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Removal of hazardous reactive blue19 dye from aqueous solutions by agricultural waste

Mahmood Abassi [a], Nima Razzaghi Asl [*,b]

[a] *Faculty of Chemistry, Bu-Ali Sina University, Hamadan, Iran*
[b] *Faculty of Pharmacy, Department of Medicinal Chemistry, Shiraz University of Medical Sciences, Shiraz, Iran*

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Abstract

Low-cost grapefruit peel (Agricultural Waste) was used for removal of reactive blue19 dye from aqueous solutions. The process was studied as a function of contact time, initial dye concentration and pH. Adsorption process was attained to the equilibrium within 45 min for initial dye concentrations of 50, 75, and 100 mg L^{-1}. An acidic medium was the optimum condition for adsorption of dye at room temperature. The maximum dye removal of 83.56 % could be achieved at initial pH 2 using adsorbent dosage of 0.5 mg in 150 ml (50 mg L^{-1} dye concentration) and agitation rate of 180 rpm. The adsorption capacity was found to be about 12.534 mg g^{-1}. The isotherm data could be well described via Langmuir equation with the correlation coefficient of 0.986 in dye concentration range of 50-100 mg L^{-1} at 25 $^{\circ}$C. Kinetic studies revealed that the experimental data correlated well with pseudo second-order model possessing regression coefficient of $R^2 \geq 0.999$. Scanning Electron Micrographs provided a supporting evidence for efficient dye sorption onto grapefruit peel.

Keywords: Agricultural waste; Grapefruit Peel; Adsorption; Reactive blue19.

1. Introduction

Color removal from industrial effluents has been of significant concern due to the environmental problems [1,2]. The presence of very low concentrations of dyes in effluent is highly visible and undesirable. Wastewaters from the textile industry commonly contain moderate concentrations (10-200 mg mL^{-1}) of dyestuffs, contributing significantly to the contamination of aquatic ecosystems [3]. Dyes may have chronic and acute effects on living organisms, affect the nature of water and inhibit sunlight penetration into the stream which avoids photosynthesis action [4]. Therefore, environmental legislation has imposed steady limits on the concentrations of contaminants, which may be discharged in aqueous effluents from manufacturing and textile industries.

Use of reactive dyes has been enhanced due to the increased consumption of cellulose fibers in which other dyes suffer from technical and economical practical limitations in comparison with reactive dyes [5]. Different methods have been applied for purification and decolorization purposes including mechanical, physical, chemical and biological or their combination [6-10]. Adsorption techniques have become more commonplace recently owing to their efficiency in the

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[*] Corresponding author. Tel.: +98 912 5968541; fax: + 98 711 2332225.
E-mail address: razzaghin@sums.ac.ir (N. Razzaghi Asl)

elimination of contaminants too stable for biological methods. Conventional treatment methods are often disadvantageous to remove certain forms of color, particularly arising from reactive dyes owing to their high solubility and low biodegradability [11]. Failure of conventional physiochemical methods as a technique for treating reactive dye waste could be overcome by adsorption. Hence, adsorption is recommended as a viable means for reactive dye removal [10].

Adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid and is bonded physically or chemically. The rate at which dye molecules are transferred to the adsorbent may be affected by the transport of dye through the bulk solution to the surface of the adsorbent, the possible adsorption of dye molecules onto this surface, and the diffusion of the dye from the surface to the interior of the adsorbent. Surface chemistry and the distribution of adsorption sites on the surface of the adsorbent play an important role in the adsorption process. Activated carbon is the most widely used adsorbent for dye molecules due to its high porosity for sorption of organic compounds, but its use is becoming limited because of high cost [12].

In recent years, the tendency toward low-cost adsorbents that have binding abilities with organic compounds has intensified. Agricultural waste in large quantities can be utilized as low-cost adsorbents. Due to abundant availability, agricultural waste such as grapefruit peel poses little economic value and moreover, causes drastic disposal problems [13]. A number of the articles have been published in literature about the application of various low cost adsorbents [14-18]. High potency of agricultural wastes in adsorption of dye compounds can be related to the fact that most adsorbents derived from this source contain cellulose, hemi-cellulose and lignin, with surface functional groups such as carboxylic, carbonyl and hydroxyl, which possess high affinity for dye molecules.

The objective of the present work is to investigate the adsorption characteristics of waste grapefruit peel for the removal of reactive blue19 dye (RB19) from aqueous solution which is widely used in textile processing industries. Effects of pH, initial dye concentration and contact time on dye removal were studied. The adsorption data were evaluated using Langmuir isotherm and kinetic parameters for pseudo first-order and pseudo second-order models were determined. Also the adsorption process was confirmed via scanning electron microscopy (SEM) images.

2. Experimental

2.1. Adsorbents and dyes

Grapefruit peel was obtained from a fruit stall, washed to removed dirt, cut into small pieces and air dried for 72 h, then powdered. The powder particle size was distributed in the range of 150-400 μm. Resulted powder was agitated in 50 ml butyl alcohol for 3 h at room temperature to remove some organic components like limonene, chlorophyll and other low molecular-weight compounds. The sample was filtered and washed with butyl alcohol twice until it had no color in the filtrate. The washed sample was dried in oven at 60 °C for 12 h and used as adsorbent. Reactive blue19 dye used in this study was purchased from Ciba Ltd. without further purification. The chemical structure of this dye is depicted in Fig.

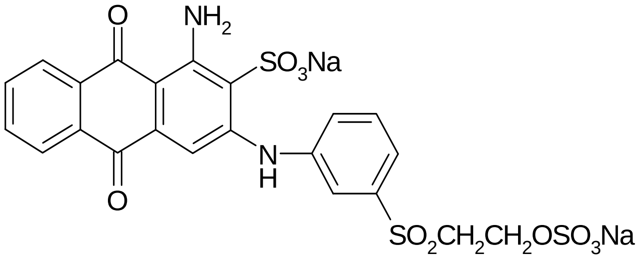


Fig. 1. Chemical structure of reactive blue19 dye.

Other chemicals were all of analytical grade from Merck Chemical Company. Distilled deionized water was used for preparation of all solutions. pH adjustments were done using dilute hydrochloric acid and sodium hydroxide solutions. The pH measurements were made by a pH meter (Hach). The agitation process for mixed adsorbent and dye solutions was carried out using shaker (model-Orbital L).

2.2. Adsorption studies

Batch sorption equilibrium experiments were performed by adding 500 mg of dry waste grapefruit peel to 150 ml dye solution with desired concentrations and pH at ambient temperature with the stirring rate of 180 rpm. After 45 min, the dye solution was separated from the adsorbent by a Hettich EBA20 centrifuge at 6000 rpm for 10 min. The amount of removed dye was determined by a CECIL 9200 spectrophotometer through monitoring the absorbance variations for all samples at 598 nm. The amount of RB19 adsorbed onto the peels, q_e (mg g^{-1}), also known as adsorption capacity was computed using the following equation:

$$q_e = (C_0 - C_e)V/W \qquad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of dye, respectively (mg L^1), V is the volume of solution (L) and W is the weight of adsorbent (g). The effect of initial dye concentration, contact time and initial pH on adsorption capacity was studied. The percentage of removed dye in solution for each treatment can be calculated using eq. (2) [19].

$$Dye\ removal\ (\%) = (A_. - A/A_.) \times 100 \qquad (2)$$

where A_0 is the initial dye absorbance and A represents the final absorbance of dye solution. Equilibrium and kinetic studies were performed under optimum experimental conditions.

2.3. Scanning Electron Microscopy studies

Scanning electron micrographs of grapefruit peel before and after adsorption process were captured by LEO 1455 VP scanning microscope. The experiment was done with 500 mg of adsorbent for 150 ml of 50 mg L^{-1} dye solution at pH 2 within 45 min contact time. The stirring rate was fixed at 180 rpm and Separation procedure was the same.

3. Results and Discussion

3.1. Concentration measurement and Calibration

In order to calculate the concentration of the sample from each experiment, a calibration curve of RB19 dye was obtained. Calibration evaluation was carried out in duplicate and the maximum absorbance of dye was plotted against concentration. Beer's law was obeyed within the experimental initial concentrations of RB19. Therefore the concentration of dye samples could be calculated from related maximum absorbance values.

3.2. Effect of contact time and initial dye concentration

Grapefruit peel and dye solutions were contacted for different intervals to study the effect of adsorption time on RB19 removal (Fig. 2). The equilibrium condition was achieved within 45 min for 50, 75 and 100 mg L^{-1} dye concentrations. The removal of dye is fluent at initial stages of contact time while gradually decreases with lapse of time till saturation.

The effect of initial dye concentration on the ability of grapefruit peel to adsorb dyes from solution suggested that the percentage color removal of reactive blue19 decreased when the initial dye concentration increased. However it remained relatively constant for concentrations more than 100 mg L^{-1} (Fig. 2). For 50 mg L^{-1} of RB19 concentration, 12.534 mg g^{-1} of dye removal was achieved while 11.267 mg g^{-1} and 9.178 mg g^{-1} removals were attained applying 75 and 100 mg L^{-1} initial dye concentrations, respectively.

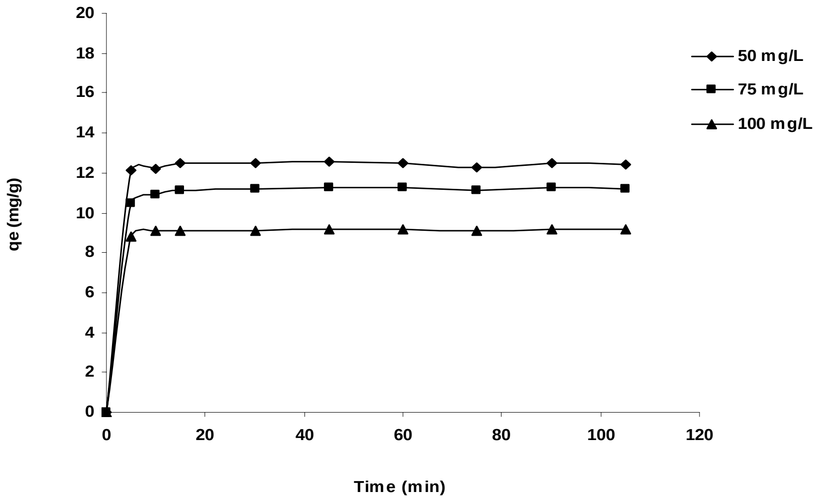


Fig. 2. Effect of contact time for different dye concentrations on dye removal by grapefruit peel; pH 2, 25 ºC, agitation rate of 180 rpm and 0.5 g adsorbent in 150 ml of 50 mg L^{-1} dye solution

3.3. Effect of pH

Spectral measurements of colored solutions containing only RB19 at various pH values (2-8) showed insignificant effect of medium acidity on the maximum absorbance wavelength (λ_{max}) of RB19. This observance demonstrated that within this range of pH, no considerable chemical structure change occurred. Therefore, during the experimental procedure pH control was ignored and initial pH values could well be considered for whole procedure. Table 1 shows the maximum absorbance wavelength of RB19 at different pH amounts.

Table 1
Maximum absorbance wavelength of aqueous RB19 solution at different pH values

pH	λ_{max} (nm)
2	597.9
4	597.9
5	598.5
6	599.1
8	597.6

The effect of pH on dye removal was investigated in the range of 2-8. pH influence on the adsorption of RB19 dye on the grapefruit peel is shown in Fig. 3. Significant decrease in dye removal could be observed as the initial pH for dye solution increased. The percentage of dye removal for various pH amounts calculated from equation (2) is shown in Fig. 4.

Solution pH would affect both aqueous chemistry and surface binding-sites of the adsorbent. As the pH of the medium increases, the number of the negatively charged sites increases as a result of dissociation of cellulose hydroxyl groups which may not have affinity for adsorption of dye anions due to the electrostatic repulsion. However, dissociation of some reactive dyes may occur in weakly alkaline region [20].

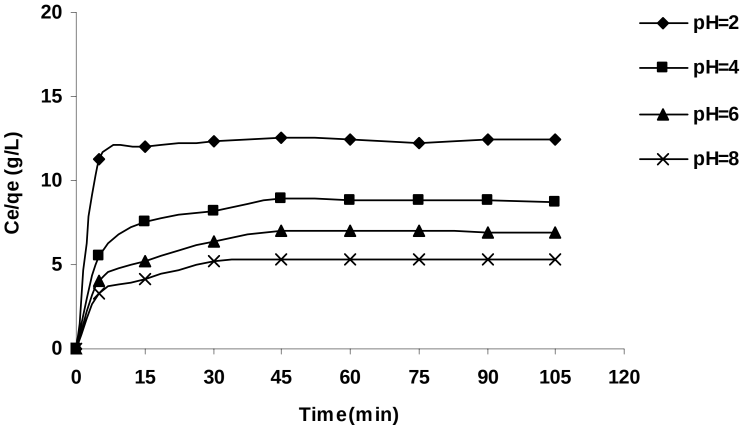


Fig. 3. Effect of pH on the removal of RB19; 45 min contact time, 25 ºC, agitation rate of 180 rpm and 0.5 g adsorbent in 150 ml of 50 mg L^{-1} dye solution.

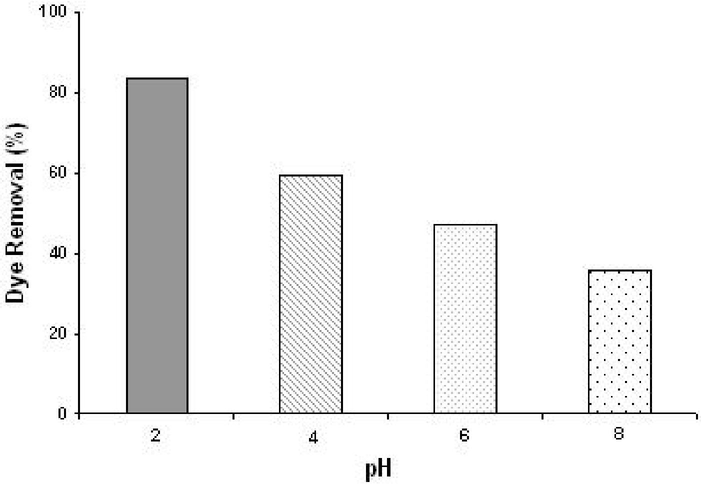


Fig. 4. Percentage of RB19 removal at different initial pH values.

Maximum removal rate was attained in acidic medium (pH 2) in which 83.56 % dye removal occurred. The similar pH effect results were reported for adsorption of reactive blue19, reactive yellow GR and reactive red RB on chitosan, reactive blue2, reactive red 4 and reactive yellow2 on activated carbon**,** brilliant blue on hen feathers and Tartrazine on hen feathers which are all sulfonated dyes [21-23].

At lower pH values, the percentage color removal of hydrolyzed reactive dye was relatively high, which may be attributed to the presence of positive charge produced via ionization of functional groups of adsorbent and significantly high electrostatic attraction. At pH values lower than 2, hydronium ions would significantly compete with dye ions for the adsorption sites of waste peel and consequently inhibiting the adsorption of dyes.

3-4. Adsorption equilibrium isotherms

Basically, adsorption is a mass transfer process in which atoms or molecules move from a bulk phase onto a solid or liquid surface. Adsorption equilibrium at a definite temperature is usually presented in the form of adsorption isotherms, which are useful for selecting the most appropriate adsorbent and also for predicting the performance of adsorption processes. Many systems can be moded by a number of the classical isotherms such as Freundlich and Langmuir together with more sophisticated isotherms [24, 25].

The Langmuir equation is applicable to homogeneous adsorbing sites where the adsorption of each molecule onto the surface has equal sorption activation energy. Langmuir adsorption model assumes that there is no interaction between adsorbed species and predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent [26]. The simplest theoretical model for monolayer adsorption due to Langmuir line arised equation can be shown as [27].

$$C_e/q_e = 1/Q_m \cdot K_L + (1/Q_m)C_e \qquad (3)$$

where q_e is the amount of dye adsorbed on grapefruit peel at equilibrium, C_e is the equilibrium concentration of dye solution, K_L is the equilibrium constant, and Q_m is the maximum adsorption capacity. The linear plot of C_e/q_e versus C_e demonstrates that the adsorption obeys Langmuir isotherm model and values of Q_m and K_L for a specific adsorption system can be determined From the slope and the intercept of a plot.

Langmuir equation (eq.3) has been successfully applied to many adsorption processes for acid dyes**,** reactive dyes**,** direct dyes and basic dyes [28-31]. Even in some literature the applicability of Langmuir model for waste agricultural adsorbents has been emphasized [32].

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. The Freundlich isotherm expresses reversible adsorption process and predicts that the dye concentrations on the adsorbent will increase so long as there is an increase in the dye concentration in the liquid. The related equation can be given by

$$q_e = K_F.C_e^{1/n} \qquad (4)$$

where q_e is solid phase adsorbate concentration in equilibrium (mg g^{-1}), C_e is liquid phase adsorbate concentration in equilibrium (mg L^{-1}) and 1/n is heterogeneity factor indicating the adsorption intensity. It has been revealed that the magnitude of heterogeneity factor indicates the favorability and capacity of the adsorbent/adsorbate systems. K_F is Freundlich constant (L g^{-1}) and can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto adsorbents for a unit equilibrium concentration. A linear form of the Freundlich expression can be given by

$$\ln q_e = \ln K_F + 1/n \ln C_e \qquad (5)$$

therefore, a plot of $\ln q_e$ versus $\ln C_e$ provides the determination of K_F and 1/n.

3.4.1. Fitting experimental data to adsorption isotherms

For the investigation of equilibrium behavior of the adsorption process, linear forms of Langmuir and Freundlich isotherms at 25 °C were applied to experimentally obtained data. The knowledge of the adsorption isotherm parameters makes it possible to determine the extent of solute removal, since the equilibrium concentration is the highest reduction level that can be achieved [33]. The plot of specific sorption C_e/q_e against the equilibrium concentration, C_e for RB19 is shown in Fig.

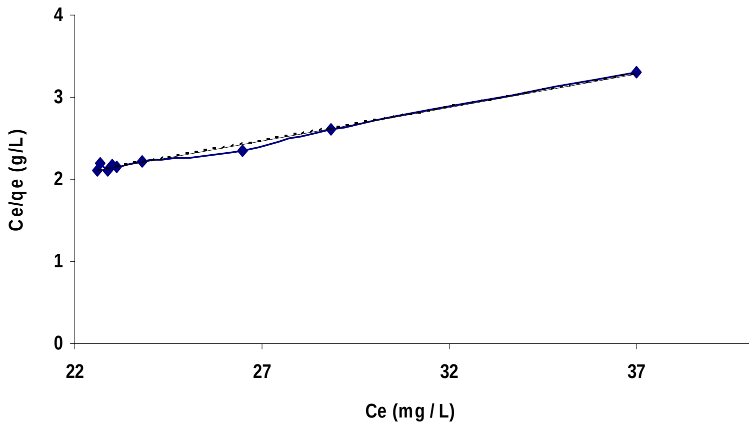


Fig. 5. Langmuir isotherm plot for reactive blue19 adsorption on waste grapefruit peel.

The correlation coefficient for Freundlich adsorption model showed a distinctive deviation from linearity for the whole concentration range ($R^2 = 0.5371$). The Q_m, K_L, r_l^2 (correlation parameters obtained for Langmuir isotherm) are given in Table 2.

Table 2
Correlation coefficients obtained for Langmuir and Freundlich equation.

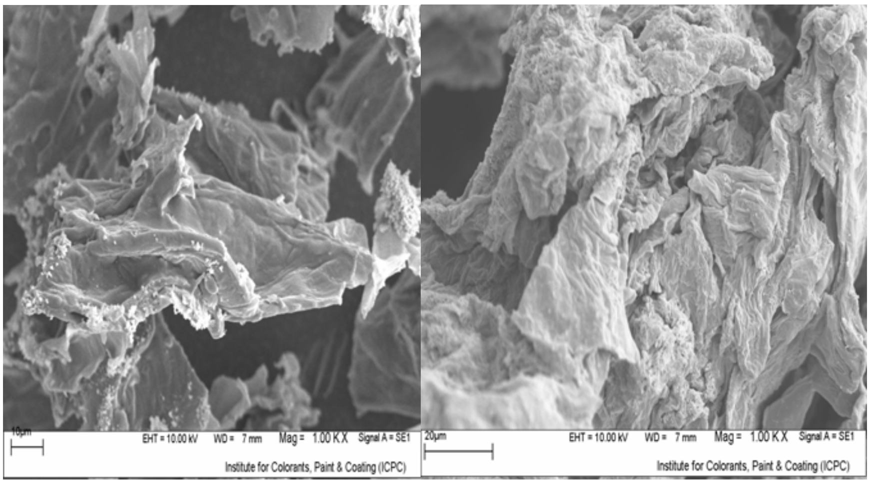
Dye	Langmuir isotherm (25 °C)		
	Q_m (mg g^{-1})	K_L (L g^{-1})	R^2
RB19	12.39	0.2789	0.986

High value of correlation coefficient in Langmuir equation (R^2=0.986) revealed that RB19 adsorption data closely followed the Langmuir model of adsorption. Fig. 5 demonstrated that the Langmuir equation could accurately describe of the experimental data with a good fit. This fact was further confirmed by high values of correlation coefficients. The model parameters and regression coefficient obtained for Freundlich isotherm showed a significant lower correlation with the experimental data compared to Langmuir model.

3.5. Scanning Electron Microscopy (SEM) analysis

Scanning Electron Microscope is a type of electron microscope capable of creating high-resolution magnified images of sample surface. The production of magnified images is due to using electrons instead of light waves which also provides SEM images with characteristic three-dimensional appearance and useful for judging the surface structure of the sample. The shape, size, porosity and arrangement of the particles making up the object that are lying on the surface of sample can be well determined by scanning electron microscopy.

The SEM image of original grapefruit peel shows the presence of significant number of pores providing a suitable position for dyes to be adsorbed. SEM images after RB19 adsorption demonstrated that the pores and cavities of adsorbent were efficiently packed with dyes (Fig. 6).



(a) **(b)**

Fig. 6. Scanning electron micrographs of (a) original grapefruit peel, (b) dye adsorbed grapefruit peel with RB19. conditions: pH 2, 0.5 g in 150 ml of adsorbent, 50 mg L^{-1} of initial dye concentration, equilibrium time of 45 min, agitation rate of 180 rpm, 25 ± 1 °C and particle size of 150-٤٠0 µm.

3.6. Adsorption kinetics

The study of adsorption kinetics is essential for investigation of solute uptake rate which controls the retention time of adsorption at the solid-solution interface. The results would be of undeniable importance for the process optimization in industry. The kinetics of RB19 adsorption on the grapefruit peel was analyzed using pseudo first-order rate expression and pseudo second-order model [34]. High correlation coefficient for pseudo second-order equation indicated that the pseudo second-order model could successfully describe the kinetic of RB19 adsorption on grapefruit peel.

3.6.1. Pseudo first order model

The Langergren equation a pseudo second-order equation, describes the kinetics of adsorption process as follows

$$\log(q_e - q_t) = \log q_e - (K1/2.303)t \qquad (6)$$

where q_t is the amount of dye adsorbed (mg g^{-1}) at time t, q_e is the amount of dye adsorbed at equilibrium, and K_1 is the rate constant of first-order sorption (min^{-1}). The pseudo first-order kinetics constants for the adsorption of RB19 on grapefruit peels are tabulated in Table 3. Results showed that the sorption data could not be fitted by this model.

3.6.2. Pseudo second-order model

The second order kinetic model can be given by

$$t/q_t = 1/\ K_2.q_e^2 + (1/q_e).t \qquad (7)$$

where K_2 is the rate constant of second-order sorption (g mg^{-1} min^{-1}). The plot of t/q_t versus t (Fig. 7) showed a linear relationship with high regression coefficient ($R_1^2 \geq 0.999$).

Kinetics parameters are tabulated in Table 3. The linear plot of t/q_t versus t shows a good compliance between experimental and theoretical q_e values (Table 3).

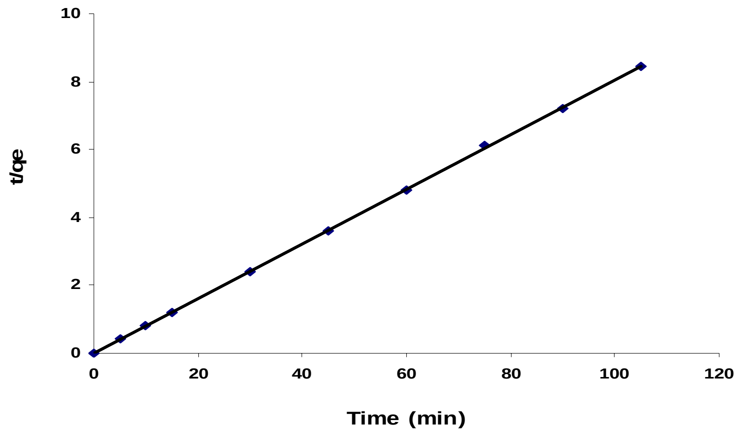


Fig. 7. Pseudo second-order adsorption kinetics of RB19 onto grapefruit peel; pH 2, 25 °C, Initial dye conc. of 50 mg L^{-1} and rate of 180 rpm.

The correlation coefficient for the pseudo second-order model is significantly higher than that of pseudo first-order model indicating the fitness of adsorption data into this equation and also demonstrated that the chemical sorption is the rate determining step instead of mass transfer. Similar observations have been reported for adsorption of reactive dyes. [35, 36].

Table 3
The adsorption kinetic model rate constants for the RB19 adsorption on grapefruit peel at pH 2.

Dye	Initial Dye conc. (mg g^{-1})	q_e (exp.) (mg g^{-1})	Pseudo first-order model		q_e (calculated) (mg g^{-1})	Pseudo second-order model		q_e (calculated) (mg g^{-1})
			K_1	R_1^2		K_2	R_2^2	
RB19	50	12.534	0.0193	0.1382	0.4454	10.8	0.9998	12.422

4. Conclusions

Waste grapefruit peel, an agricultural waste which is thrown away, can be well applied as a suitable and low-cost adsorbent for the removal of reactive blue19 dye (RB19) from wastewater. Equilibrium and kinetic evaluations at ambient temperature revealed that the sorption process obeyed Langmuir isotherm model. The initial adsorption equilibrium was achieved within 45 min at pH 2 (optimum pH) for all concentrations of RB19. The kinetics of the adsorption was found to follow a pseudo second-order rate equation. Under the experimental conditions (C_0=50 mg L^{-1}, adsorbent dosage of 0.1 g in 50 ml of dye solution, pH 2 and agitation rate of 180 rpm) maximum dye removal of 89.9 % could be attained. According to the results, low-cost grapefruit peel, being a cheap and available material, could be an alternative for some costly adsorbents in the removal of reactive dyes in wastewater treatment process. As the investigations about the adsorption properties of grapefruit peel have been much limited, so it was considered to be important to study on the ability of this agricultural waste to remove reactive anionic dyes from industrial wastewater. The feasibility of using grapefruit peel as an adsorbent for the treatment of solution containing other types of dyes is an important purpose to study in further investigations.

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