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Assessment on the modelling of the kinetic parameter for the removal of crystal violet dye using Ag-soil nanocomposite: linear and non-linear analysis

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ABSTRACT

In recent decades, handling of bio-hazardous dyes such as crystal violet in various discharges is a growing concern which can affect the global aquatic scenario. A low-cost environment-friendly nanocomposite was synthesized for the removal of crystal violet dye from industrial effluent solution. The efficacy of plant(*Azadirachta indica*)-mediated synthesized silver nano soil composite as an adsorbent was evaluated in a batch reactor. A composite model system was introduced linear and non-linear responsiveness towards the kinetics of adsorption of crystal violet onto Ag-nano soil composite during batch experimental study. The equilibrium kinetics was analysed using pseudo-second-order kinetic model system. The coefficient of determination and chi-square tests were implemented to explore the best fit of the equation. The experimental data were better represented by non-linear model system than that of linear model system.

Keywords: Crystal violet; Clay; Adsorbent; Ag-NP; Composite model system; Linear and non-linear model

1. Introduction

Despite enormous applicability of crystal violet dye in textiles, pharmaceuticals, pathological and day-to-day medical practices, the adversity of this dye encompasses various dreadful life-threatening ecological impacts too during its discharge in to local water bodies. The crystal violet present in effluent wastewater leads to pollution and contamination of the aquatic environment affecting the concerned biota. The widespread use of crystal violet and its direct discharge in to effluent water without prior and proper treatment adds an extra alarming burden to environmental pollution. This dye affects the water bodies and as a result, the marine lives as well as human health are affected in direct and indirect ways. Due to the presence of the dye, dissolved oxygen concentration in water bodies decreases and water toxicity increases, which affect the water physiology proportionally. This dye is carcinogenic, non-biodegradable and also toxic to mammalian cells, which causes skin irritation and inflammation. Besides this, this dye also causes respiratory and kidney failure. Nowadays, treatment of this dye affecting water bodies is a very essential measure for the local agencies involved and environmental pollution control boards. In recent years, there has also been an increasing interest in finding innovative solutions for efficient removal of contaminants from

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water, soil and air [1–8] to check the environmental pollution towards creating a healthy environment. Current scientific studies are involved in the search for a sustainable way for reduction and control of water pollution that arise due to bio-hazardous crystal violet dye in water bodies [6,7].

One of the powerful treatment processes for the removal of dye from water is adsorption, which has been proved successful in removing coloured organics. As an effective, efficient, economic and scientific physicochemical approach for water purification, adsorbents and adsorption processes have been widely studied and applied in different aspects for a long time in environmental engineering for pollution-control measures.

More recently, plant-mediated synthesis (green synthesis) of silver nanoparticles have gained more importance than those prepared chemically or microbially owing to the effectiveness (cost, time, ease of accessibility, etc.) of the process [9–14].

Azadirachta indica leaf is selected for plant extract preparation. It has been selected as an effective and invaluable as well as a cheaper and chief source of reducing and capping agent for silver nano particle preparation due to its ease of availability in various climatic conditions. Clayey soil is used with slight modification towards a novel aim of plant-mediated biomimetic nano soil composite adsorbent preparation and has to be implemented practically as an effective and economic bioadsorbent for removal of toxic crystal violet dye released in effluent. This nanocomposite material is analysed and found to have excellent capability of toxic dye adsorption in laboratory scale.

The kinetic parameters of plant-(*A. indica*) mediated synthesized silver nano soil composite adsorbent is scientifically analysed by pseudo-second-order linear and non-linear mathematical model systems. The transformation of non-linear equations to linear forms may change the error structure and as a result, error variance may be changed [15,16].

In the present study, linear least squares method and non-linear method in estimating the kinetic parameters of the kinetic models were carried out based on the batch experiment of Crystal violet adsorption onto the silver nano soil composite as adsorbent to compare the results associated with linearization of a non-linear equation.

2. Materials and methods

2.1. Adsorbate

Crystal violet dye used in this study was used without further purification. Stock solution was prepared by dissolving accurately weighed quantity of the dye in double-distilled water. Experimental dye solutions of different concentrations were prepared by diluting the stock solution with suitable volume of double-distilled water. The initial solution pH was adjusted using 0.1 (N) HCl and 0.1 (N) NaOH solution.

2.2. Adsorbent

2.2.1. Plant material

The mature healthy leaves of plant *A. indica* were obtained from the area in and around Durgapur, West Bengal (India). The leaves were washed properly followed by washing with double-distilled water. Then leaves were dried for 20 d and made into a fine powder. 20 g of the powder was poured in 100 mL of double-distilled water and kept in water bath at 313 K for 60 min. The extract was filtered through Whatman No. 1 filter paper to remove all unextractable matter, including cellular materials and other constituents which are insoluble in the extraction solvent. The entire extract was concentrated to dryness using lyophilizer under reduced pressure. The dried plant extract was redissolved in double-distilled water to yield solution (1 g/100 mL). The solution was used as reducing agent for silver nano particle preparation and stored for further use in future experimental work.

2.2.2. Microwave assisted leaf extract-mediated synthesis of silver nanoparticles

One millimole of 95 mL silver nitrate solution was prepared in an Erlenmeyer flask. Five Millilitre of aqueous leaf extract was then added drop wise to the silver nitrate solution. The colour change of the aqueous leaf extract, silver nitrate and the composite mixture were monitored carefully in each and every step of the procedure. Then the mixture was placed on the turntable of a microwave oven for complete bioreduction at a power level of 300 W for 5 min. The colour change from faint light green to light yellowish-brown to reddish brown to colloidal brown was observed followed by the absorption maxima measurement of each type of the solution by a spectrophotometer periodically, throughout the reaction. After completion of microwave irradiation, the dilute colloidal solution was cooled to room temperature. Then the saturated colloidal mixture solution was stored properly for experimental purpose. Control samples were introduced and analysed for ease of observation and checking the uniformity of the practical performance.

2.2.3. Preparation of AgNP-soil composite adsorbent

Air dried clayey soil was added in 50 mL of plant mediated synthesized saturated AgNP solution (freshly prepared). The soil and colloidal AgNP solution mixture was left overnight in shaker incubator (at particular temperature and agitation speed) for silver nano soil composite to be formed. Then the colloidal composite mixture solution was centrifuged and the supernatant was discarded to get the pure colloidal composite material. The wet composite sediment was air dried after proper washing. The dried soil was uniformly and finely powdered to specific particulate size and taken as composite adsorbent for further experimental study after proper characterization.

2.2.4. Batch adsorption experiments

Batch experiment is a valuable primary experimental scientific tool to check and optimize dye adsorption kinetics during newer adsorbent introduction in the field of environmental engineering and industrial effluent treatment experiments.

Batch adsorption experiments were carried out in 250 mL Erlenmeyer flasks. Experimental adsorbate dye solutions were prepared from stock solutions carefully. Known specific amount of adsorbent dose was added in to each flask containing 100 mL of dye solution at required pH and temperature 303 K in a shaker incubator (REMI, India). Control samples without adsorbent were put along with each experimental set up. Periodically, sampling was done for analysing the concentration of crystal violet in the solution for ease of analysis and the rate of dye removal from solution by composite adsorbent. After the practical adsorption of Crystal violet on to the composite adsorbent inside the flask, the concentration of the adsorbate, if present, was checked and observed by using ultraviolet/visible (UV/VIS) spectrophotometer (Model Hitachi, model 2,800) at $\lambda_{\max}$ of 589 nm. The amount of dye adsorbed per unit mass of the composite adsorbent (mg g^{-1}) was calculated according to a mass balance of the dye in liquid phase using the following equation:

$$q_e = \frac{(C_i - C_e)V}{m} \quad (1)$$

where C_i is the initial dye concentration (mg L^{-1}), C_e is the equilibrium dye concentration in solution (mg L^{-1}), V is the volume of the solution (L) and m is the mass of the biosorbent used (g).

All the experiments were performed in triplicates and the average results were taken for more accuracy in readings and avoiding minimum possible manual errors.

3. Results and discussion

The characterization of the synthesis Ag-nanocomposite and Ag-soil nanocomposite were reported to the previous study [13,14]. The mechanism of crystal violet dye adsorption on the Ag-soil nanocomposite was also reported [13,14].

3.1. Pseudo-second-order kinetic equation

The differential form of pseudo-second-order kinetic model used for the sorption of CV using Ag-soil nanocomposite [15] was:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (2)$$

where q_t and q_e are the amount of dye adsorbed at time t and at equilibrium (mg g^{-1}) and k_2 (g mg^{-1} min^{-1}) is the pseudo-second-order rate constant for the adsorption process. Integrating and applying boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, Eq. (2) became:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (3)$$

The Eq. (3) was linearized into four different forms. The different linearized forms of the pseudo-second-order equation were given in Table 1.

The most popular linear form used was category 1 (9). For Linear form 1 model, q_e and k_2 had been calculated using the expression [15–19]:

$$q_e = \frac{1}{\text{slope}}; \quad k_2 = \frac{\text{slope}^2}{\text{intercept}} \quad (4)$$

For Linear form 2, the q_e and k_2 were calculated by:

$$q_e = \text{intercept}; \quad k_2 = \frac{-1}{(\text{intercept } x \text{ slope})} \quad (5)$$

For Linear form 3, the q_e and k_2 were calculated by:

$$q_e = \frac{-\text{intercept}}{\text{slope}}; \quad k_2 = \frac{\text{slope}^2}{\text{intercept}} \quad (6)$$

Table 1
Different linearized forms of the pseudo-second-order equation

Category	Linear form of pseudo-second-order model	Plotting
Category 1	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	t/q_t vs. t
Category 2	$q_t = q_e - \frac{1}{k_2 q_e} \frac{q_t}{t}$	q_t vs. q_t/t
Category 3	$\frac{q_t}{t} = k_2 q_e^2 - k_2 q_e q_t$	q_t/t vs. q_t
Category 4	$\frac{1}{q_t} = \frac{1}{q_e} + \frac{1}{k_2 q_e^2} \frac{1}{t}$	$1/q_t$ vs. $1/t$

For Linear form 4, the q_e and k_2 were calculated by:

$$q_e = \frac{1}{\text{intercept}}; \quad k_2 = \frac{\text{intercept}^2}{\text{slope}} \tag{7}$$

To evaluate the fit of the equations to the experimental results, an error functions were required. In the present study, the coefficient of determination (r^2) and the chi-square (χ^2) tests were used in order to quantitatively compare the applicability of each model:

$$r^2 = \frac{(q_{e,meas} - \overline{q_{e,cal}})^2}{\sum (q_{e,meas} - \overline{q_{e,cal}})^2 + (q_{e,meas} - q_{e,cal})^2} \tag{8}$$

$$\chi^2 = \sum \frac{(q_{e,meas} - q_{e,cal})^2}{q_{e,cal}} \tag{9}$$

Where $q_{e,meas}$ and $q_{e,cal}$ (mg g^{-1}) are the measured and calculated adsorbate concentration at equilibrium, and $\overline{q_{e,cal}}$ (mg g^{-1}) is the average of $q_{e,cal}$.

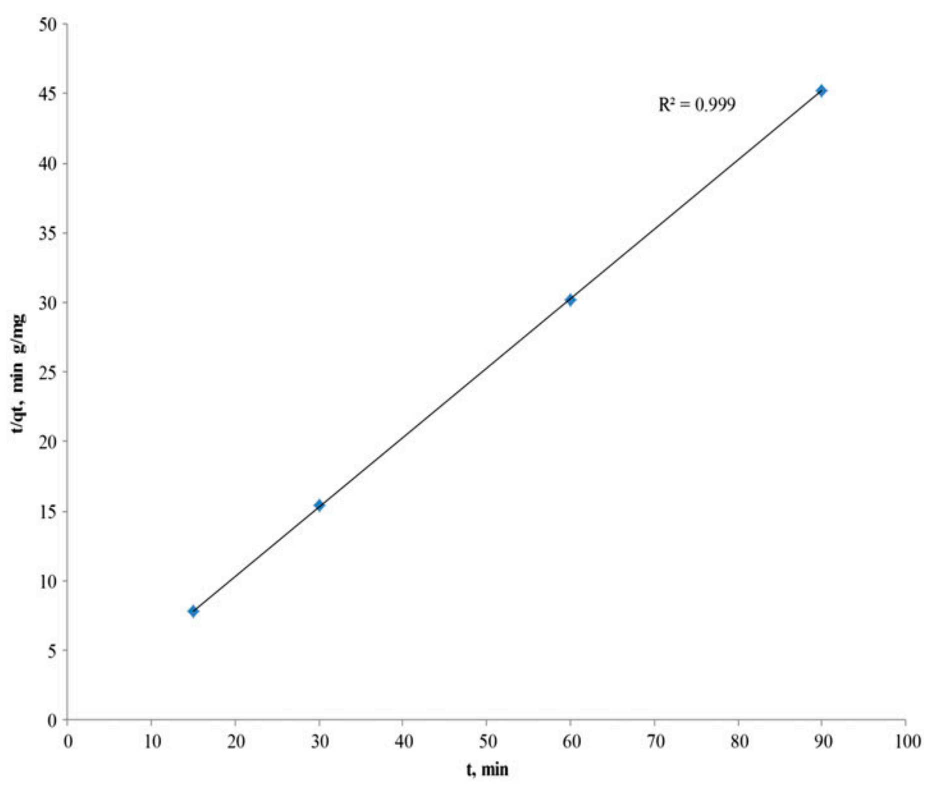

Fig. 1. Pseudo-second-order kinetic expression obtained by using linear method for the sorption of crystal violet onto Ag-nanocomposite using Linear form 1.

3.1.1. Linear and non-linear method

The experimental results were tried to be fitted to pseudo-first- and pseudo-second-order kinetic model. It was observed that the experimental data were better represented by pseudo-second-order kinetics.

Least square analysis method was used to find out the kinetic parameters from second-order kinetics. Four different linearized forms of pseudo-second-order kinetic model were used (Table 1) for this purpose to study the efficacy of the models. For linearized form 1, theoretical q_e and kinetic constant k_2 were determined using the plot of t/q_t vs. t [Fig. 1]. q_e was calculated using 1/slope and k_2 using: slope^2/intercept. Similarly, q_e and k_2 for linearized form 2, linearized form 3 and linearized form 4 were calculated by the expressions given, respectively [Figs. 2–4; Eq. (5)–(7)]. The method for determination of q_e and k_2 from figure was given in Table 2. The detailed values of k_2 and q_e, error function values were given in Table 2. It was observed from the kinetics constant and q_e value that parameters using different linearized pseudo-second-order expression were different from each other. It was observed that r^2 was low and $\chi^2$was high for linearized form 2, linearized form 3 and linearized form 4 models. So it was suggested that these models were not appropriate to use pseudo-second-order expressions and so the sorption of crystal violet using the nanocomposite was better represented by the expression of linearized form 1.

During the transformation of nonlinear to linear form, different axis settings were changed accordingly along with regression. As a result, the accuracy was influenced and the theories behind the kinetic model system were greatly violated. Also, due to this conversion, some assumptions of non-linear model formation related–such as assumption of normality of least square analysis was distorted as most of the kinetic models are non-linear due to the different mechanisms occurred simultaneously. For the same non-linear expressions, pseudo-second-order kinetic equation was found to be a poor fit to the experimental data of category—3, category—4 than that of category—1 experimental data obtained. The variation in the results were found in four linear forms due to various axial settings change and ultimately the direct impacts were on the determination level. Furthermore, using linear method, slope and intercept were reported only from the linear trend line of the experimental values and the resulting errors were predicted in limiting the best fit of kinetics of the adsorption study. Whereas, in non-linear regression analysis, these drawbacks and errors were minimized as in this case on the same

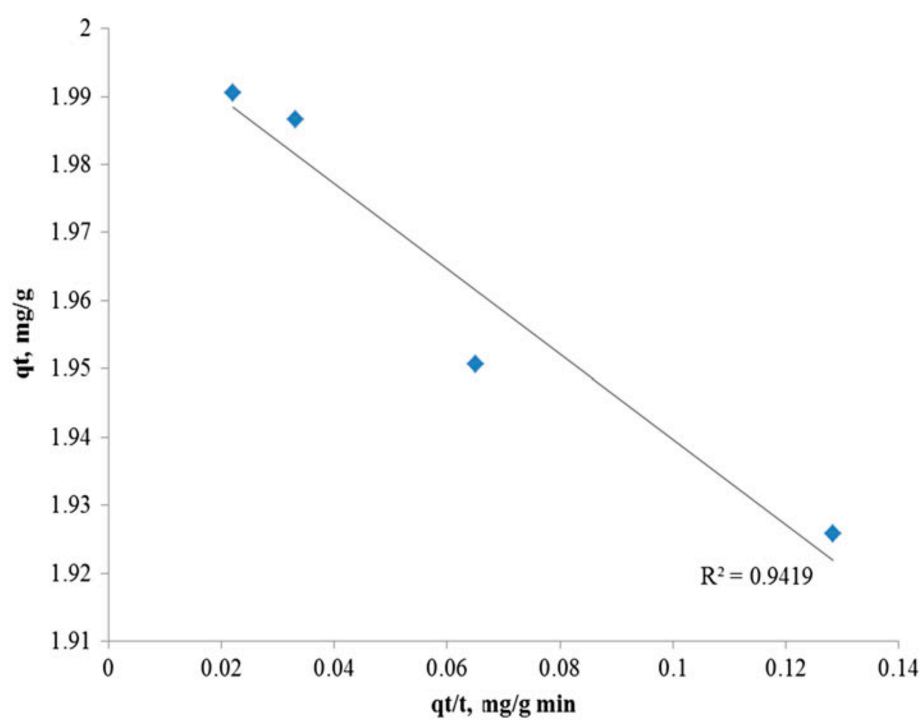

Fig. 2. Pseudo-second-order kinetics obtained by using linear method for the sorption of crystal violet onto Ag-nanocomposite using Linear form 2.

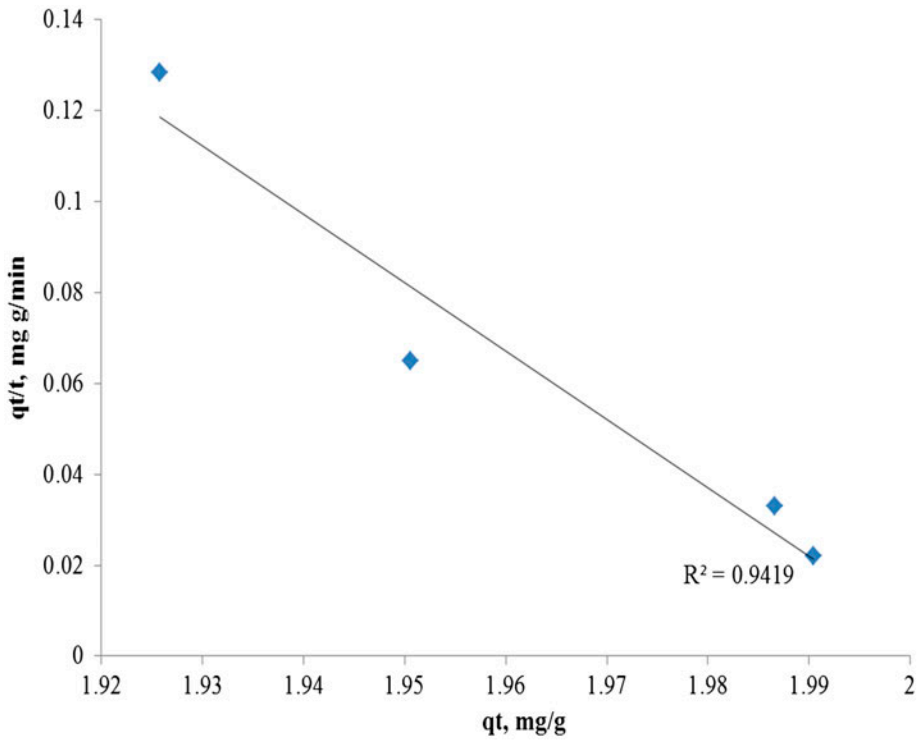

Fig. 3. Pseudo-second-order kinetics obtained by using linear method for the sorption of crystal violet onto Ag-nanocomposite using Linear form 3.

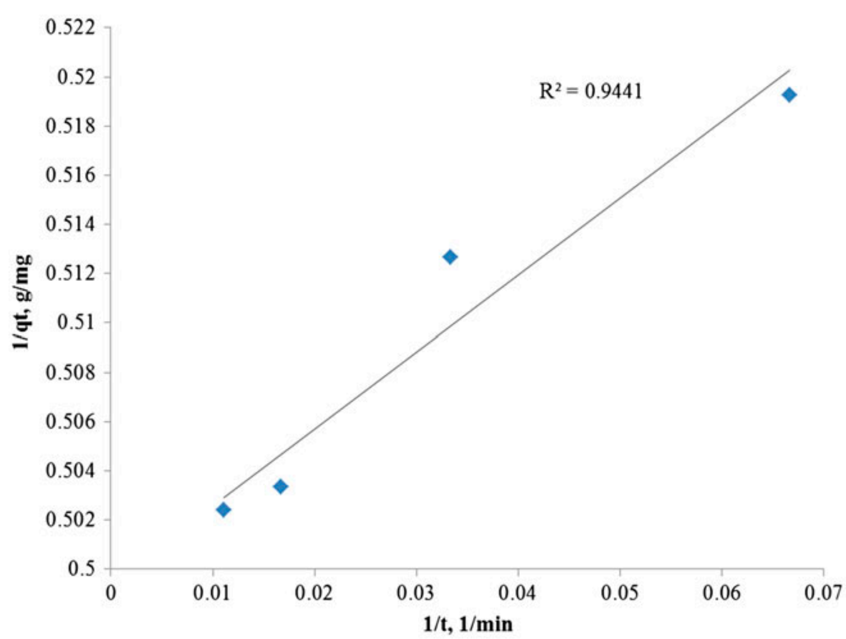

Fig. 4. Pseudo-second-order kinetics obtained by using linear method for the sorption of crystal violet onto Ag-nanocomposite using Linear form 4.

Table 2
Pseudo-second-order kinetic parameters obtained by using the linear and non-linear methods

Kinetic Models	q_e, exp (mg g^{-1})	q_e, (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	r^2	χ^2
Linear Type 1	1.997	2.019	0.676	0.999	0.0042
Linear Type 2		2.002	0.797	0.941	0.0043
Linear Type 3		2.005	0.749	0.941	0.0047
Linear Type 4		2.002	0.798	0.944	0.0043
Nonlinear		2.002	0.793	0.999	0.004

Note: For non-linear equation, *F*-value: 145340.29.

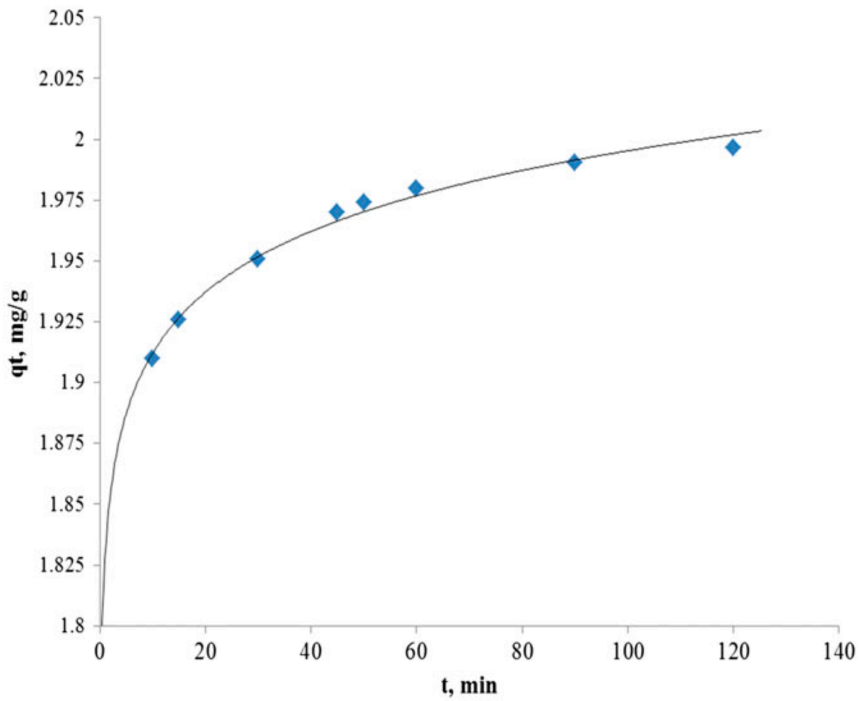

Fig. 5. Pseudo-second-order kinetics obtained by using non-linear model for the sorption of crystal violet onto Ag-nanocomposite.

abscissa and ordinate, the regression resulting in same error distribution structure [19,20].

The experimental values and the values of pseudo-second-order kinetics of non-linear methods were represented by Fig. 5. The k_2 and q_e were listed in Table 2. From the analysis of r^2 and χ^2 of non-linear expression, it was observed that non-linear expression was the best fit expression to represent the pseudo-second-order kinetics expression to linear form with error function. Due to non-linear expression, the error function distribution was found to remain unaltered, and so, the model was better represented along with the theoretical data than the different linear model systems. Linear model 1 was proved to be the best fit among the other linear forms due to the highest coefficient of data found that was calculated from equation. So it was inferred that it would be more reliable to interpret the adsorption kinetic data through a non-linear regression analysis.

4. Conclusion

The adsorption kinetics of crystal violet dye using Ag-nanocomposite was studied using non-linear and linear forms of pseudo-second-order kinetic models. The kinetic models were analysed in detail for confirmation using four linear forms and a non-linear form for the comparative assessment. It was observed that using linear form of kinetic models in determining the kinetic parameters were not appropriate due to the error distribution getting altered. The drawbacks were minimized by transformation and use of non-linear expression of pseudo-second-order model. It was observed that the adsorption kinetics of crystal violet onto Ag-nanosoil composite was suitably fitted and better described by non-linear kinetic model.

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