

Equilibrium and Kinetics Study for Adsorption of 2,4-Dinitrophenol from Aqueous Solutions by Using *Cucumis Sativus* Peels and Kidney Bean Shells as New Low-cost Adsorbents

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Abstract Main goal of this study was to investigate the adsorptive potential of 2,4-Dinitrophenol (2,4-DNP) from aqueous solutions onto *Cucumis Sativus* peels (CSPs) and kidney bean shells (KBS). These adsorbents were used first time to adsorb 2,4-DNP from aqueous solutions. Both the adsorbents were pretreated with 37% HCl to enhance the 2,4-DNP uptake ability. Adsorption parameters such as influence of pH, adsorbent dose, contact time and initial concentration of 2,4-DNP were determined. Maximum % adsorption of 2,4-DNP take place, at pH of 4.0, initial concentration of 40 mg/L, contact time of 120 min and adsorbent dose of 100 mg which was 93.13% for *Cucumis sativus* peels and 99.02% for kidney bean shells. Kidney bean shells was found to be more efficient in adsorption of 2,4-DNP from aqueous solutions as compared to *Cucumis sativus* peels. Kinetic study indicated that the adsorption of 2,4-DNP was best followed by pseudo second order kinetic model. Results show that the rate of adsorption was better controlled by intra-particle diffusion as well as film diffusion. It was accomplished that the adsorption of 2,4-DNP onto *Cucumis sativus* peels and kidney bean shells was best defined by Langmuir adsorption model and maximum adsorption capacities of both the adsorbents were obtained by Langmuir equation which were 47.61 mg/g for *Cucumis sativus* peels and 52.63 mg/g for kidney bean shells. It is concluded that agricultural waste such as *Cucumis sativus* peels and kidney bean shells can be used as low-cost adsorbents for adsorption of 2,4-DNP from aqueous solution at large scale in replacement of high cost adsorbents.

Keywords: equilibrium, kinetics, 2,4-DNP, adsorption, *cucumis sativus* peels, kidney bean shells

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1. Introduction

Water is fundamental for life and health. It limited natural resource. The availability of pure water is being reduced with the growth of mankind, society, science and technology. Due to rapid growth of world population environmental disorder especially water pollution translated to a critical aspect.

Dyes, heavy metals and phenols generally nitro-phenols belong to the most dangerous class of pollutants found in wastewater [1]. These water pollutants enter to life cycle through water body and disturb the life even at low concentration. United State Environmental Protection Agency (USEPA) specified the list of water contaminants on the basis of their behavior to the environment in which phenols are on 11th position out of 126 compounds [2]. Phenolic compounds degrade the quality of water and serve as persistent in different forms.

Nitro phenols have been indicated ≥ 14 of dangerous wastewater contaminants out of 1177 hazardous compounds in National Priorities List (NPL) [2]. Nitro phenols are those pollutants which play the main role to reduce the dissolved oxygen in wastewater and also cause adverse effects in living organisms [3]. They are delivered into environment through water body and cannot be degraded biologically [4]. Wastewater discharged by various industries like steel, coal, plastic, shaving cream, soap, electroplating, oil, color and pharmaceutical contain high concentration of phenolic compound [5]. The maximum permissible concentration of nitro phenol in wastewater is < 1 mg/L which was set by United State Environmental Protection Agency (USEPA) [6,7].

2,4-Dinitrophenol (2,4-DNP) is considered to be the most toxic environmental pollutant among phenolic family. It is a component of wood stabilizers and also used for the preparation of different types of dyes [8]. 2,4-DNP may also use as an indicator in various chemical laboratories for determination of particular ions. It is

applied for manufacturing of herb killer materials and also used as intermediate in explosive items [9]. It is also used to prevent polymerization of many organic compounds which is used in various industries [10]. Literature indicated that 2,4-DNP was also found in wastewater which is discharged by paper industry [11].

The Environmental Protection Agency has designated 2,4-dinitrophenol as being 121st out of 275 most poisonous substances [12,13]. 2,4-dinitrophenol is a nitro-aromatic compound which is dangerous for living beings [14,15]. 2,4-DNP has excessive impact on human health and causes nausea, sweating, vomiting, headaches, dizziness and weight loss [16]. Additionally, skin lesions and cataracts are formed by exposure to 2,4-dinitrophenol [17]. 2,4-DNP toxin also affects the bone marrow, cardiovascular system and Central Nervous system [18].

Due to various destructive effects of 2,4-DNP its removal becomes necessary. The Clean Water Act designates 2,4-dinitrophenol as a chief contaminant [19], which emphasizes on the need to adopt efficient and cost-effective methods for 2,4-dinitrophenol removal from wastewater.

Various methods are being useful for the removal of nitro-phenols from aqueous medium like chemical oxidation [20,21], precipitation [22], solvent extraction [23], photo-catalytic degradation [12], microbial degradation, reverse osmosis, membrane separation [18] and adsorption [24,25].

Adsorption acts as an efficient phenomenon at low concentration of target pollutant in wastewater due to its proficiency [26,27]. Numerous adsorbents like lakhra coal [28], zeolite [29], waste tires [30], sludge [31], activated carbons [32], molecular imprinted polymers [33] and surface modified smectite clays [34] are being used for adsorption.

Regularly activated carbon is not profitable and it also causes secondary pollution [35]. Due to high cost of activated carbons, chemists are continuously searching the ways to make lucrative adsorbents for adsorption process [36]. Recently, some profitable adsorbents have been studied as adsorbents for adsorption of nitro-phenolic compounds which include agricultural waste biomass. Agricultural waste biomass is mainly studied because it is not costly and is available in abundance [37].

Cucumis sativus peels (CSPs) and kidney bean shells (KBS) constitute the list of cost-effective adsorbents and are excellent for the process of adsorption because they are among the very few agricultural wastes which are cheap and abundantly available. The main aim of this work is to explore the feasibility and potentiality of utilizing *Cucumis sativus* peels (CSPs) and kidney bean shells (KBS) as innovative and money-making adsorbents for the adsorption of 2,4-dinitrophenol from water. *Cucumis sativus* is a local fruit which is abundantly available in Pakistan. The peels of *Cucumis sativus* and shells of kidney bean are removed before consumption and usually discarded as waste [38]. This waste has become one of the main sources of municipal solid waste, which has increasingly been tough environmental issue. So, it is very essential to manage such waste properly. Peel of *Cucumis sativus* fruit was previously investigated to adsorb cationic dyes [38,39].

Cucumis sativus peels (CSPs) and kidney bean shells (KBS) were used first time to remove 2,4-dinitrophenol from aqueous solution. The comparative adsorption study of both the adsorbents was done to evaluate the effects of certain parameters like initial concentration of 2,4-dinitrophenol, pH, adsorbent dose and contact time.

2. Materials and Methods

The following materials were used in this study: *Cucumis sativus* peels (CSPs); Kidney bean shells (KBS); 2,4-dinitrophenol (2,4-DNP) (Analytical standard, Sigma Aldrich, USA); Sodium hydroxide (NaOH) (Merck, Germany); Hydrochloric acid (HCl) (Analytical grade, Pakistan) and Deionized water (Ultra- Pure, Gujranwala Pakistan).

2.1. Analytical Instruments

A pH meter (pH-107), ARE Magnetic Stirrer (VELP Scientifica), Centrifuge (SIMPLEX 54701), UV-Visible Double Beam Spectrophotometer (Dynamica DB-20S), Electrical oven (Schwabach FRG,) and Electronic balance (Sartorius).

2.2. Preparation of Adsorbents

Cucumbers and kidney beans were obtained from market in Kacha Fattomand Gujranwala, Punjab, Pakistan. These were separated into peels (CSPs) and shells (KBS). CSPs and KBS were thoroughly washed with tap water to remove all the dirt and then with deionized water to remove all the adhered material and were dried in an oven at 80°C for 4 hours. The dried samples were then pretreated with chemical solvent to enhance the 2,4-dinitrophenol uptake ability. For this purpose, 25 g of CSPs and KBS were boiled in 500 ml of 37% HCl separately. The acid slurries were filtered and then washed with deionized water until the pH of residual solution become neutral. After washing, these samples were placed in oven at 70°C for 24 hours. Finally, the dried residues were grounded into powder form and sieved into -100/+120 mesh size. These powders were labeled and stored in air tight glass bottles.

2.3. Preparation of Adsorbate Solution

Stock solution of 500 mg/L was prepared by dissolving appropriate amount of adsorbate (2,4-DNP) in 1000 mL pyrex flask and filled up to mark with distilled water. Desired concentrations (10 - 60 mg/L) of adsorbate were prepared by dilution method.

2.4. Experimental Procedure

Adsorption experiments were conducted in batch mode to recognize the effects of various factors as well as contact time (30-180 min), initial 2,4-DNP concentration (10-60 mg/L), pH (2 - 7) and adsorbent dose (20 - 120 mg) on adsorption of 2,4-DNP by using CSPs and KBS. All the experiments were conducted in the laboratory

temperature ($25\pm 2^\circ\text{C}$) were then stacked at 400 rpm (Revolutions per minute) of 100 mL 2,4-DNP solution in 250 mL Erlenmeyer flask. After induction the samples were centrifuged and analysed in UV-visible spectrophotometer at 354.5 nm (λ_{max}). Percentage adsorption of 2,4-DNP and sorption capacity of both the adsorbents were determined by equation (1) and (2):

$$\% \text{ Adsorption} = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

$$q_e = \frac{C_o - C_e}{m} \times V \quad (2)$$

Where C_o is the concentration of 2,4-DNP before adsorption (mg/L), C_e is the concentration of 2,4-DNP in solution after adsorption at equilibrium (mg/L), V is the volume of 2,4-DNP solution taken for adsorption (100 mL), m is the mass of adsorbents used for adsorption (mg) and q_e is amount of 2,4-DNP adsorbed on adsorbents at equilibrium (mg/g).

2.5. Adsorption Kinetics Study

2.5.1. Pseudo First Order Kinetic Model

Pseudo first order model of kinetic was set forth in 1898 by Lagergren [40]. For several instances of total adsorption period this model is not appropriate. It can be commonly used for the preliminary minute of adsorption procedure, in other words for the periods ahead to reaching equilibrium [41]. Hence the adsorption rate can be expressed on the basis of equation (3);

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

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

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

Where q_e is the amount of 2,4-DNP adsorbed on adsorbent at equilibrium (mg/g), q_t is the amount of 2,4-DNP adsorbed at time t (mg/g) and k_1 is the rate constant of adsorption (min^{-1}). Compatibility of adsorption data with pseudo first order kinetic model can be checked by a plot of $\ln(q_e - q_t)$ versus t is a line, k_1 and $\ln q_e$ can be obtained from the slope and intercept of the graph.

2.5.2. Pseudo Second Order Kinetic Model

Another model used for analyzes of adsorption kinetic data is the pseudo second order kinetic model. It is most companionable with the mechanism of rate controlling step throughout the adsorption procedure as compared to the pseudo first order kinetic model. It is given by the following equation (5) [42]:

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

After rearrangement it becomes (6):

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

Where k_2 is a pseudo second order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$). Compatibility of adsorption data with pseudo second order kinetic model can be checked by a plot of t/q_t versus t is a line, k_2 and q_e can be obtained from the intercept and slope of the graph.

2.5.3. Intra-particle Diffusion Model

Intra-particle diffusion model was applied for the monitoring of adsorption progress and for the determination of rate controlling step. It is given by the following equation (7) [43]:

$$q_t = k_{id} \sqrt{t} + C \quad (7)$$

Where k_{id} is a rate constant of intra-particle diffusion model ($\text{mg g}^{-1} \text{min}^{-1/2}$) and C is a boundary layer thickness constant (mg/g). k_{id} and C can be obtained by plotting a graph between q_t and \sqrt{t} as slope and intercept.

Multilinear correlation can be observed in q_t versus \sqrt{t} plot. Film diffusion can be seen from first part of a line where film diffusion act as rate controller. The most advance part of the line is a second section where intra-particle diffusion acts as rate controlling grade. The equilibrium section of a line is a third part of the line where intra-particle diffusion starts to slow down because remaining concentration of 2,4-DNP in the solutions become low [44]. If the linear section in the second part of the line, that is the intercept of the line (C) representing intra-particle diffusion goes through the origin, then it is concluded that only intra-particle diffusion acts as rate controlling step, if not, it can be stated that adsorption rate can be controlled by more than one mechanisms [45].

2.6. Adsorption Isotherms Study

2.6.1. Langmuir Adsorption Isotherm

Theory explains the phenomenon of adsorption in such a way that if any atoms, ions or molecules came to contact with active regions of a crystalline surface are deemed to be adsorbed on these regions. One site of the surface can contain only one atom, ion or molecule and hence it forms monolayer of adsorbed atom, ion or molecule which is also called homogeneous layer [46]. The following equation (8) expressed the nonlinear Langmuir isotherm:

$$q_e = \frac{b C_e}{1 + b C_e} \quad (8)$$

After rearrangement it converted into linear form and becomes equation (9) which is given bellow:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\text{max}}} + \frac{1}{b q_{\text{max}}} \quad (9)$$

Where q_e is the amount of 2,4-DNP adsorbed at equilibrium (mg/g), q_{max} is the maximum monolayer adsorption capacity (mg/g) C_e is the amount of 2,4-DNP retained in a solution after adsorption at equilibrium and b is a constant related to adsorption enthalpy (L/mg). Compatibility of adsorption data with Langmuir adsorption isotherm was determined by a plotting a graph between C_e/q_e and C_e . q_{max} and b were determined by the slope and intercept of this graph.

The most important parameter of Langmuir isotherm is R_L which is non-dimensional constant and commonly known as separation factor or equilibrium parameter. It is represented by following equation (10) [47]:

$$R_L = \frac{1}{1 + bC_0} \quad (10)$$

Where C_0 is concentration of 2,4-DNP in solution before adsorption (mg/L) and b is the Langmuir constant (L/mg). R_L parameter explains the signal of adsorption compatibility for selected adsorbents- adsorbate pair. The following possibilities for R_L has been observed [47]:

If $0 < R_L < 1$ then adsorption is favorable. If $R_L > 1$ then adsorption is unfavorable. If $R_L = 1$ then it shows linearity of adsorption. If $R_L = 0$ then adsorption is irreversible.

2.6.2. Freundlich Adsorption Isotherm

According to Freundlich adsorption takes place on surfaces with different energy of adsorption and different character. He also claimed that the amount of adsorbate adsorbed on the surface of adsorbent increases with increasing concentration or pressure. Freundlich adsorption isotherm model is represented by following equation (11) [48]:

$$q_e = K_f C_e^{1/2} \quad (11)$$

After rearrangement equation (11) converted into linear form and becomes equation (12) which is given below:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (12)$$

Where q_e is amount of 2,4-DNP adsorbed on adsorbent at equilibrium (mg/g), K_f is the adsorption constant (mg/g) and n is an empirical parameter associated with adsorption intensity. The value of K_f and $1/n$ was determined by plotting a graph between $\ln q_e$ and $\ln C_e$ as intercept and slope.

3. Results and Discussion

3.1. Influences of pH on 2,4-DNP Adsorption

Adsorption of 2,4-dinitrophenol depends on the pH of the solution. The pH impacts the surface charge of adsorbent as well as the speciation of adsorbate [3]. 2,4-dinitrophenol is acidic with $pK_a = 4.09$ and at $pH > 4.09$, 2,4-DNP is found mostly in anionic form [49].

To study the effects of pH on adsorption of 2,4-DNP for both the adsorbents, pH was scanned from 2 to 7 by adjusting the other parameter like adsorbent dose 80 mg, initial concentration of 2,4-DNP 40 mg/L and samples were stirred at constant speed for 120 minutes. It is clear from the Figure 1 that % adsorption decreased from 92.72% to 45.19% for CSPs and also decreased from 98.42% to 60.13 for KBS when the pH was increased from 4 to 7.

With an increase in pH, a decrease in percentage adsorption of 2,4-dinitrophenol has also been observed [50]. It can be seen from the Figure 1 that the percentage adsorption of 2,4-DNP is maximum at $pH = 4$. This is due to the acidic nature of 2,4-DNP. Similar results had also been given by [50] and [11].

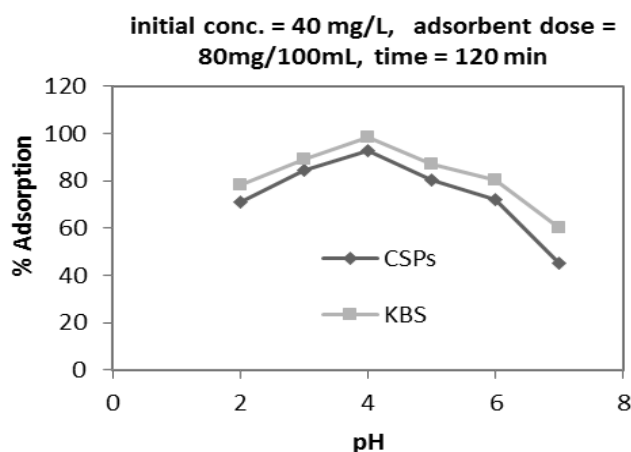


Figure 1. Effect of pH on % adsorption of 2,4-DNP

Correspondingly, it can be seen from the Figure 2 that by increasing the pH from 4 to 7 the sorption capacity (q_e) decreased from 46.36 mg/g to 22.59 mg/g for CSPs and also decreased from 49.21 mg/g to 30.06 mg/g for KBS.

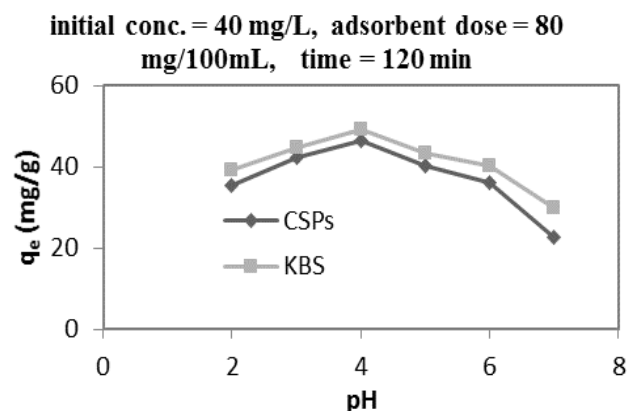


Figure 2. Effect of pH on adsorption capacity q_e

3.2. Influences of adsorbent dose on 2,4-DNP adsorption

The effect of adsorbent dose of CSPs and KBs were studied starting from 20 mg and increasing 20 mg with each experiment up-to 120 mg of both the adsorbents. These experiments were performed by adjusting the pH of 4, initial concentration of 2,4-DNP 40 mg/L at constant agitation speed for 120 minutes.

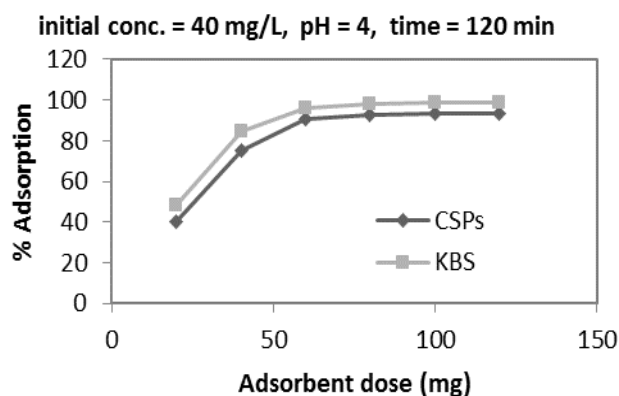


Figure 3. Effect of adsorbent dose on % adsorption of 2,4-DNP.

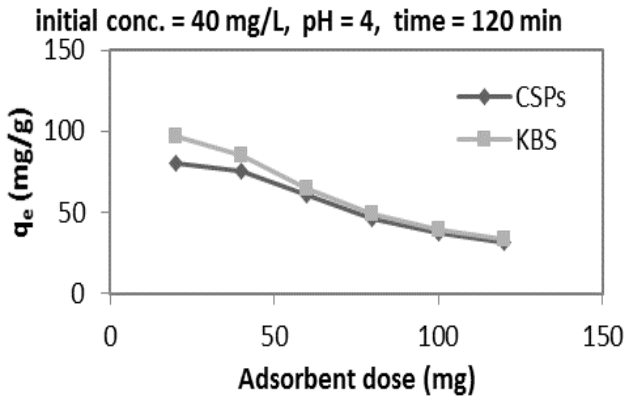


Figure 4. Effect of adsorbent dose on sorption capacity q_e .

From the Figure 3, it is shown that percentage adsorption increased from 40.12% to 93.13% for CSPs and 48.23% to 99.02% for KBS with increasing adsorbent dose from 20 mg to 100 mg respectively. With further

increase in adsorbent dose from 100 mg to 120 mg, there is no change in percentage adsorption of 2,4-DNP and equilibrium is established.

The Figure 4 showed that the sorption (q_e) capacity decreased from 80.25 mg/g to 31.05 mg/g for CSPs and also decreased from 96.45 mg/g to 33.01 mg/g for KBS by increasing adsorbent dosage of both the adsorbents from 20 mg to 120 mg respectively.

3.3. Influences of Contact Time and Adsorption Kinetics of 2,4-DNP

The effect of contact time on 2,4-DNP adsorption of CSPs and KBS were studied starting experiment time from 30 min and increasing 30 min with each experiment up to 180 min of both the adsorbents. These experiments were performed by adjusting the pH of 4, initial concentration of 2,4-DNP 40 mg/L and adsorbent dose for both the adsorbents of 80 mg at constant agitation speed.

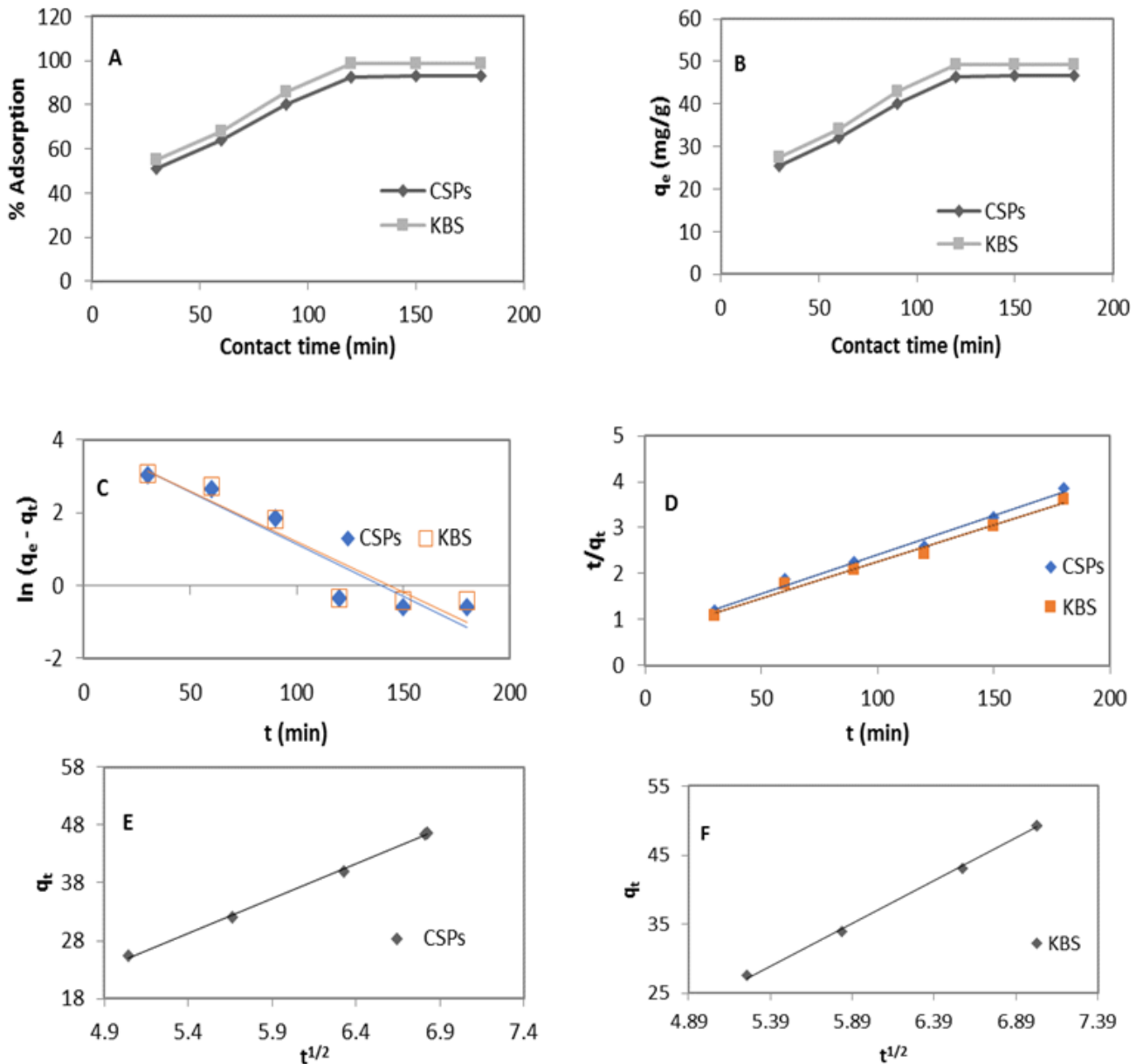


Figure 5. Effect of contact time and adsorption kinetics of 2,4-DNP, A: effect of contact time on % adsorption, B: effect of contact time on sorption capacity q_e (mg/g), C: pseudo first order kinetic model of 2,4-DNP adsorption, D: pseudo second order kinetic model, E: intra-particle diffusion model of 2,4-DNP adsorption by CSPs, F: intra-particle diffusion model of 2,4-DNP adsorption by KBS

Table 1. Kinetics models constants for 2,4-DNP adsorption

Adsorbent	q_e (exp) mg/g	Pseudo first order kinetics			Pseudo second order kinetics			Intra-particle diffusion model		
		q_e (cal) mg/g	k_1 min ⁻¹	R^2	q_e (cal) mg/g	k_2 g mg ⁻¹ min ⁻¹	R^2	C mg/g	k_{id}	
									g mg ⁻¹ min ^{-1/2}	R^2
CSPs	46.36	3.937	-2.7×10^{-3}	0.8712	46.22	4.05×10^{-4}	0.9872	35.42	11.99	0.9988
KBS	49.21	4.01	-2.8×10^{-3}	0.8914	49.11	3.91×10^{-4}	0.9873	37.85	12.39	0.9989

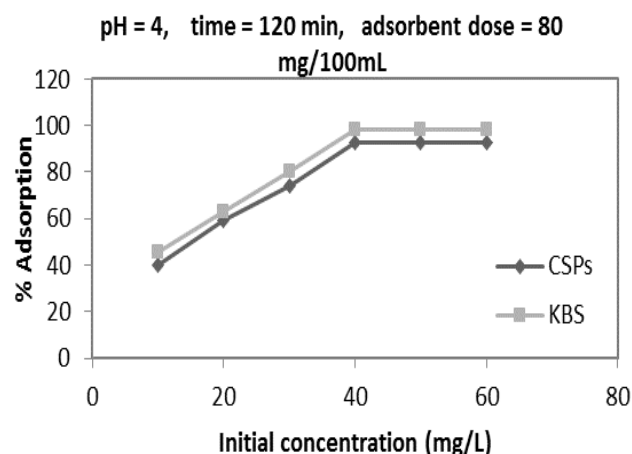
The Figure 5A indicated that percentage adsorption increased from 50.91% to 92.72% for CSPs and also increased from 55.10% to 98.42% for KBS by increasing the contact time from 30 minutes to 120 minutes respectively and with further increase of contact time from 120 minutes to 150 minutes for both the adsorbents, the percentage adsorption remains almost same and equilibrium was established. From the Figure 5B it can be seen that the sorption capacity increased from 25.45 mg/g to 46.36 mg/g for CSPs and also increased from 27.55 mg/g to 49.21 mg/g for KBS by increasing the contact time from 30 minutes to 120 minutes respectively and with further increase of contact time from 120 minutes to 150 minutes for both the adsorbents, the sorption capacity remains almost same and equilibrium was established.

Three different models were used to investigate the adsorption kinetics of 2,4-DNP onto CSPs and KBS: pseudo first order, pseudo second order and intra-particle diffusion. The graph, between $\ln(q_e - q_t)$ and t for pseudo first order (figure 5C), between t/q_t and t for pseudo second order (figure 5D) and q_t versus \sqrt{t} for intra-particle (Figure 5E and 5F) were plotted, with data obtained from experiments and different constants were calculated from each plot which are given in Table 1, for the kinetics study of 2,4-DNP adsorption. It can be seen from Table 1 that pseudo second order kinetic model with correlation coefficients (R^2) 0.9872 and 0.9873 be a symbol of good time dependent function of equilibrium as compared to pseudo first order kinetic model with correlation coefficients (R^2) 0.8712 and 0.8914 for CSPs and KBS. Furthermore, it is indicated that the value of q_e (cal) obtained from pseudo second order kinetic model show good compatibility with the experimental value of q_e (exp). Intra-particle diffusion model was applied for satisfaction of adsorption mechanism and determination of rate controlling step.

Figure 5E and 5F for intra-particle diffusion model indicated that adsorption was carried out in two steps with both the adsorbents, in first step adsorption was take place in first minutes which was very fast in the film layer on adsorbents and is termed as film diffusion. In second step intra-particle diffusion of 2,4-DNP molecules in the direction of both the adsorbents starts, which shows the movement of 2,4-DNP molecules on the way to the site where actual adsorption occurred. Furthermore, constants obtained from intra-particle diffusion model C from the Table 1 which were not approach to zero for both the adsorbents, it come into view that intra-particle diffusion model is not only sufficient to control the adsorption rate [51]. Hence, adsorption rate can be controlled by film diffusion model along with intra-particle diffusion model. Therefore, it is indicated that the most adsorption take place in the film layer of both the adsorbents in first 60 minutes.

3.4. Influences of Initial Concentrations and Adsorption Isotherms of 2,4-DNP

To study the effect of initial concentration, 10 mg/L to 60 mg/L solutions were prepared and the contact time was set to 120 minutes, adsorbent dosage taken was 80 mg/100 mL and pH of the solution for both adsorbents was set at 4. It is indicated from the Figure 6 that by increasing the concentration of 2,4-DNP from 10 mg/L to 40 mg/L, the % adsorption increased from 40.19% to 92.82% for CSPs and 45.33% to 98.92% for KBS.

**Figure 6.** Effect of initial concentration on % adsorption of 2,4-DNP

It can be seen from the Figure 7a that by increasing the concentration of 2,4-DNP the sorption capacity (q_e) of both the adsorbents also increases. Hence, sorption capacity of both the adsorbents is determined by further increasing in initial concentration of 2,4-DNP [52].

In present study Freundlich and Langmuir adsorption isotherms were used to describe the equilibrium established between both the adsorbents and concentrations of 2,4-DNP. Linear Langmuir and Freundlich graphs of both the adsorbents are shown in Figure 7b, c, e and f. High values of correlation coefficients (R^2) of the graphs show good linearity and it is indicated that adsorption of 2,4-DNP onto CSPs and KBS follow both the Langmuir and Freundlich isotherms but it can be seen that adsorption of 2,4-DNP onto both the adsorbent was best defined by Langmuir adsorption model. The values of Langmuir parameter (R_L) from Figure 7d indicated, which were less than one and greater than zero, that adsorption is favorable.

Maximum adsorption capacity of CSPs and KBS for 2,4-DNP adsorption was determined by Langmuir adsorption which were 47.61 mg/g and 52.63 mg/g at 80cmg of adsorbent dose. Maximum adsorption capacity of KBS and CSPs is much higher than other studies of low cost adsorbents in literature, like 23.331 mg/g of bagasse

fly ash [52], 49.87 mg/g of coconut shells AC [53], 46.076 mg/g of date pits [54], 13.45 mg/g of Tectona grandis

sawdust [55], 74.12 mg/g of Commercial granular AC [56] and 40.121 mg/g of clay [57].

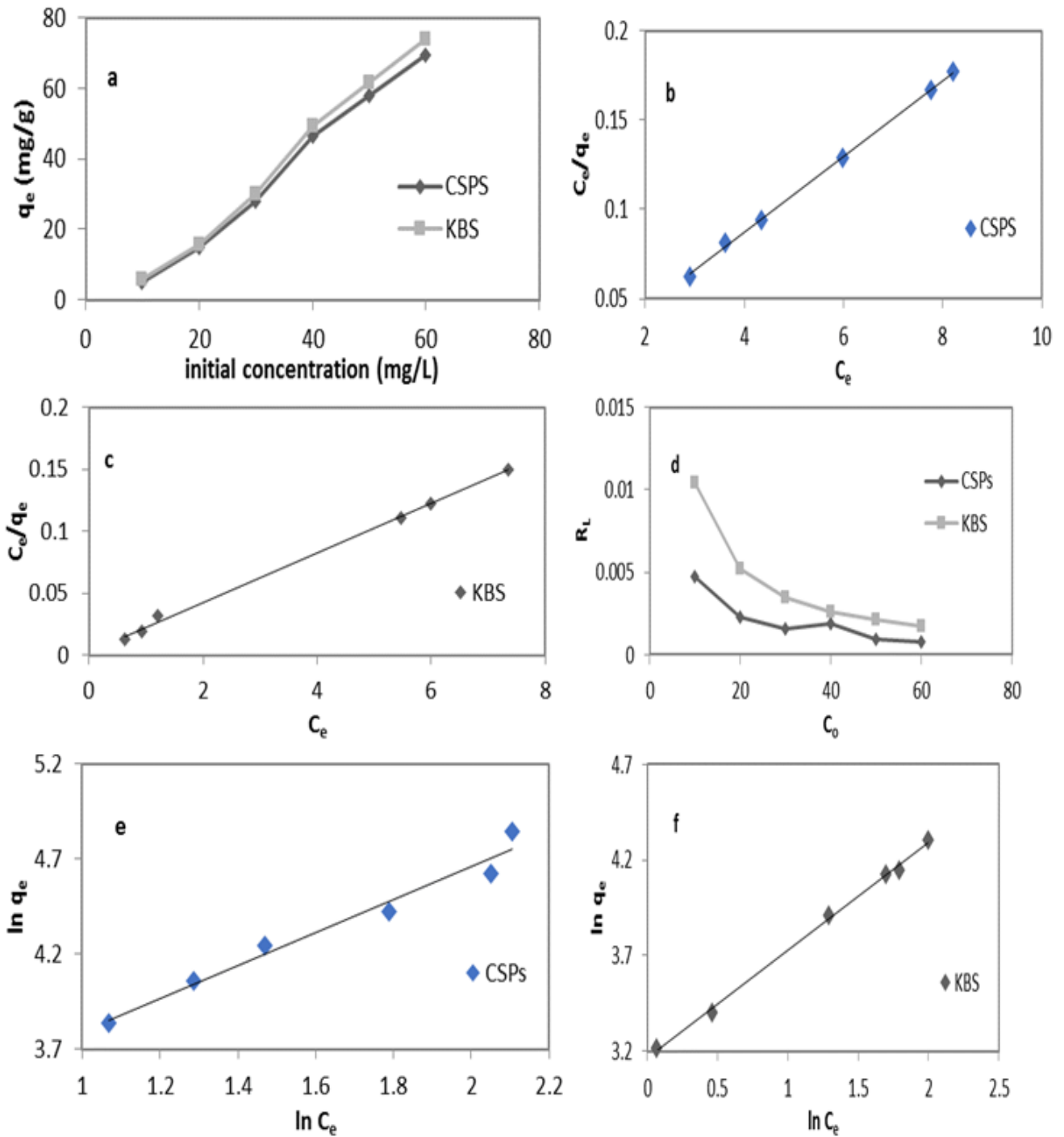


Figure 7. Effect of initial concentration and isotherm models of 2,4-DNP adsorption study, **a:** effect of initial concentration of 2,4-DNP on sorption capacity (q_e), **b:** Langmuir isotherm of 2,4-DNP adsorption on CSPS: C_0/q_e versus C_e , **c:** Langmuir isotherm of 2,4-DNP adsorption on KBS: C_0/q_e versus C_e , **d:** R_L versus C_0 , **e:** Freundlich isotherm of 2,4-DNP adsorption on CSPS: $\ln q_e$ versus $\ln C_e$, **f:** Freundlich isotherm of 2,4-DNP adsorption on KBS: $\ln q_e$ versus $\ln C_e$

Table 2. Isotherm models constants for 2,4-DNP adsorption

Adsorbent	Langmuir adsorption isotherm model			Freundlich adsorption isotherm model		
	q_{max} (mg/g)	b (L/mg)	R^2	K_f (mg/g)	N	R^2
CSPs	47.61	21.01	0.9998	18.69	1.156	0.9694
KBS	52.63	3.17	0.9971	23.71	1.779	0.9963

4. Discussion

This result mainly shows that agricultural waste material has a high potential to reduce water pollution in terms of waste water treatment by adsorption. The present study proves that *Cucumis sativus* peels (CSPs) and kidney bean shells (KBS) act as low cost, efficient and environmental friendly adsorbents for adsorption of 2,4-DNP from aqueous solutions. The maximum adsorption capacities of KBS and CSPs were 52.63 mg/g and 47.61 mg/g at 80 mg of adsorbent dose respectively, which were significantly good and much higher than other low- cost adsorbents.

The maximum % adsorption of 2,4-DNP attained at pH of 4.0, initial concentration of 40 mg/L, contact time of 120 min and adsorbent dose of 100 mg which was 93.13% for CSPs and 99.02% for KBS. KBS was found to be more efficient adsorbent for adsorption of 2,4-DNP in aqueous solutions as compared to CSPs. It is concluded that the % adsorption of 2,4-DNP is to some extent reduced in very acidic and very basic region and by increasing adsorbent dose of both the adsorbents the % adsorption increases nonlinearly. The results also show that by increasing contact time the % adsorption increases but at 120 min it does not increase further and equilibrium is established for both the adsorbents. Kinetics study revealed that 2,4-DNP adsorption onto CSPs and KBS followed pseudo second order kinetic model and intra-particle diffusion model as well as film layer diffusion were helpful to control adsorption rate. It is also concluded that adsorption of 2,4-DNP onto CSPs and KBS were better described by Langmuir adsorption isotherm model as compared to as compared to Freundlich adsorption isotherm model and adsorption was favorable according to Langmuir parameter.

5. Conclusion

2,4-DNP was best removed by kidney bean shells as compared to *Cucumis sativus* peels. It is concluded that agricultural waste such as *Cucumis sativus* peels and kidney bean shells can be used as low-cost adsorbents for adsorption of 2,4-DNP from aqueous solution at large scale in replacement of high cost adsorbents.

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