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Application of Treated and Untreated Cucumis Sativus Peels for Elimination of Congo Red Dye from Aqueous Solutions: An Adsorption Study

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Abstract

Chief objective of present study was to examine the eliminative potential of congo red dye from aqueous solutions by using adsorption process with the help of untreated Cucumis sativus peels (UCSP) and treated Cucumis sativus peels (TCSP) in the form of comparison. An adsorptive elimination of congo red dye was attain first time by using Cucumis sativus peels from aqueous solutions. The effects of different parameters in adsorption process like effect of pH, dose of adsorbent, initial concentration and agitation time were also investigated. Maximum percentage elimination of congo red dye by using untreated Cucumis sativus peels was occurred at pH of 7, adsorbent dose of 300 mg, initial concentration of 150 ppm and agitation time of 250 minutes, which was 95.31% and using treated Cucumis sativus peels, it was occurred at pH of 7, adsorbent dose of 500 mg, agitation time 250 minutes and initial concentration of 120 ppm, which was 98.48%. Adsorption kinetics study indicated that adsorption of congo red dye was best followed by pseudo second order kinetics model as compared to pseudo first order kinetics model. Treated Cucumis sativus peels was found to be performed well for elimination of congo red dye from aqueous solutions as compared to untreated Cucumis sativus peels.

Keywords: Cucumis sativus peels; Elimination; Congo red dye; Adsorption.

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1. Introduction

Most of the dyes acts as a main component of the pollutants in wastewater and are widely utilized in many industries. These are colour substances used in textile, paper, plastic and cosmetic industries [1]. About 10,000 tonnes of dyes are consumed worldwide in several industries and one third of these dyes are discharged into water body as waste [2]. Existence of very small amount of these colours in wastewater is dangerous to environment [3]. Little concentration of dyes in wastewater increase oxygen demand, which adversely affects metabolic functions of phytoplankton, aquatic flora and fauna by reducing light penetration and thus photosynthesis [4]. Dyes containing wastewater show adverse effects on microorganisms and other microbial populations presents in water body. They are highly toxic and can be carcinogenic to living body [5].

There are three types of dyes which are classified as anionic, cationic and non-ionic. Anionic dyes referred to acidic, direct and reactive while cationic dyes referred to basic and non-ionic referred to disperse and vat dyes [6, 7]. Amongst them anionic dyes (azo dyes) are considered to be major class of organic dyes due to the presence of nitrogen-nitrogen double bond [8, 9] and they cannot be despoiled easily due to their structural complication and poor biodegradability [10, 11].

Congo red dye belongs to benzidine based azo dye having composite chemical structure with great solubility in water medium. High concentration of this dye is discharged from textile, rubber, paper, printing and dying industries into water body and cause water pollution [12]. When congo red dye enter into the food chain it persist and cause hazardous effects. Congo red may metabolized into benzene and could able to cause carcinogenicity in human [13]. It acts as irritant to eye and skin and persuade somnolence and respiratory difficulties [14, 15]. Due to its harmful effects it must be eliminate from water body before discharging into natural environment.

Bundle of techniques can be used for elimination of congo red dye from aqueous medium like coagulation, chemical oxidation, membrane separation, flocculation and microbial degradation [16-20] but these are not favourable because they are destructive and produce sludge which is another problem. Adsorption is considered to be most favourable, low cost, simple, ease in processing, efficient, and protective technique as compared to other techniques [21-25]. Many low cost adsorbents have been investigated previously for elimination of congo red dye from aqueous solutions but it is need to explore some new adsorbents which show awesome results against congo red dye elimination. The main objective of this study was to explore the behaviour of *Cucumis sativus* peels as a new low cost adsorbent for elimination of congo red dye from aqueous medium.

2. Material and Method

Following materials were used in present study: *Cucumis sativus* peels; Congo red (CR) (Microscopical stain, BDH); Sodium hydroxide (NaOH) (Merck, Germany); Hydrochloric acid (HCl) (Analytical grade, Pakistan).

2.1. Adsorbent preparation

Cucumis sativus peels were obtained from Kacha Fattomand Gujranwala, Punjab, Pakistan. These peels were washed many times with tap water and finally washed with distilled water. The washed peels were allowed to dry in drying oven at 70 ± 0.2^{o}C for 36 hours. Then the dried peels were grounded into powder form and sieved into -100/+200 mesh size. This powder was termed as untreated *Cucumis sativus* peels (UCSP) (Figure 1) and stored in polyethylene bag.

Figure 1: Untreated *Cucumis sativus* peels powder

The treatment of *Cucumis sativus* peels was down by boiling, 25 g of dried peels into 500 mL of 37% HCl, for 45 min [26]. After this process colloidal solution was filtered and residue was washed with distilled water until the pH of residual solution become neutral. Then the residue was allowed to dry in drying oven at 70 ± 0.2^{o}C for 36 hours. Finally, dried residues grounded into powder form and sieved -100/+200 mesh size. This powder was termed as treated *Cucumis sativus* peels (TCSP) (Figure 2) and stored in polyethylene bag.

Figure 2: Treated Cucumis sativus peels powder

2.2. Adsorbate solution preparation

Stock solution of 500 ppm was prepared by dissolving appropriate amount of adsorbate that was congo red (CR) in 1000 mL Pyrex flask and filled up to mark with the help of distilled water. Desired concentrations (30-180 ppm) of adsorbate were prepared by dilution method.

2.3. Adsorption study

Adsorption study was carried out with the help of batch experiments for elimination of Congo red dye by under taken the various parameters effects like effect of pH (5-10), agitation time (50-300 min), initial dye concentration (30-180 ppm) and adsorbent dose (100-600 mg) by using UCSP and TCSP. All experiments were performed at agitation speed of 300 rpm (revolutions per minute) in the laboratory temperature (25 ±2^{o}C) by taking 100 mL of CR solution in 250 mL Erlenmeyer flask. After induction the samples were centrifuged and analysed in UV visible spectrophotometer (Dynamica, Halo DB-20S) at 495 nm (λ_{max}). Percentage elimination of CR and adsorption capacity of UCSP and TCSP were determine by equation (1) and equation (2).

$$Elimination(\%) = \frac{C_i - C_f}{C_i} \times 100 \qquad (1)$$

$$adsorption\ capacity = Q_e = \frac{C_i - C_f}{M} \times V \qquad (2)$$

where ‘Q_e’ is the amount of CR adsorbed on adsorbent (mg/g) at equilibrium [27], ‘C_i’ and ‘C_f’ are the concentration of CR before and after adsorption (ppm), ‘M’ is the mass of adsorbent (mg) and ‘V’ is the volume of CR taken for adsorption (100 mL).

2.3. Adsorption kinetics study

2.3.1. Pseudo first order kinetic model

Pseudo first order model of kinetics was set forth in 1898 by Lagergren [28]. For several instances of total adsorption this model some time is not appropriate. It can be commonly used for the preliminary minute of adsorption procedure, in other words for the periods ahead to equilibrium [29]. Hence the adsorption rate can be expressed on the basis of equation (3);

$$\frac{dq}{dt} = k_1 (q_e - q) \qquad (3)$$

Integrating the above equation (3) by applying limits in which t = 0, q = 0 and q = q_t and it becomes equation (4) which is given bellow;

$$ln(q_e - q_t) = ln\, q_e - k_1 t \qquad (4)$$

Where ‘q_e’ is the amount of CR adsorbed on adsorbent at equilibrium (mg/g), ‘q_t’ is the amount of CR adsorbed at time t (mg/g). Compatibility of adsorption data was checked by the help of pseudo first order kinetic model by plotting a graph of ln (q_e - q_t) versus t, k_1 and ln q_e can be obtained from the slope and intercept of the graph.

2.3.2. Pseudo second order kinetic model

Adsorption kinetic data can also be analysed by the help of pseudo second order kinetic model. It is the most companionable with the mechanism of rate controlling step throughout the adsorption procedure as compared to pseudo first order kinetic model [30]. It can be expressed by the following equation (5);

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (5)$$

After rearrangement it become equation (6) which is given bellow;

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \qquad (6)$$

Where k_2 is a pseudo second order rate constant (g/mg min). Compatibility of adsorption data was analysed by plotting a graph t/q_t versus t, a straight line where k_2 and q_e can be obtained from the intercept and slope of the graph.

3. Results and Discussion

3.1. Effect of pH on CR dye elimination

Elimination of CR dye depends upon the pH of the solution. The pH effects the surface charge of adsorbents as well as the speciation of adsorbate. Effect of pH on % elimination of CR dye was studied by scanning the pH from 5 to 10 and adjusting the other parameters like initial concentration of CR dye 120 ppm, adsorbent dose 300 mg and agitation time 250 min. According to previous literature congo red dye is widely used as indicator in acid specific acid base reactions. During experimental work it was seen that congo red dye change its colour from red to blue when pH drawn to 5. Due to this reason effect of pH on CR dye elimination was studied staring from pH of 5 to pH of 10, where red colour of dye does persist.

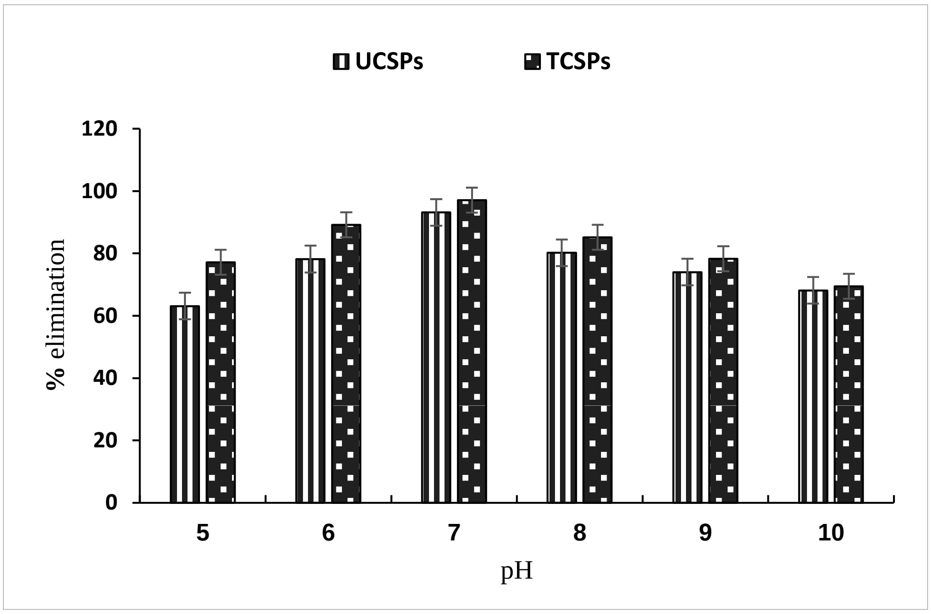

Figure 3: Effect of pH on % elimination of CR dye

It can be seen from the Figure 3, % elimination of CR dye increased from 63.13% to 93.17% for UCSP and also increased from 77.16% to 97.13% for TCSP when pH enlarged from 5 to 7 and % elimination of CR dye decreased from 93.17% to 68.16% in terms of UCSP and 97.13% to 69.44% in terms of TCSP when pH increased from 7 to 10. Figure 4 depicted that by increasing the pH from 5 to 7 the adsorption capacity (Q_e) of CR dye was increased for both UCSP and TCSP.

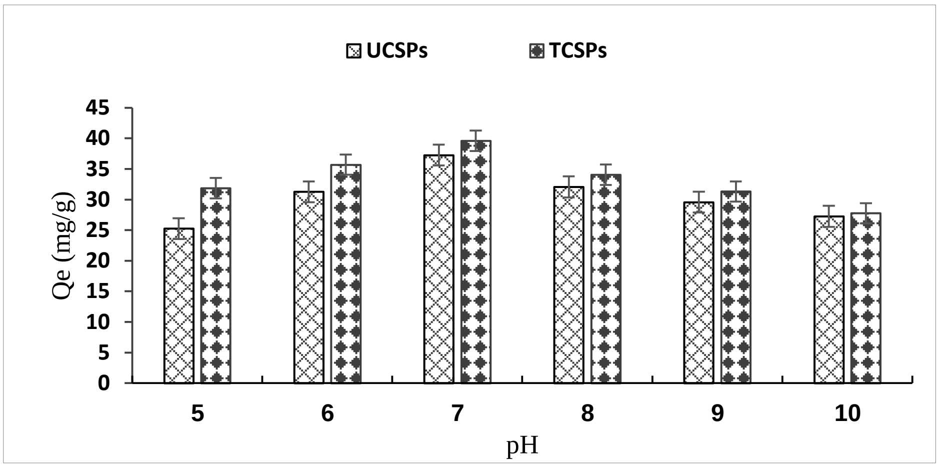

Figure 4: Effect of pH on adsorption capacity of CR dye

3.2. Effect of adsorbent dose on CR dye elimination

Adsorbent dose effect is fundamental approach to study the behaviour of adsorbent. Generally, literature depicted that use of low adsorbent dose results high adsorption efficiency is property of ideal adsorbent. Effect of adsorbent dose of UCSP and TCSP on percentage elimination of CR dye was investigated by skim through 100 mg to 600 mg of adsorbent dose of both the adsorbents by adjusting the pH of 7, initial concentration 120 ppm and agitation time of 250 minutes.

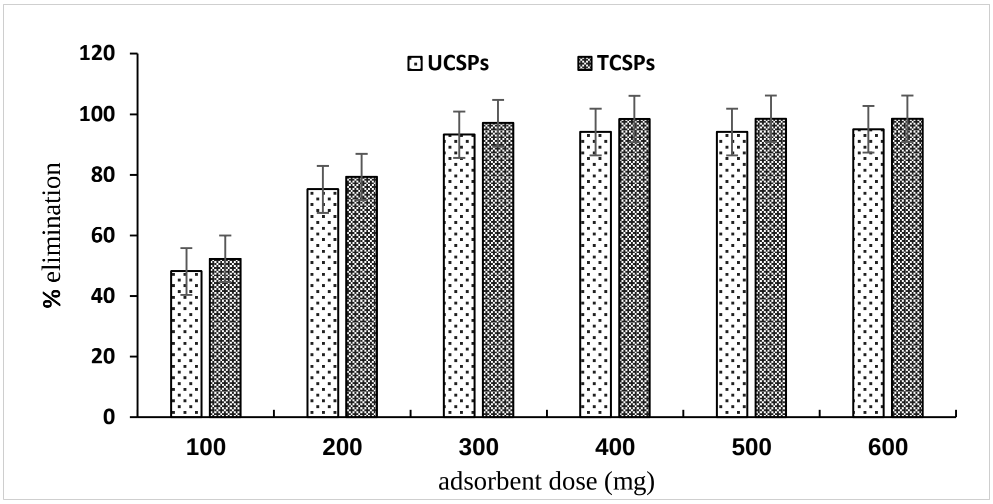

Figure 5: Effect of adsorbent dose on % elimination of CR dye

Figure 5 represented that % elimination of CR dye increased from 48.10% to 94.14% for UCSP and 52.29% to 98.39% for TCSP with increasing adsorbent dose from 100 mg to 500 mg. With more increase in adsorbent dose up to 600 mg, there is no change in % elimination of CR dye and hence equilibrium was established. From the Figure 6, the adsorption capacity (Q_e) decreased from 57.72 mg/g to 19.02 mg/g for UCSP and also decreased from 62.75 mg/g to 19.70 mg/g for TCSP by increasing adsorbent dose of both the adsorbents from 100 mg to 600 mg respectively.

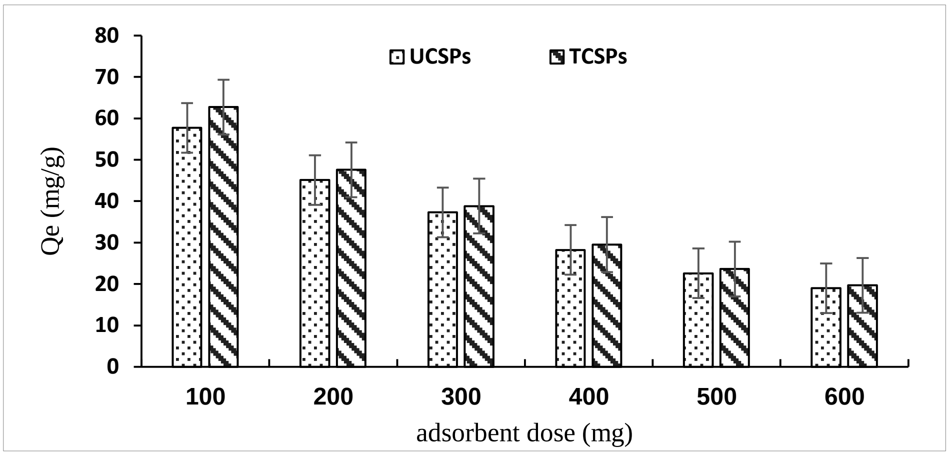

Figure 6: Effect of adsorbent dose on adsorption capacity of CR dye

3.3. Effect of initial concentration on CR dye elimination

Theory explains that the increase in initial concentration of adsorbate the extent of adsorption increases. This effect was investigated by increasing the initial concentration of CR dye from 30 ppm to 180 ppm and adjusting the agitation time of 250 min, adsorbent dose of 300 mg and pH of 7. Figure 7 showed that by increasing the concentration of CR dye from 30 ppm to 150 ppm, the % elimination increased from 31.31% to 95.31% for UCSP and 39.30% to 98.44% for TCSP and after increasing from 150 ppm to 180 ppm of CR dye concentration, there was not any increase in % elimination of CR dye was seen. *Bhaumik* and his colleagues [29], *Zulfikar* and *Setyanto* [30] and *Lieu* and his colleagues [17] have concluded that % elimination of CR dye increased by increasing initial concentration of CR dye with adsorption by reference adsorbents.

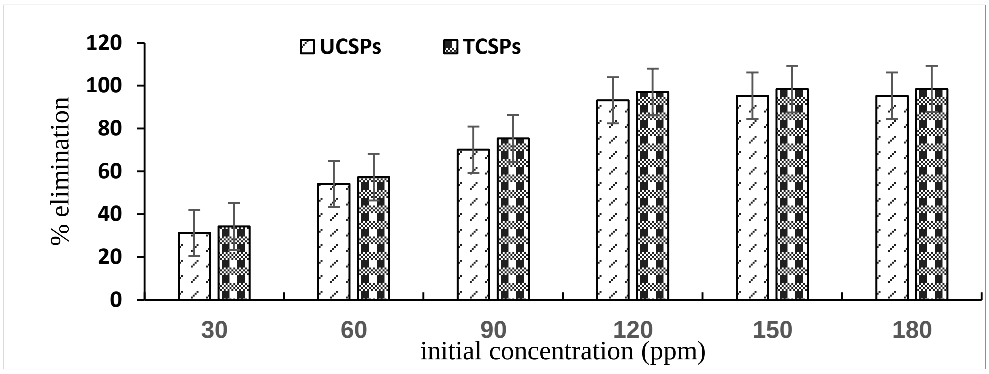

Figure 7: Effect of initial concentration of CR dye on % elimination

Figure 8 indicated that adsorption capacity (Q_e) increased from 3.13 mg/g to 57.19 mg/g for UCSP and 3.43 mg/g to 59.08 mg/g for TCSP when initial concentration of CR dye increased from 30 ppm to 180 ppm.

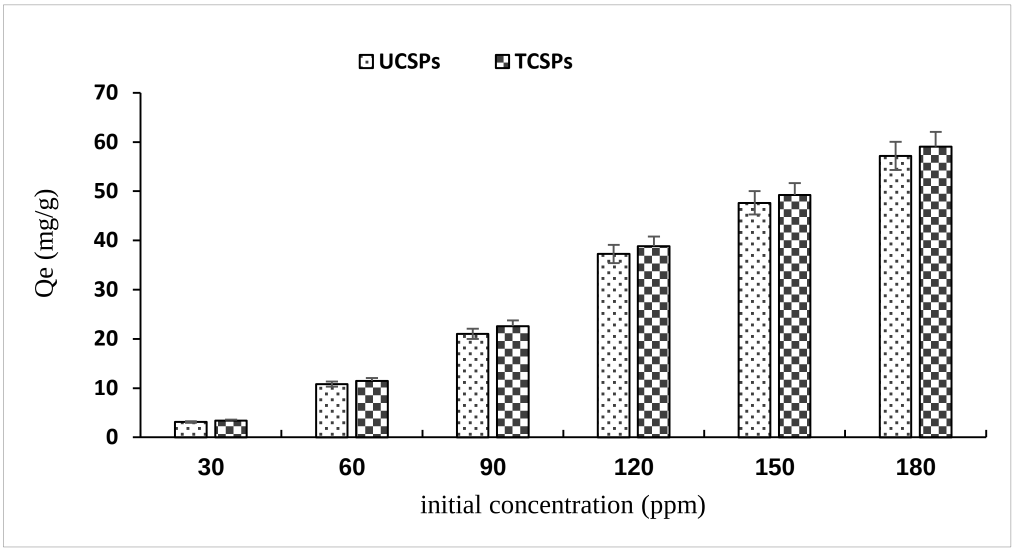

Figure 8: Effect of initial concentration of CR dye on adsorption capacity

3.4. Effect of agitation time on CR dye elimination and adsorption kinetics study

Effect of agitation time was studied staring experiment time from 50 min and increasing 50 min with each experiment up to 300 min of both the adsorbents. These experiments were performed by regulating the pH of 7, initial concentration 120 ppm and 300 mg of adsorbent dose of both the adsorbents. Figure 9 depicted that % elimination of CR dye increased from 58.39% to 93.19% for UCSP and also increased from 60.14% to 97.31% for TCSP by increasing the agitation time from 50 to 250 minutes respectively and with further increase in agitation time from 250 min to 300 min for both the adsorbents, the % elimination remains almost same and equilibrium was established.

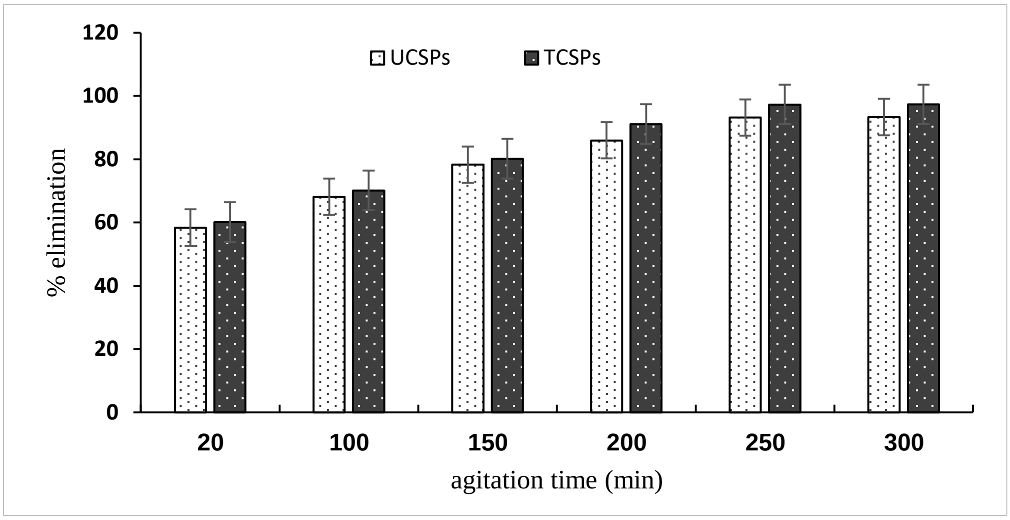

Figure 9: Effect of agitation time on % elimination of CR dye

Figure 10 explains that the adsorption capacity (Q_e) increased from 23.35 mg/g to 37.28 mg/g for UCSP and also increased from 28.05 mg/g 38.92 mg/g for TCSP by increasing the contact time from 50 min to 250 min.

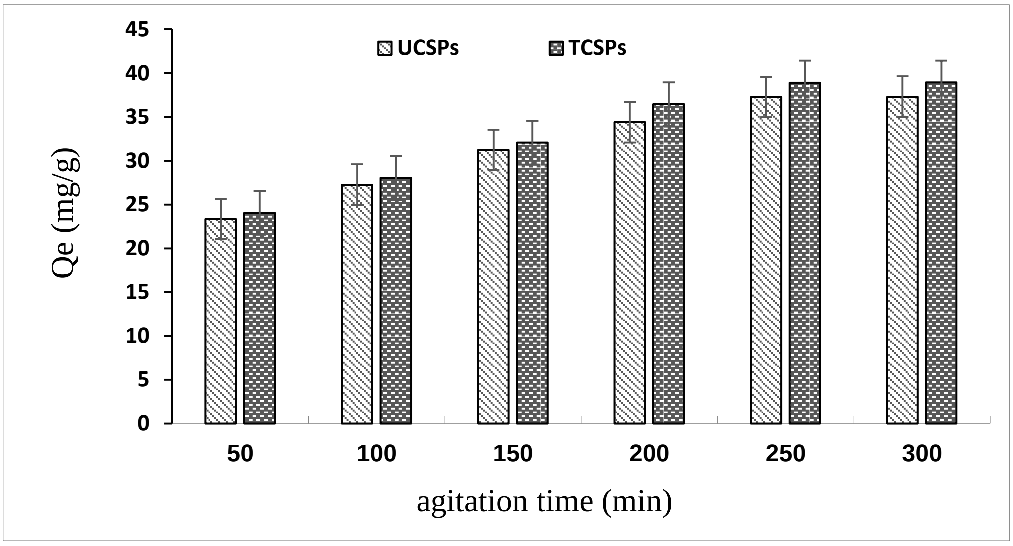

Figure 10: Effect of agitation time on adsorption capacity of CR dye

Two different models were used to investigate the adsorption kinetics of CR dye elimination by using UCSP and TCSP which are pseudo first order and pseudo second order. The graph between ln (q_e – q_t) and t for pseudo first order (Figure 11) and between t/q_t and t for pseudo second order (Figure 12) were plotted with data obtained from experiments and their constants were calculated for each plot which are given in Table 1.

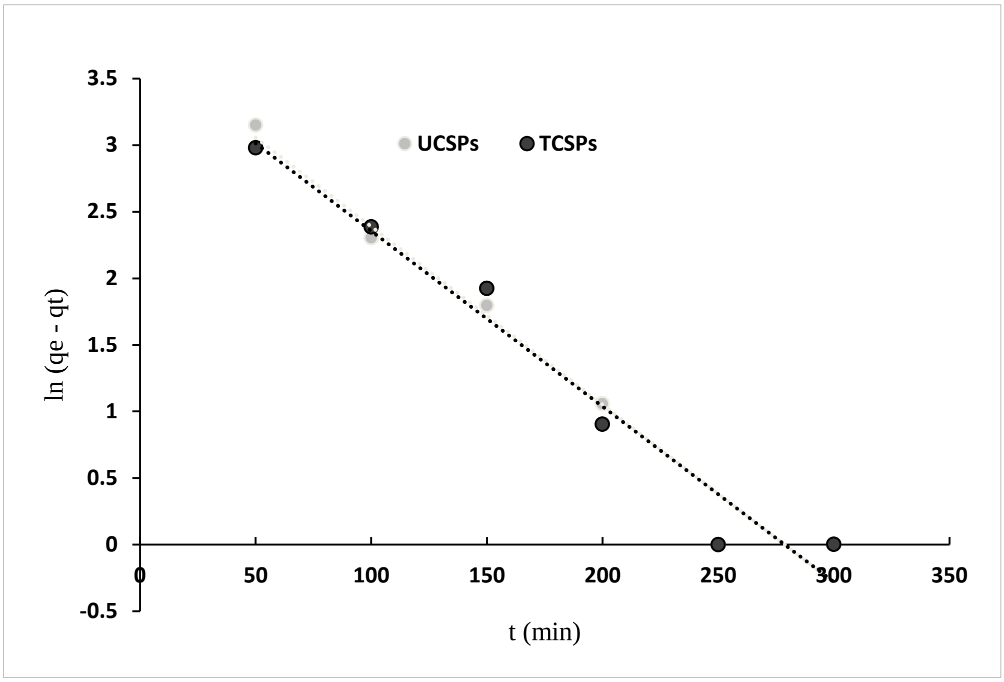

Figure 11: Pseudo first order kinetic model

Table 1: Adsorption kinetics study data for elimination of CR dye

Adsorbent	Pseudo first order kinetics			Pseudo second order kinetics		
	q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	k_2 ($gmg^{-1}min^{-1}$)	R^2
UCSP	3.672	-0.015	0.9681	44.25	1.233	0.9935
TCSP	3.725	-0.013	0.9683	46.73	1.238	0.9916

Table 1 represented that pseudo second order kinetic model with correlation coefficients (R^2) 0.9935 for UCSP and 0.9916 for TCSP, be a symbol of good time dependent function of equilibrium as compared to pseudo first order kinetic model correlation coefficients (R^2) 0.9681 for UCSP and 0.9623 for TCSP. Hence, adsorption kinetics study with the help of *Cucumis sativus* peels strongly followed by pseudo second order kinetic model. This behaviour of *Cucumis sativus* peels was also reported by recently performed experimental work which corresponds to adsorption of phenolic compounds [31]. Further, more it is indicated that the value q_e (calculated) obtained from pseudo second order kinetic model show good compatibility with the experimental value (Q_e).

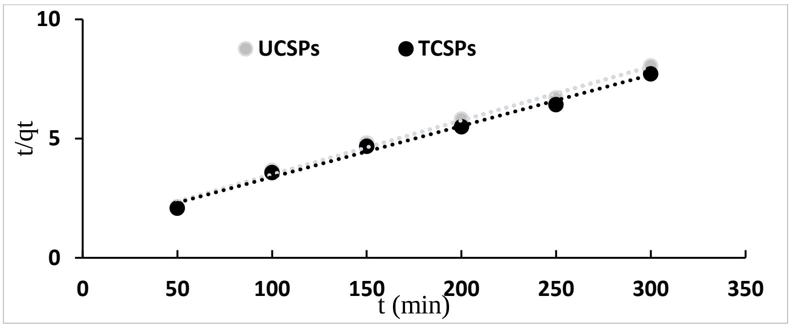

Figure 12: Pseudo second order kinetic model

4. Conclusions

Present paper describes the compatibility of *Cucumis sativus* peels with congo red dye in terms of adsorption. Results show that the agriculture waste materials such as *Cucumis sativus* peels has a high potential to eliminate congo red dye concentration from aqueous medium and can be used to decrease water pollution in terms of wastewater treatment by adsorption. *Cucumis sativus* peels acts as a low cost, safe, environmental friendly and more efficient adsorbent for elimination of congo red dye. It is also concluded that treated *Cucumis sativus* peels (TCSP) was found to be more efficient as compared to untreated *Cucumis sativus* peels (UCSP) for elimination of congo red dye from aqueous solutions. Kinetics study revealed that elimination of congo red dye by adsorption process was best followed by pseudo second order kinetic model as compared to pseudo first order kinetic model. Previous investigations explain that adsorption rate can be increased by increasing the temperature of the solution, in this regards present investigation incapable to study temperature effect on adsorption rate, which acts as a limitation of this study. This study also fails to evaluate thermodynamic behaviour, point zero charge, surface analysis, and elemental analysis of *Cucumis sativus* peels.

5. Recommendations

Present piece of work strongly recommends environmental scientists and chemists to search out further dynamic behaviours of *Cucumis sativus* peels and other low cost adsorbents which have capability to treat wastewater with different modes of their applications. *Cucumis sativus* peels was found to be efficient adsorbent for elimination of congo red dye but further research work is needed to enhance its competency against treatment of dye containing wastewater.

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