_{eq} values. The concurrence of calculated q_{eq} and experimental q_{eq} up to 150 ppm was found to be good. This ensured with R^2 values. From 175 ppm to 250 ppm the concurrence of calculated q_{eq} with experimental q_{eq} was found not to be satisfactory expect 225 ppm. The pseudo second order kinetic model is built on the postulation that the rate limiting step is chemical adsorption involving valency forces through sharing or exchanging the electrons between the sorbent and sorbate. The uncertainty between experimental and calculated q_{eq} values in this investigation, thought that pseudo second order kinetic model is not more accurate to describe the entire adsorption process and not confirms adsorption of Cr (VI) onto blue green algae is not a chemisorption. Fig. 3 and 4 represents the Pseudo second order kinetic model for the initial concentration from 25 ppm to 125 ppm and from 150 ppm to 250 ppm respectively.

Table 2: Pseudo Second Order kinetics for the initial Concentration of 25 ppm to 250 ppm.

Cin	Slope (1/qeq)	q _{eq} Cal	Intercept	K2	R2	q _{eq} Exp
25	0.1885	5.31	48.118	0.00074	0.9312	4.4
50	0.0964	10.37	17.655	0.00053	0.9637	9.0
75	0.0622	16.08	12.327	0.00031	0.8825	13.6
100	0.0477	20.96	7.5224	0.00030	0.9784	18.4
125	0.0391	25.58	4.9799	0.00031	0.9726	23.2
150	0.0287	34.84	7.9721	0.00010	0.9294	27.8
175	0.0221	45.25	8.7319	0.00006	0.4535	32.6
200	0.0194	51.55	8.6804	0.00004	0.7750	37.4
225	0.0236	42.37	3.4586	0.00016	0.9381	37.2
250	0.0197	50.76	7.3646	0.00005	0.3810	37.0

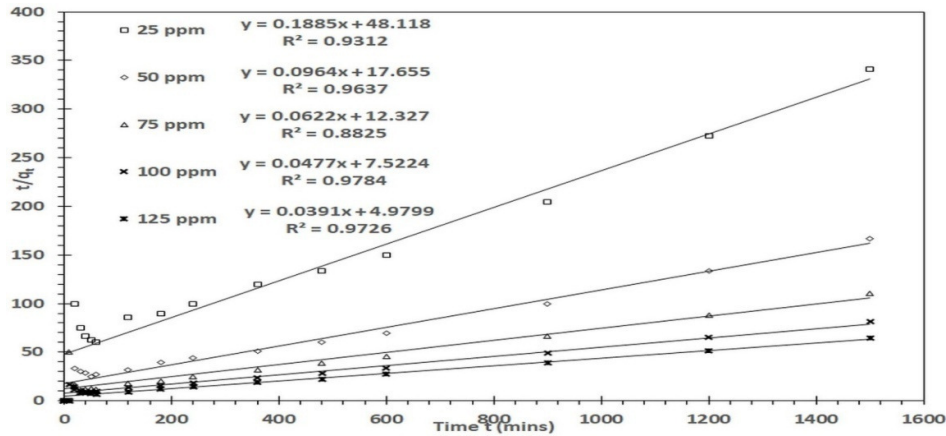


Fig. 3. Pseudo Second Order kinetics for the initial Concentration of 25 ppm to 125 ppm.

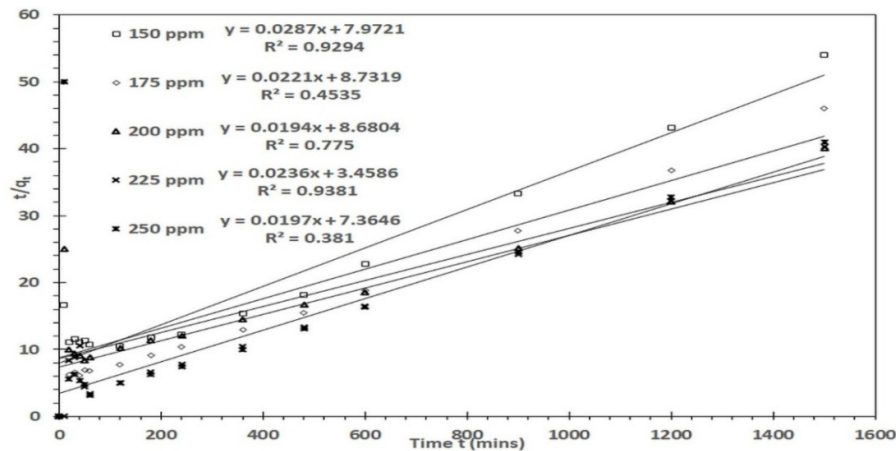


Fig. 4. Pseudo Second Order kinetics for the initial Concentration of 150 ppm to 250 ppm.

External Mass Transfer Model: Prediction of rate limiting step is an essential criterion in adsorption process. In the solid-liquid adsorption, the solute transfer is usually characterized by either external mass transfer mode (boundary layer diffusion) or Intra-particle diffusion mode. Thus, the uptake of metal ions can be controlled either by mass transfer through the boundary film of liquid or by intra-particle mass transfer. The following linear Equation was used to evaluate the external mass transfer coefficient βL (cm/s) for adsorption of Cr (VI) ions from aqueous solution using blue green algae.

$$\ln\left(\frac{C_t}{C_o} - \frac{1}{1+mK_a}\right) = \ln\left(\frac{mK_a}{1+mK_a}\right) - \left(\frac{1+mK_a}{mK_a}\right)\beta_L S_s t \quad (5)$$

where C_t (mg/L) and C_o (mg/L) are the concentration of Cr (VI) ion solution at time t (min) and time zero (min) respectively. K_a (L/g) is a constant defined as the

product of the Langmuir constants b_L (L/mg) and q_{max} (mg/g).

The m (g/L) and S_s (cm²) are the adsorbent mass and surface area respectively. The coefficient β_L is estimated from the slope of the plot of $\ln[(C_t/C_o) - (1/(1+mK_a))]$ versus t . Fig. 5 and 6 represents the external mass transfer model for the initial Cr (VI) ion concentration from 25 to 125 ppm and from 150 ppm to 250 ppm respectively.

It is observed that the linear relationship between $\ln[(C_t/C_o) - (1/(1+mK_a))]$ and t is very poor for the entire range on initial Cr (VI) ion concentration employed in this investigation. The regression coefficient has very low value for all the initial Cr (VI) ion concentration employed in this investigation. It results clearly that the uptake rate of Cr (VI) ions by blue green algae from aqueous solution was not controlled by mass transfer through a liquid film boundary such as convective mass transfer. Hence it was reached that the Cr (VI) ions may probably be transported from the aqueous bulk solution into the solid surface by intra-particle diffusion process.

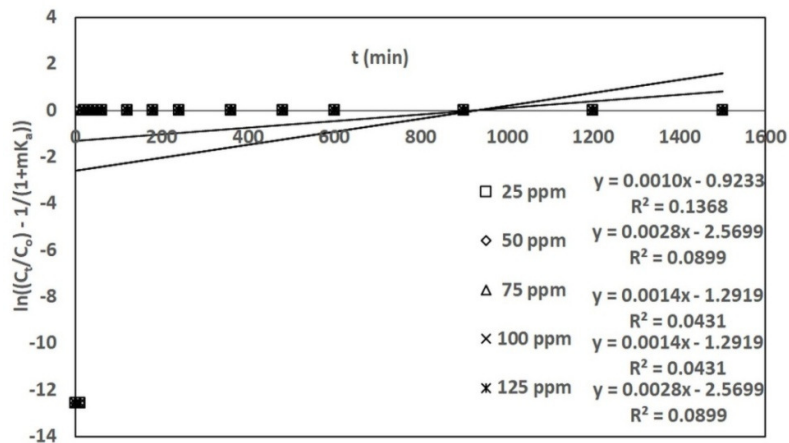


Fig. 5. External Mass Transfer Model for initial Cr (VI) ion concentration from 25 ppm to 125 ppm.

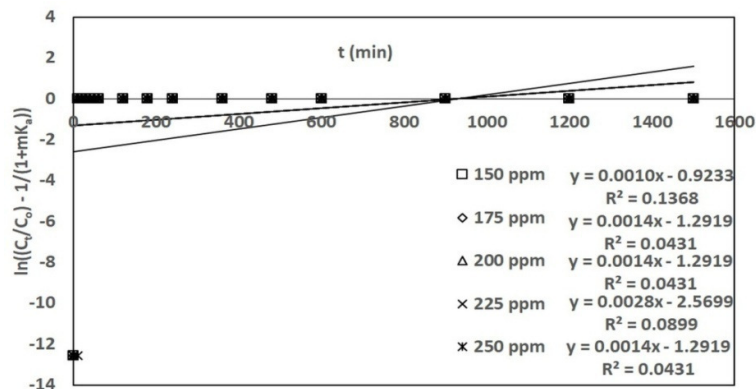


Fig. 6. External Mass Transfer Model for initial Cr (VI) ion concentration from 150 ppm to 250 ppm.

Weber and Morris Intra-Particle Diffusion Model: The consequences of external mass transfer model enforced to test the experimental data with Weber and Morris intra-particle diffusion model to find the mechanism of adsorption. Eqn. 6 shows the linear form of Weber and Morris intra-particle diffusion model.

$$q_t = K_{dif} t^{\frac{1}{2}} + C \quad (6)$$

Where C is the intercept and K_{dif} is the Weber and Morris intra-particle diffusion rate constant. The

intercept C and Weber and the slope Morris intra-particle diffusion rate constant K_{dif} can be calculated from the plot of q_t versus t . The slope K_{dif} and intercept C along with regression coefficient R^2 was given in Table 3 for Weber and Morris intra-particle diffusion model Fig. 7 and 8 represents the Weber and Morris intra-particle diffusion model for the initial Cr (VI) ion concentration from 25 to 125 ppm and from 150 ppm to 250 ppm respectively.

Table 3: Weber and Morris Intraparticle Diffusion model () kinetics for the initial Concentration of 25 ppm to 250 ppm.

C_{in}	K_{dif}	C	R_2
25	0.1328	0.0796	0.9366
50	0.2840	0.1638	0.9100
75	0.4044	1.3372	0.8729
100	0.5563	1.5057	0.8789
125	0.7063	1.7698	0.8609
150	0.8310	1.8989	0.8715
175	0.9983	2.3232	0.8713
200	1.0196	2.5049	0.9289
225	1.1730	3.1321	0.8858
250	1.1324	4.3838	0.8608

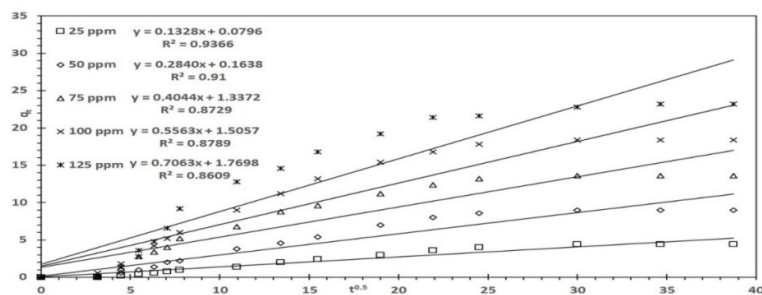


Fig. 7. Weber and Morris Intraparticle Diffusion model kinetics for the initial Concentration of 25 ppm to 125 ppm.

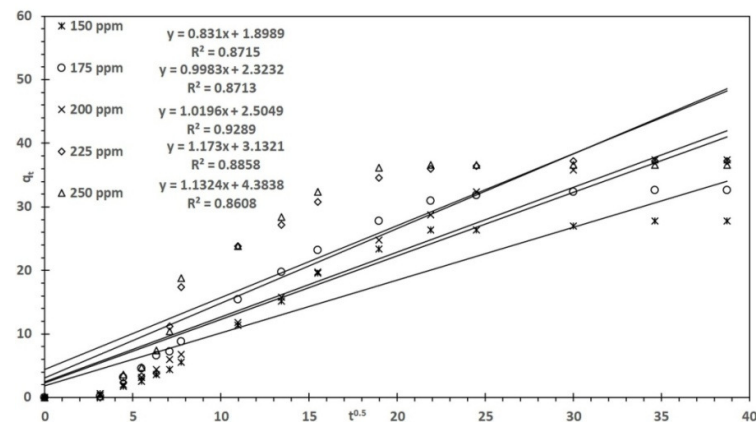


Fig. 8. Weber and Morris Intraparticle Diffusion model kinetics for the initial Concentration of 150 ppm to 250 ppm.

The values of intercept C in Table 3 indicates the thickness of boundary layer, the resistance to the external mass transfer. It was surprise to found that the intercept value goes on increasing with an increase in initial Cr (VI) ion concentration. The larger the intercept is the higher the external resistance to mass transfer. The R^2 values in Table 3 are close to unity, confirming that the rate-limiting step is actually the intra-particle diffusion process. The intra-particle diffusion rate constant K_{dif} , was in the range of 0.1328 to 1.1324 $\text{mg/g min}^{0.5}$ for the initial Cr (VI) ion concentration from 25 to 250 ppm. The linearity in the Fig. 9 and 10 demonstrated that the intra-particle diffusion played a significant role in the uptake of Cr (VI) ions by blue green algae. This is also confirming that the adsorption of Cr (VI) on to blue green algae was a multi-step process into the interior. Surprisingly, at higher concentrations, from 175 to 250 ppm, an intersection between the linear lines were noticed Fig. 10. If the steps are independent of an another, the plot usually shows two or more intersecting lines depending on the exact mechanism, the first one of these lines representing surface adsorption and the second one

intra-particle diffusion. The absence of such feature in Fig. 9 indicates that the steps were indistinguishable from one another and the intraparticle diffusion was prominent process right from the initial Cr (VI) ion concentration of 25 ppm to 150 ppm. Thereafter the notification of interaction in Fig. 10, i.e., from the initial Cr (VI) ion concentration of 175 ppm to 250 ppm, indicates that the adsorption process was two-step process, i.e., surface adsorption followed by intra-particle diffusion. Further it was noticed that for all the initial Cr (VI) ion concentration investigated in this study, the plot of q_t versus $t^{0.5}$ shown in Fig. 9 and 10 has definite intercept values and the linear lines does not pass through the origin. If the intra-particle diffusion is the sole rate limiting step, the linear lines would pass through the origin. Since this was also not the case in the range of initial Cr (VI) ion concentration investigated in this study, it has to be concluded that surface adsorption and intra-particle were concurrently operating during the adsorption of adsorption of Cr (VI) on to blue green algae.

Shrinking Core Model: The effect of contact time data was further tested with Shrinking Core Model. It defines

that the reaction occurs first at the outer skin of particle and then the reaction zone moves into the deeper unreacted zone. The zone where reaction has occurred will become ash layer and the layer is assumed to be inert. Adsorption of Cr (VI) is a heterogeneous process [4] which involves more than one phase i.e. the solid-liquid phase. Thus, this process would be controlled by three main steps, such as diffusion through liquid film layer, diffusion through ash layer, and chemical reaction.

The overall rate of the process is determined by the slowest step. Types of the shrinking core models in adsorption process can be summarized in the following equations. The overall adsorption rate of binding of the adsorbate onto the adsorbent depends mainly on diffusivity (D). In case the adsorption process is controlled by the diffusion of Cr (VI) ions through the liquid film (film diffusion control), the extent of adsorption of Cr (VI) ions onto blue green algae as a function of time is given by the following equation.

Diffusion through Liquid Film Layer Control

$$X = \frac{3D}{\delta RC} \alpha$$

where X is equal to the extent of adsorption = $\frac{C_0 - C_t}{C_0 - C_{eq}}$; $\alpha = \int_0^t C dt$; D (m²/s) is the diffusion coefficient; C₀ (mg/l) is the initial Cr (VI) ion concentration; C (mg/l) is the Cr (VI) ion concentration at time t; δ (m) is the film thickness; R (m) is the radius of the blue green algae adsorbent particle.

If the film diffusion is the rate controlling step in the adsorption of Cr (VI) ions onto blue green algae, the plot X versus α gives a straight-line relationship. Fig. 9 and 10 shows the Diffusion through liquid film layer control – Shrinking Core model for the initial Concentration of 25 ppm to 125 ppm and for the initial Concentration of 150 ppm to 250 ppm respectively. It is clearly seen that the model does not fit the experimental data over the total time range employed in this investigation. This is ensured by the subsequent R² values.

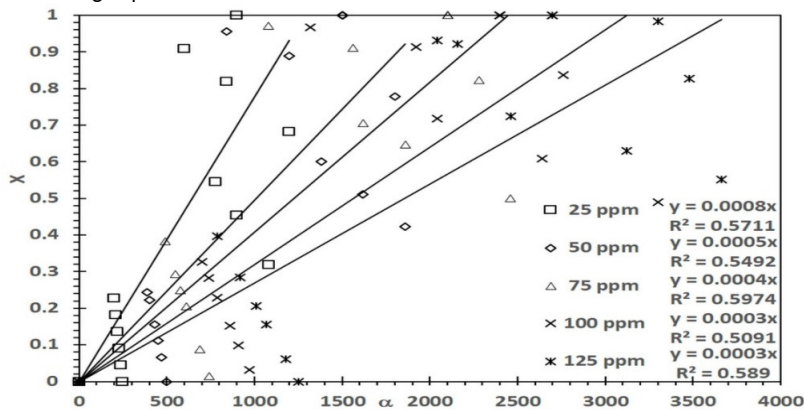


Fig. 9. Diffusion through liquid film layer control – Shrinking Core model for the initial Concentration of 25 ppm to 125 ppm.

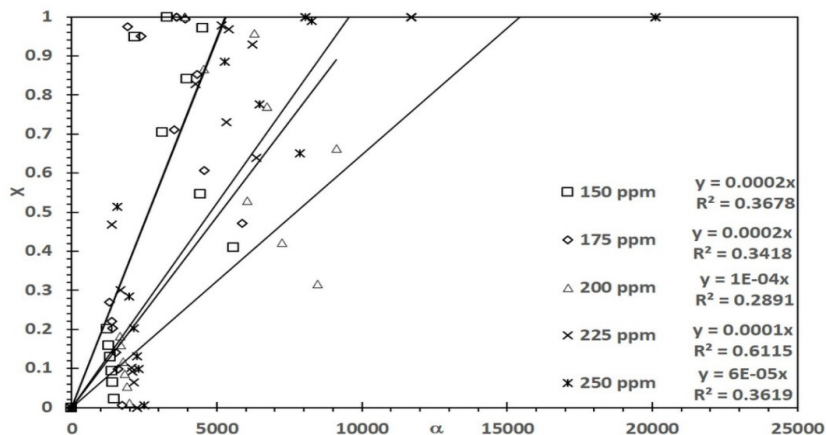


Fig. 10. Diffusion through liquid film layer control - Shrinking Core X model for the initial Concentration of 150 ppm to 250 ppm.

Diffusion through Ash Layer Control: If the adsorption process is controlled by the diffusion through the reacted shell (particle diffusion control) then the model is given by the following expression.

$$F(X) = 1 - 3(1 - X)^{2/3} - 2(1 - X) = \frac{6D}{R^2 C_0} \alpha$$

In case of particle diffusion control, a plot of F(X) versus α should give a straight-line relationship and the diffusivity of Cr (VI) ions onto blue green algae could be

calculated from the slope of the plot. Fig. 11 and 12 shows the Diffusion through ash layer control – Shrinking Core model for the initial Concentration of 25 ppm to 125 ppm and for the initial Concentration of 150 ppm to 250 ppm respectively. It is clearly seen that the model does not fit the experimental data over the total time range employed in this investigation. This is ensured by the subsequent R² values.

Chemical Reaction Control: If the adsorption process is controlled by the chemical reaction through the reacted shell (chemical reaction control) then the model is given by the following expression.

$$F(X) = 1 - (1 - X)^{\frac{1}{3}} = \alpha = \int_0^t C dt$$

where x is the reacted fraction; t is time; K_F , K_D , and K_R are reaction rate constants. Most of models used for adsorption process are of diffusion through ash layer control model. The kinetic models have been used to estimate the mass transfer characteristics of adsorption process. It is shown in Fig. 13 and 14.

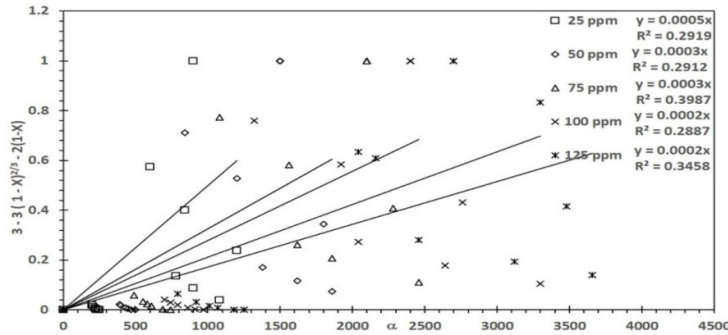


Fig. 11. Diffusion through ash layer control - Shrinking Core model for the initial Concentration of 25 ppm to 125 ppm.

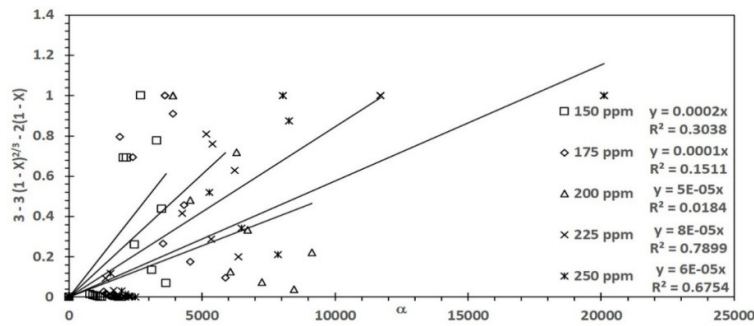


Fig. 12. Diffusion through ash layer control - Shrinking Core model for the initial Concentration of 150 ppm to 250 ppm.

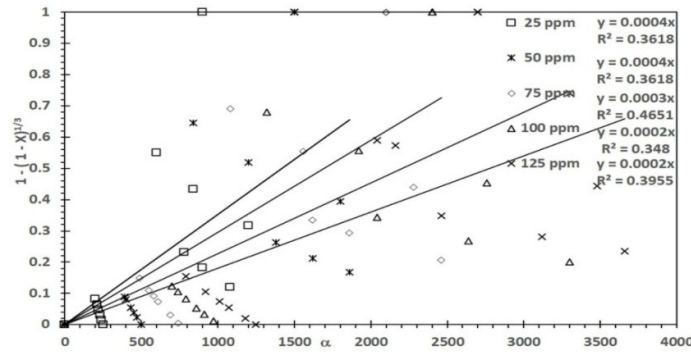


Fig. 13. Chemical reaction control - Shrinking Core model for the initial Concentration of 25 ppm to 125 ppm.

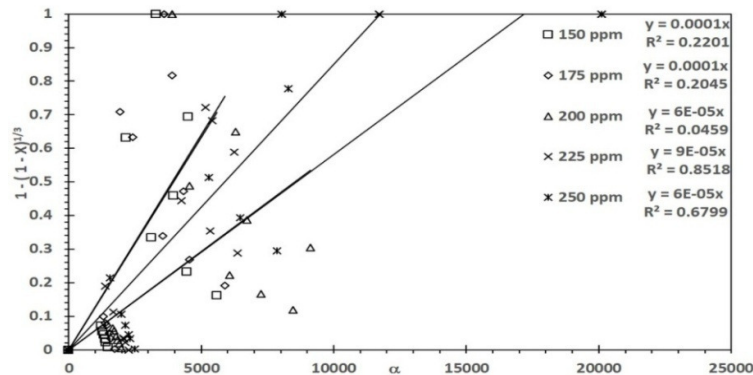


Fig. 14. Chemical reaction control - Shrinking Core model for the initial Concentration of 150 ppm to 250 ppm.

Elovich Model: The linear form of Elovich equation is generally expressed as Eqn. 7.

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (7)$$

Where α is the initial adsorption rate (mg/min) and β is related to the extent of surface coverage and the activated energy for chemisorption (g/mg). The Elovich equation has been shown to be useful in describing chemisorption on highly heterogeneous adsorbents. The initial adsorption rate, α and extent of coverage, β were calculated from the slope and the intercept of the plot of q_t against $\ln t$, respectively and the plot is shown in Fig.

15 and 16 for the initial Concentration from 25 ppm to 125 ppm and for the initial Concentration from 150 ppm to 250 ppm respectively. The results of Elovich model for the adsorption of Cr (VI) ions using blue green algae is shown in Table 4. Fig. 15 and 16 is linear with good regression coefficient R^2 values. The initial adsorption rate α , increases with an increase in initial metal ion concentration from 0.0924 to 1.3895 mg/min while increasing the initial Cr (VI) ion concentration from 25 ppm to 250 ppm.

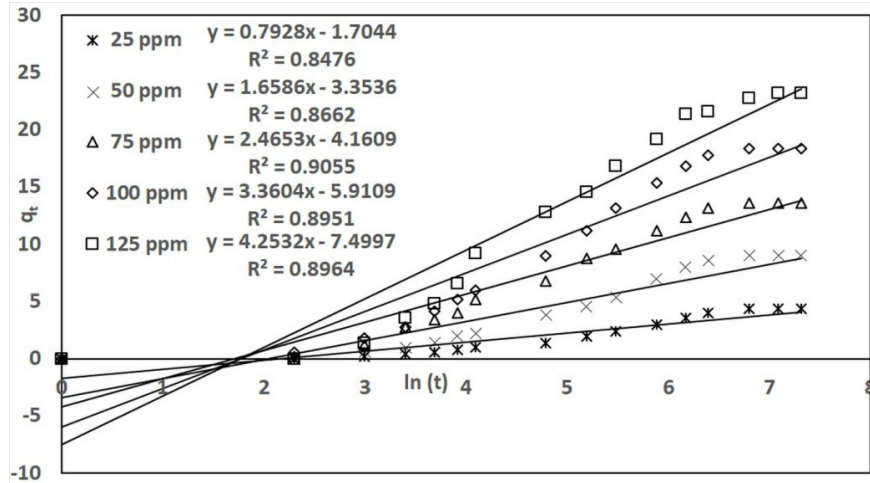


Fig. 15. Elovich model for the initial Concentration from 25 ppm to 125 ppm.

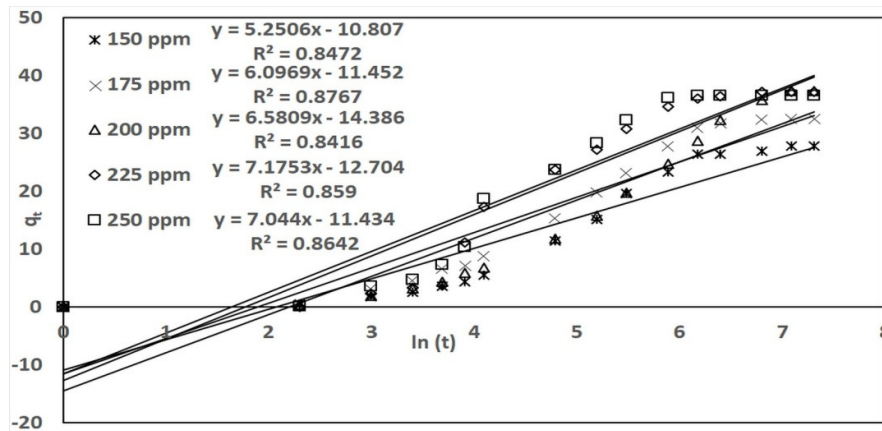


Fig. 16. Elovich model for the initial Concentration from 150 ppm to 250 ppm.

Table 4: Elovich kinetic model for the initial Concentration of 25 ppm to 250 ppm.

Initial Concentration (ppm)	Slope ($\frac{1}{\beta}$)	β	Intercept ($\frac{1}{\beta} \ln(\alpha\beta)$)	α	R^2
25	0.7928	1.261352	-1.7044	0.092363	0.8476
50	1.6586	0.602918	-3.3536	0.219595	0.8662
75	2.4653	0.40563	-4.1609	0.455904	0.9055
100	3.3604	0.297584	-5.9109	0.578725	0.8951
125	4.2532	0.235117	-7.4997	0.729325	0.8964
150	5.2506	0.190454	-10.809	0.670133	0.8472
175	6.0969	0.164018	-11.4520	0.93188	0.8767
200	6.5809	0.151955	-14.3860	0.739448	0.8416
225	7.1753	0.139367	-12.7040	1.221557	0.8590
250	7.0440	0.141965	-11.4340	1.389509	0.8642

Boyd Model: The effect of contact time data was tested with the Boyd kinetic plot to predict the actual slowest step in the adsorption process. The Boyd kinetic model is given in Eqn. 8

$$F = \frac{q_t}{q_{eq}} = 1 - \frac{6}{\pi^2} \exp(-B_t) \quad (8)$$

The linear form of Eqn. 8 is

$$B_t = -0.4977 - \ln(1 - F) \quad (9)$$

where q_{eq} is the amount of Cr (VI) ions adsorbed onto the blue green algae at equilibrium (mg/g). q_t is the amount of Cr (VI) ions adsorbed onto the blue green algae at any time t . F is the fraction of Cr (VI) ions adsorbed at any time t . B_t is a mathematical function of F . The B_t values at different contact times can be calculated using Eqn. 9 for various time intervals. The calculated B_t

values were plotted against time t . If the plots of B_t versus time t are linear and pass through the origin, then the actual slowest step in the adsorption process is the intraparticle diffusion (internal diffusion). Table 5 shows the Boyd Kinetic model parameters for the initial Concentration of 25 ppm to 250 ppm

The Boyd plots are shown in Fig. 17 and 18 for the adsorption of Cr (VI) ions onto blue green algae for the initial Cr (VI) ions concentration of 25 ppm to 125 ppm and 150 ppm to 250 ppm respectively. From these two Figures, it is clear that the plots are linear for the entire initial concentrations investigated in this research. Hence the actual slowest step in the adsorption process is the intraparticle diffusion.

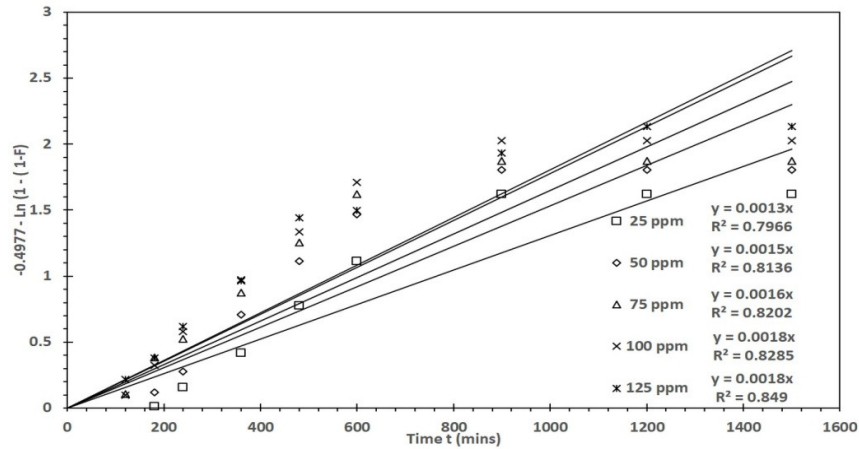


Fig. 17. Boyd model for the initial Concentration from 25 ppm to 125 ppm.

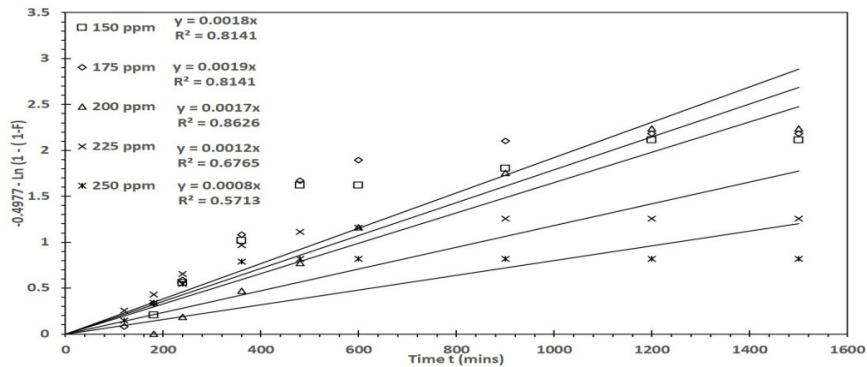


Fig. 18. Boyd model for the initial Concentration from 150 ppm to 250 ppm.

Table 5: Boyd Kinetic model parameters for the initial Concentration of 25 ppm to 250 ppm.

C _{in} ppm	B = $\frac{\pi^2 D_t}{r^2}$	D _i (X10 ⁸) cm ² /s	R ²
25	0.0013	6.7920	0.7966
50	0.0015	7.8370	0.8136
75	0.0016	8.3594	0.8202
100	0.0018	9.4044	0.8285
125	0.0018	9.4044	0.8490
150	0.0018	9.4044	0.8141
175	0.0019	9.9268	0.8147
200	0.0017	8.8819	0.8626
225	0.0012	6.2696	0.6765
250	0.0008	4.1797	0.5713

V. CONCLUSION

Blue green algae is used for adsorption of hexavalent chromium from synthetic solution and its removal efficiency is investigated kinetically. The kinetic data were tested with Pseudo first order, Pseudo second order, Weber and Morris Intra Particle diffusion model, Boyd model, Homogeneous diffusion model, shrinking core model and Elovich model for different initial Cr (VI) concentration. This confirms that it is not appropriate to use the Lagergren first order kinetic model to predict the adsorption kinetics for Cr (VI) onto blue green algae for the range of initial Cr (VI) ion concentrations except 200 ppm. The uncertainty between experimental and calculated q_{eq} values in this investigation, thought that pseudo second order kinetic model is not more accurate to describe the entire adsorption process and not confirms adsorption of Cr (VI) onto blue green algae is not a chemisorption. The uptake rate of Cr (VI) ions by blue green algae from aqueous solution was not controlled by mass transfer through a liquid film boundary such as convective mass transfer. Hence it was reached that the Cr (VI) ions may probably be transported from the aqueous bulk solution into the solid surface by intra-particle diffusion process. If the intra-particle diffusion is the sole rate limiting step, the linear lines would pass through the origin. Since this was also not the case in the range of initial Cr (VI) ion concentration investigated in this study, it has to be concluded that surface adsorption and intra-particle were concurrently operating during the adsorption of adsorption of Cr (VI) on to blue green algae. It is clearly seen that when compared to Weber and Morris Intra-Particle Diffusion Model, the Shrinking core model, Elovich model and Boyd model does not fit the experimental data over the total time range employed in this investigation.

VI. FUTURE SCOPE

Further investigation is needed for comparison with earlier investigation.

Conflict of Interest. The authors (Ramadoss Ramsenthil and Subramaniam Dhanasekaran) declare that there are no conflicts of interest regarding the publication of this paper.

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