ISSN-1996-918X

Pak. J. Anal. Environ. Chem. Vol. 19, No. 1 (2018) 44 – 52

http://doi.org/10.21743/pjaec/2018.06.04

Biosorptive Decontamination of Acid Red-87 Dye from Wastewater by *Citrus limonum* Peels: Ecofriendly Approach

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Received 20 February 2018, Revised 23 April 2018, Accepted 30 April 2018

Abstract

Batch adsorption experiments were conducted to evaluate efficiency of lemon peels (*Citrus limonum*) for adsorption of Acid Red-87 dye from aqueous media. The effects of various parameters, i.e. particle size, pH, sorbent dose, sorbate concentration, temperature, contact time and agitation speed on biosorption efficiency were optimized. Isotherm models: Langmuir and Freundlich were employed to understand the mechanism of adsorption. The monolayer adsorption capacity calculated by Langmuir isotherm was found to be 0.6240 mg/g. Thermodynamic studies revealed exothermic and spontaneous nature of sorption process, while kinetics guided pseudo-second order behaviour. All these factors indicated that *Citrus limonum* peels are potential adsorbent for the removal of Acid Red-87.

Keywords: Lemon peels, dye, adsorption isotherms, waste water.

Introduction

Waste of many major industries contains organic dyes, which are chemically stable, therefore can't be removed easily and are discharged along with the wastewater. It remained utmost demand of textiles, leather, cosmetics, paper printing, plastic, pharmaceuticals and foods industries to explore cost-effective means to remove them from wastewater [1].

In textile industry, two third of total dyestuff production is used. Worldwide over 7×10^5 tons of dyes are produced annually [2]. Such effluents not only affect their aesthetic nature but also reduce photosynthetic action, eventually affecting man through the food chain [3]. Acid Red-87 dye (Eosin) is an acidic dye and is commonly used for dyeing wools, cotton, silk, leather, papers and nylon. This dye may be harmful by inhalation, in contact with skin, and if swallowed [1].

Various treatment methods and technologies have been reported in literature to remove such effluents. Among them notable are chemical coagulation/flocculation, chemical precipitation, oxidation processes, ultrafiltration, reverse osmosis and ion exchange etc [4]. However, majority of these used methods could not use due to high price, synthesis of harmful byproducts or severe energy demands [5-8]. Adsorption is another conventional, most adaptable and commonly used method since its low cost and eases of operation.

Numbers of low cost sorbents have been explored previously for the removal of pollutants of varying chemical nature. For example, peanut hulls were explored as very promising sorbent materials for the removal of heavy metal ions from aqueous solutions [9]. Batch experimentation was carried out to removal Cd(II) and Pb(II) from aqueous solutions using sawdust [10]. Similarly,

significant removal of Pb(II) was carried out from wastewater employing maize bran as sorbent [11]. Removal of large range of divalent metal ions was carried out using sugar beet pulp as biosorbent material [12] and study revealed very good removal efficiency. For the removal of dyes, number of sorbents has been successfully tried, for example, chitosan hydrobeads were successfully used for the removal of eosin dye from aqueous media [13] with removal efficiency more than 90%. Additionally, corn starch [14], chitin [15], rice husks [16], granular kohlrabi peels [17], raw barley straws [18], orange wastes [19], egg shells [20], aqua cultural shell powders [21] and many other sorbent materials have been successfully employed for the removal of sorbates / pollutants of varying chemical nature.

Lemon (*Citrus limonum)* peels are commonly available in our country as lemon is consumed more or less throughout the year, however its demand is more enhance in the long summer season of this country. In an earlier report, lemon peel has been evaluated as a potential adsorbent to remove methyl orange and Congo red [22]. We have also previously contributed the function of lemon peel [23], as low cost adsorbent to remove the Trypan Blue dye from aqueous solution [24].

In continuation of our previous effort, in present work, *Citrus limonum* peels have been investigated to remove another important anionic dye (Acid Red-87 dye) from aqueous media. The structure of dye molecule is shown in Fig. 1.

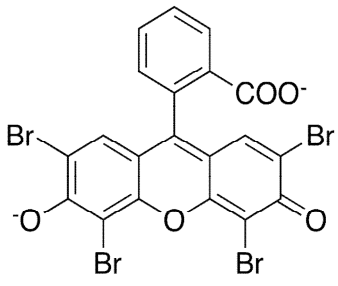

Figure 1. **Acid Red-87 dye (Also known as eosin yellow)**

It is a fluorescent dye usually employed in detergents, hair dyes, cosmetics, histology, photovoltaic devices, nano-scale host material, color filter, and in inks used for detection of latent fingerprints. Its various properties are: CI NO.: 45380; Physical appearance: Red; Insoluble in Water: 0.5 %; Ash Content: 0.3 % and pH: 9.5 – 10. Numbers of serious safety concerns and health implications have been associated with the release of Acid Red-87 dye in aqueous media including modification of hydraulic characteristics of water, leading to emergence of carcinogenic compounds on biodegradation and increased COD [25]. Factors (initial dye concentration, adsorbent dose, and contact time) influencing the *Citrus limonum* peels adsorption capacity had been studied. The purpose of the work is to evaluate the adsorption efficiency of *Citrus limonum* peels for the removal of Acid Red-87 dye from aqueous solutions. Feasibility of the process has been investigated by studying various isotherm models in addition to kinetic and thermodynamic investigations.

Materials and Methods

All chemicals and solvents used during this study were analytical grade and purchased from Merck. Glassware was dried at 110 ^{o}C before its use. *Citrus limonum* (Lemon) peels were collected from local market.

Preparation of standard dye solution

Stock solution of Acid Red-87 dye (1000 ppm) was prepared by dissolving 0.1 g/100 mL distilled water. Further standards and working solutions were prepared by its dilution.

Preliminary treatment to Citrus limonum peels

Citrus limonum peels were washed with distilled water several times and then dried in sunlight for five days. Then in oven at 110 ^{o}C for 24 hours for complete moisture removal. The dried *Citrus limonum* peels were ground to obtain mesh size in the range 20-80 microns.

Adsorption experiments

Absorption study was carried out at 30 ^{o}C. A known quantity of adsorbent added to sample solution of dye (25 mL) and allowed to stay for one hour on orbital shaker (model OSM-747).

Then the mixture was filtered and dye concentration was monitored by UV/VIS spectrophotometer (Labomed UVD = 3500) at λ_{max} = 515 nm. Different parameters were varied, such as: particle size of adsorbent (10 – 80), adsorbent dose (0.1 – 2 g), time (10 – 80 min), stirring rate (50 – 250 rpm), temperature (20 – 60 ^{o}C) and pH (2 – 8). Equation-1 was used to find out the Acid Red-87 dye adsorbed:

$$q_e = V (C_o – C_i)/ m \quad (1)$$

q_e (mg g^{-1}) is at equilibrium, the Acid Red-87 dye adsorbed amount, V (L) is dye volume, C_o (mg L^{-1}) is initial concentration of dye, C_i (mg L^{-1}) is dye concentration at any time and 'm' (g) is *Citrus limonum* peels dosage. Optimized conditions were further employed for adsorption modeling of equilibrium data.

Results and Discussion

Characterization of *Citrus limonum* peels

It was done using standard methods and the composition of various components is reported in (Table 1).

Elemental analysis was carried out to determine percentage of C, H and N in raw sorbent by elemental analyzer and results indicated their high amounts in peels. It revealed the significant potential of *Citrus limonum* peels as sorbents. Efficiency of a sorbent material for the removal of dyes of varying chemistry, i.e. polarity, from its surface is strongly influenced by content of carbon. Carbon content, upon burning, gives activated carbon, which has very established removal efficiency. Proximate analysis was carried out to find percentage of fiber, cellulose, hemicelluloses and lignin in dried *Citrus limonum* peels, and it was found that they were rich in these contents. *Citrus limonum* peels contained appreciable quantities of cellulose and hemi-cellulose contents which have high adsorption efficiency due to the presence of large quantities of hydroxyl, methoxyl, and carbonyl groups that can adsorb various contaminants from waste water. Same trend is found by Tejeda [26]. Small variations can be attributed to seasonal, topographical and climatic variations.

Table 1. **Composition of *Citrus limonum* peels**

Parameters (%)	***Citrus limonum* peels**
Carbon	33.35 – 36.56
Hydrogen	5.29 – 7.34
Nitrogen	1.25 – 3.36
Sulfur (in ppm)	0.03
Ash	3.51
Pectin	5.17
Lignin	7.16
Cellulose	17.59
Hemicellulose	5.91
Moisture	8.73
Volatile matter	5.15
Fiber	37

FTIR spectrum reveals the presence of amines, alcohol, carboxylic acid, hydroxyl groups, phenol, amino acids etc in both form of this peel. The peaks observed near 2900 cm^{-1} may be associated with the stretching vibrations of CH bond of methyl, methylene and methoxy groups [24-27]. Shifting of various peaks in below spectrum occurred after adsorption of dye molecules as is clear from (Fig. 2).

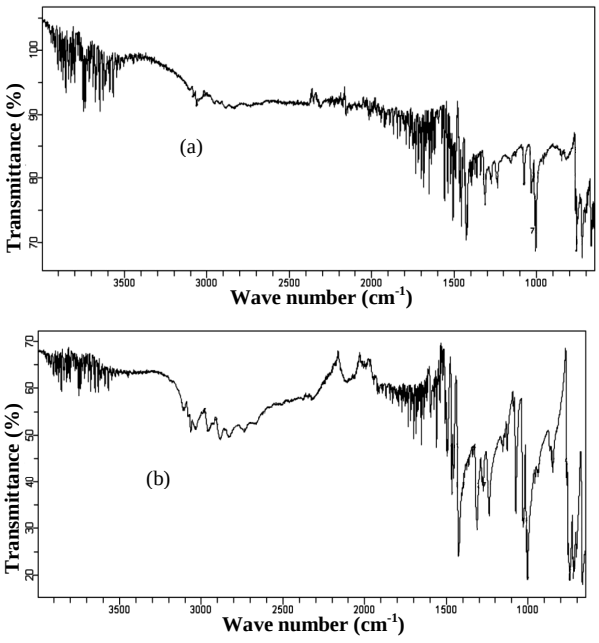

Figure 2. **FTIR spectra of *Citrus limonum* peels (a) before and (b) after adsorption of dye**

Scanning electron microscopic analysis of *Citrus limonum* peels by SEM (JSM-6700F, JEOL, Japan) revealed presence of different sized pores with different depths on its surface as indicated in Fig. 3. From apparent view, irregular shaped pores are present in it.

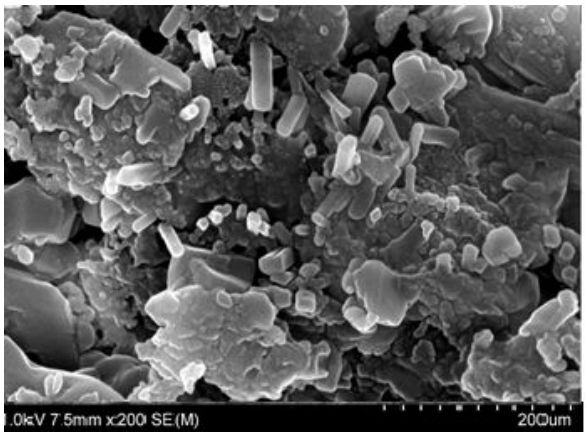

Figure 3. **SEM micrograph of *Citrus limonum* peels**

Thermo gravimetric analysis provides information about thermal decomposition pattern of materials under investigation. It is an effective tool to examine the pattern of chemical changes in the lingo-cellulosic matrix. Lignin, cellulose and hemicelluloses show sharp thermal decomposition at specific temperatures. Hemicellulose, being highly unstable compound, decomposes first followed by lignin and cellulose. As indicated from Fig. 4 that these peels exhibited the decomposition in three stages. Initial decrease in weight was noted below 200 ^{o}C and may be attributed to loss of light volatiles; mainly water. The second weight loss is mainly observed between 200 - 400 ^{o}C and may be related to breakdown of lignin and cellulose. These two components pyrolyzed into monomeric phenols, aromatic rings and piranose structures. Above 500 ^{o}C, a continuous weight loss was noticed, which may be attributed to slow decomposition of the remaining heavy components, which may consist of stable micronutrients like metal oxides [24-27].

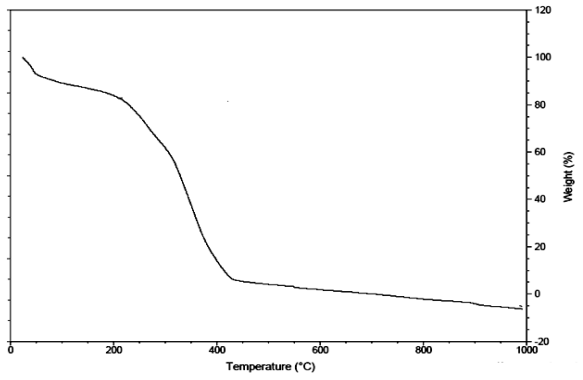

Figure 4. **TGA curve for *Citrus limonum* peels**

Optimization of operational parameters of adsorption

Various operational conditions were optimized one by one in order to carry out mathematical modeling of equilibrium data as followed:

Adsorbent size (mesh)

To evaluate the effect of particle size of adsorbent, different mesh sizes (20-80) of *Citrus limonum* peels were used. Results are graphically shown in Fig. 5. Generally adsorption increased by increasing 20-80 mesh sizes (80 > 60 > 40 > 20) and agrees as reported [27].

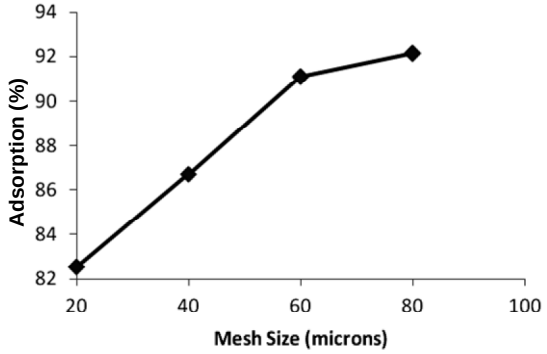

Figure 5. **Effect of adsorbent particle size (mesh) on % adsorption of Acid Red-87 dye by *Citrus limonum* peels**

Adsorbent dose

The adsorption efficiency influenced by adsorbent dose is shown in Fig. 6.

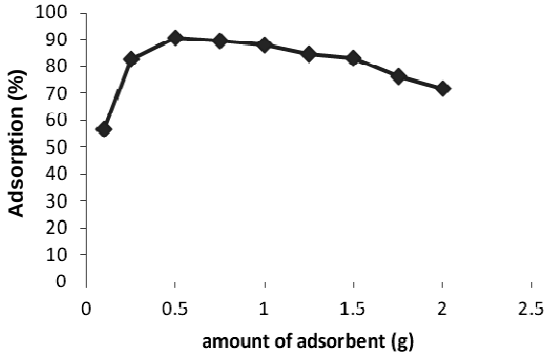

Figure 6. **Effect of *Citrus limonum* peels amount on % age adsorption of Acid Red-87 dye by *Citrus limonum* peels**

The dosage was changed from 0.1-2.0 g. As predicted pattern, adsorption efficiency increased as the dosage was increased. In this work, maximum adsorption was found at adsorbent dosage of 0.5g and beyond 0.5g, it started decreasing. The results can be compared with related literature [28].

Contact time

The adsorption efficiency of *Citrus limonum* peels studied at variable contact time (10-80 min). It was illustrated that as contact time increased, dye adsorption decreased especially after 60 min (Fig. 7). It is established in the related literature that the adsorption process has been increased rapidly initially at the external surface of the adsorbent proceeded slow internal diffusion processes [29].

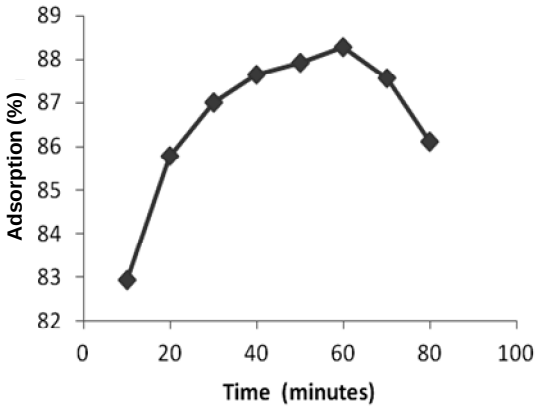

Figure 7. **Effect of time on % age adsorption of Acid Red-87 dye by *Citrus limonum* peels**

Initial dye concentration

This effect on adsorption capacity was evaluated by taking dye concentrations in the range of 5-25 ppm at pH (2). Fig. 8 shows that the percentage adsorption increases by enhancing dye concentration. *Citrus limonum* peels shown minimum adsorption at 5 ppm and maximum adsorption at 25ppm. The trend is comparable with related literature [29].

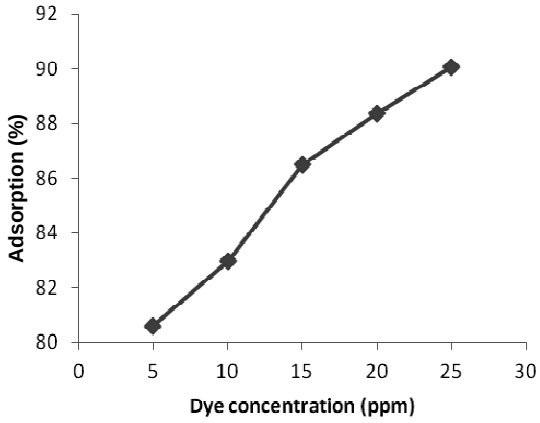

Figure 8. **Effect of initial dye concentration (ppm) on % age adsorption of Acid Red-87 dye by *Citrus limonum* peels**

Dye solution pH

The results of pH effect are graphically represented in Fig. 9. Maximum Acid Red-87 dye adsorption was observed at pH 2, thereafter it decreased, because in acidic conditions it is more ionized and that's why ionized species of Acid Red-87 dye in aqueous form could be easily chemisorbed on protonated adsorbent binding sites. In acidic conditions, oxygenated functional groups of cellulose and hemi-cellulose, usually found in agro-waste materials (like: *Citrus limonum* peels) get protonated which can adsorb more anionic contaminants easily.

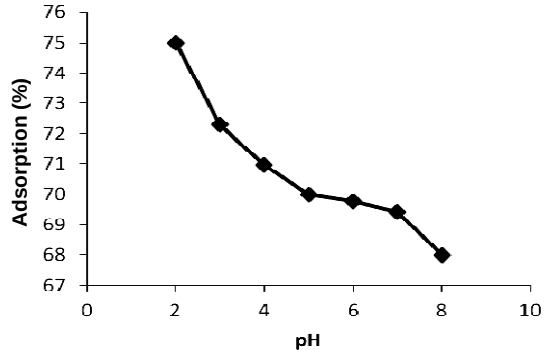

Figure 9. **Effect of pH on % adsorption of Acid Red-87 dye by *Citrus limonum* peels**

Stirring speed

Stirring speed was varied from 50 - 250 rpm in order to see its effect on adsorption capacity. Results are represented in Fig. 10. It

revealed that the dye was best absorbed at 150 rpm i.e. at low stirring speed. After that, adsorption efficiency of *Citrus limonum* peels decreases and no further increase in adsorption of Acid Red-87 dye was observed.

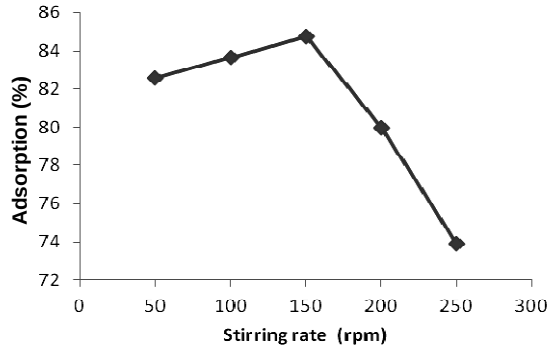

Figure 10. **Effect of stirring rate on % adsorption of Acid Red-87 dye by *Citrus limonum* peels**

Temperature

To see the influence of temperature, adsorption process was carried out in temperature range i.e.; 20-60 °C. Obtained results are given in Fig. 11. It shows that adsorption efficiency decreases at elevated temperature and was found maximum at 30 °C. It might be due to fast movement of dye molecules thereby rendering less interaction with adsorbent material.

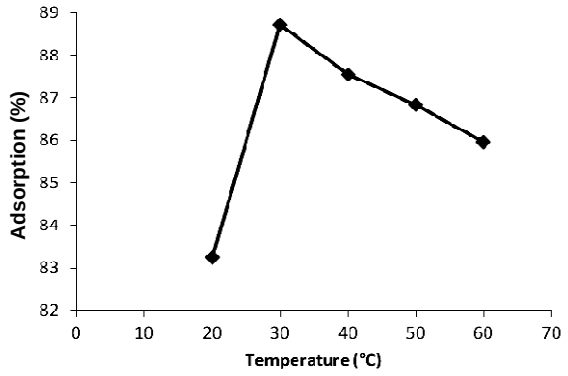

Figure 11. **Effect of temperature on % age adsorption of Acid Red-87 dye by *Citrus limonum* peels**

Adsorption isotherm

Adsorption isotherms shown in Fig. 12 & 13 used to identify interaction behavior between adsorbate and the adsorbent (2) using following equation 2 and 3:

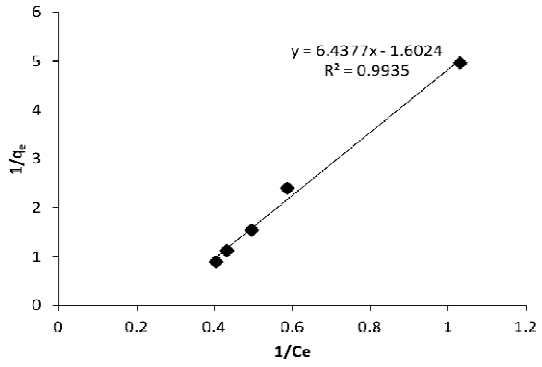

Figure 12. **Langmuir isotherm for adsorption of Acid Red-87 dye by *Citrus limonum* peels**

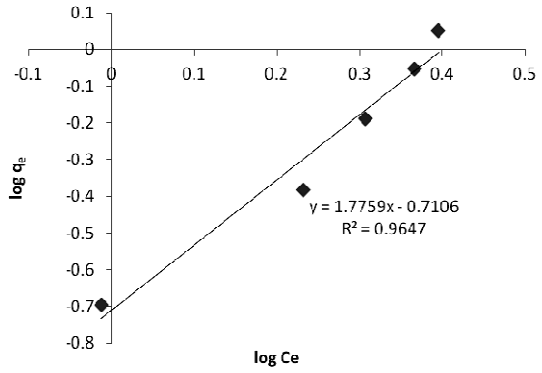

Figure 13. **Freundlich isotherm for adsorption of Acid Red-87 dye by *Citrus limonum* peels**

Langmuir isotherm:

$$1/q = 1/(q_m b)C_e + 1/q_m \quad (2)$$

Freundlich isotherm:

$$\log q_e = \log Kf + \frac{1}{n} \log C_e \quad (3)$$

These equation parameters provide details regarding adsorption procedure, the surface property and affinity for adsorbate [30]. The monolayer adsorption capacity in this experiment observed from Langmuir was 0.6240 $mg.g^{-1}$ and from Freundlich was 0.1947 (mg/g) $(L.mg^{-1})^{1/n}$. R^2 values shown that Langmuir model is favorable (Table 2).

Table 2. **Isothermal, Thermodynamic and Kinetic parameters for adsorption of Acid Red-87 dye by *Citrus limonum* peels.**

Langmuir Parameters			**Freundlich Parameters**		
q_{max} (mg/g)	**b (L/ g)**	**R^2**	**K_f**	**n**	**R^2**
0.6240	0.017	0.980	0.1947	0.5630	0.9647
Thermodynamic parameters					
Temperature (^{0}C)	**30**		**40**		**50**
ΔS^o	-30.84		-30.84		-30.84
ΔH^o	-6.98		-6.98		-6.98
ΔG^o	-2.36		-2.67		-2.98
Kinetic parameters					
Pseudo-second order	**K_f (min^{-1})**	**q_e (exp) mg/g**	**q_e (cal) mg/g**		**R^2**
	0.0675	1.1035	0.1246		0.9977

Thermodynamic parameter

Thermodynamic parameters such as enthalpy (ΔH°) (KJ/mole), entropy (ΔS°) (KJ/(K mole) and change in free energy (ΔG°) (KJ/mole) was also calculated by using equations 4 – 6 at different range of temperatures i.e., 30 °C, 40 °C, 50 °C and shown in Table 1 and graphically represented in Fig. 14.

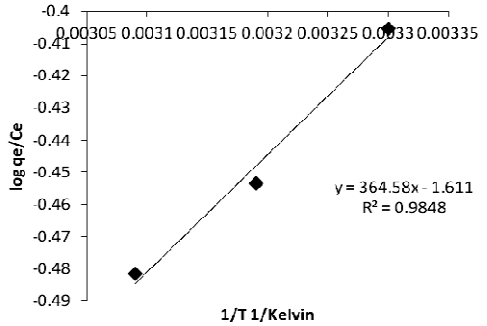

Figure 14. **Thermodynamic parameters graph for adsorption of Acid Red-87 dye by *Citrus limonum* peels**

$$\Delta G° = - RT\ln(K) \quad (4)$$

$$\ln\frac{K_2}{K_1} = \frac{\Delta H^o}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (5)$$

$$\Delta G° = \Delta H° - T\Delta S° \quad (6)$$

Where *R* is the universal gas constant (1.987 cal/deg/mol) and *T* is the temperature in kelvin. At negative values of enthalpy change, adsorption method was exothermic. However, negative value of entropy shows the decreased randomness of adsorbate molecules during adsorption process.

Kinetic studies

The kinetic study illustrated that adsorption process follow pseudo-second order kinetics as it's R^2 value is 0.9977 as shown in Table 1 and represented graphically in Fig. 15 according to equation 7 [31]:

$$\frac{1}{q_1} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

Moreover, theoretical q_e values and experimental q_e values well agreed in the case of pseudo-second order model.

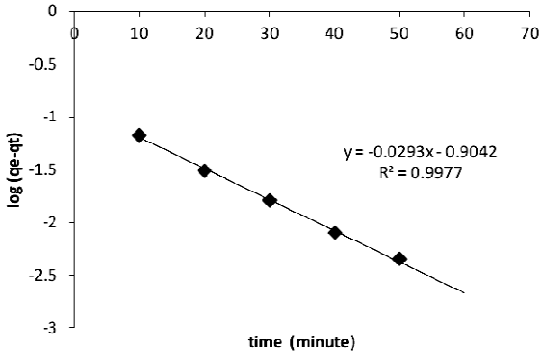

Figure 15. **Pseudo-second order parameters graph for adsorption of Acid Red-87 dye by *Citrus limonum* peels**

Conclusion

So it is obvious from results that Acid Red-87 dye can be easily removed from waste water streams using *Citrus limonum* peels which are indigenously available in Asian countries from local markets and confectionaries' juice factories. Textile dyes becoming very crucial to use for our industries, but later on their removal in non-toxic way is also important. Various biological methods were tried to remove dyes in effective way. We have tried *Citrus limonum* peels in this study, which is a common biological material found abundantly as agro-waste in arid countries during hot and rainy seasons. The results indicated that it is very effective for decontamination of synthetic

waste water. Isothermal and thermodynamic modeling of equilibrium data indicated that this process is feasible and spontaneous following chemisorption mode of removal of Acid Red-87 dye by *Citrus limonum* peels, which shows maximum adsorption capacity 0.624 mg/g.

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