Kinetic modelling and thermodynamic studies on purification of Polyvinylpyrrolidone by Adsorption

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Abstract

Polyvinylpyrrolidone (PVP), a highly water soluble polymer, with many technological, engineering and pharmaceutical applications, obtained by polymerization of N-vinylpyrrolidone, has been purified by adsorption onto activated carbon and strong acidic ion-exchange resin using PVP aqueous solution. Various parameters that can affect the process have been studied such as effect of contact time, effect of adsorbent dosage, effect of temperature, effect of PVP concentration and effect of NVP initial concentration. It has been clearly demonstrated that NVP adsorption is affected by all these factors. Adsorbent capacities have been determined by mathematical fitting of equilibrium data using the most common isotherms: Freundlich isotherm and Langmuir isotherm.

Several kinetic models have been applied to the process. Thermodynamic parameters: $\triangle S^o$, $\triangle H^o$, $\triangle G^o$ *and Ea (kJ/mol) have been determined. It was found out that the process follows pseudo-second-order kinetic model suggesting that the adsorption mechanism might be a chemisorption process; thermodynamic studies showed that this process is spontaneous and endothermic. These results are very important in optimization of this purification process.*

Keywords: *Polyvinylpyrrolidone (PVP), adsorption, activated carbon, resin, modelling.*

1. Introduction

Polyvinylpyrrolidone (PVP), Povidone or Polyvidone is a member of a large family of chemicals termed Poly-N-vinylamides they are highly water-soluble synthetic polymers with a weighted average molecular weight between 2.5 and 1200 kDa. PVP is obtained by free-polymerization of N-vinyl pyrrolidone (NVP) in water or isopropanol. (Trimpin, et al., 2001).

Polymers of N-vinylpyrrolidone are being widely used in the fields of cosmetics preparations, chemicals, pharmaceutical preparations, food additives and personal care articles. It is used as binder in many pharmaceutical tablets. It is used in coatings for photo-quality ink-jet papers and transparencies. As well as in inks for inkjet printers and in other numerous technical applications. Today, soluble PVP (e.g. Kollidon, Polyvidone and Plasdone) is one of the most and widely used in pharmaceutical auxiliaries (Reppe, 1954, Ushakov, et al. 1961, Denzinger, et al., 1977 and Friendrich,et al., 1989)

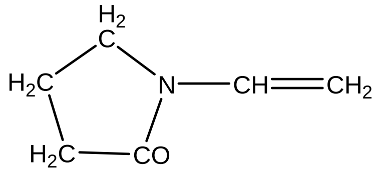
Since PVP has some similarities to polyvinylchloride (PVC) whose monomer, vinyl chloride (VC), is known to be carcinogenic to humans, the lack of information on the amount of vinylpyrrolidone monomer (NVP) in pharmaceutical and cosmetic products containing PVP and the dearth of knowledge concerning its metabolism and toxicity is cause for some concern (Lawrence, et al., 1979). However the polymer PVP in its pure form is so safe that not only is it edible to humans, but also it was used as a blood expander for trauma victims after half of 20th century (Ushakov, et al., 1961).

In these fields, requirements for high purity products and for removing odor and color forming impurities are strong. As little as 500 ppm N-vinyl pyrrolidone monomer produces a faint but unpleasant odor. Particularly for toxicological and aesthetic reasons, polymer should in principle be as free as possible of monomer. This applies in particular to polymers for cosmetics and especially for pharmaceutical applications (Denzinger, et al., 1977).

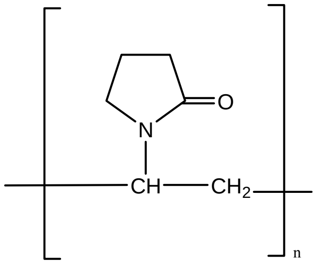
There are several previous research works aiming at PVP purification by adsorption (Nuber, et al., 1989, Marilyn, et al., 1993 and Liu, et al., 1998). But to the best of our knowledge none of them has established optimal conditions of PVP purification process by adsorption. The aim of the present research is to establish these conditions by studying various parameters which can affect this process. From the results of this work it could result in a method for obtaining a high purified PVP from PVP containing a small amount of N-vinylpyrrolidone monomer.

2. MATERIALS AND METHODS

Polyvinylpyrrolidone (PVP) and N-Vinylpyrrolidone (NVP) were kindly provided by Anhui Harvest Fine Chemicals Industry Co, dichloromethane was obtained from Sinopharm, activated carbon was supplied by Henan Sheng Gongyishin Dahua Gong Chang and resin was gotten from Shanghai Huazhen Sci.&Tech.Co., Ltd of ECUST, People's Republic of China. Pure PVP K-30 and N-vinylpyrrolidone were used to prepare different solutions needed in this work. The powdered activated carbon and granular strongly acidic ion-exchange resin were used as adsorbents; tables1 and 2 present their physical and chemical properties. Distilled water and dichloromethane were solvents.



N-Vinylpyrrolidone



Polyvinylpyrrolidone

Table 1. Properties of activated carbon SJ-300

Parameter	Value
Molasses decolorization (%)	120
Moisture content (%)	10
Ash content (%)	4.0
Ion content (%)	0.1
Chloride (%)	0.2
pH value	3-4
Acid soluble content (%)	1.5
Bulk mass (g/dm^3)	540
Specific surface (m^2/g)	1000
Methylene blue number mg/g)	162
Iodine number (mg/g)	1050

Table 2. Physicochemical Properties of HD-8 resin

Type	Strong acidic cation exchange resin
Active group	-SO3-
Matrix	Polystyrene
Ion form	H^+
Water retention	55-65%
Total exchange capacity (mmol/g)	4
Density	1.2

The effect of time on the adsorption of NVP onto both adsorbents was studied by taking 100 ml of PVP solution 20% mixing with 10% weight percent of polymer as adsorbent in different stoppered flasks at various temperatures. The NVP initial concentrations were 0.1 and 0.18 weight percent of the solution for the solution treated by carbon and by resin respectively. The flasks were mildly stirred by magnetic stirrer for 6 hours. Samples were taken after every one- hour time interval to analyze the content of NVP.

The effect of adsorbent dosage was investigated using the same experimental conditions as in previous section but varying the concentration of adsorbent from 1 to 20 % weight percent with respect to PVP weight. The effect of temperature was studied using the same solution with 10% weight percent of PVP weight as adsorbent content in a temperature range from 30 to 50 ^{o}C.

PVP concentration effect was investigated by varying its concentration from 20 to 50% weight percent in the solution; adsorbent dosage was 10% weight percent with respect to PVP weight in the temperature range of 30 to 50^{o}C.

The effect NVP initial concentration was studied by varying the concentration of NVP in range of 0.1 to 2 % weight percent in the solution the temperature range of 30 to 50^{o}C. Adsorbent concentration was 10% weight percent of the polymer weight.

Langmuir and Freundlich adsorption isotherms were established using equilibrium data obtained by varying NVP initial concentration from 0.1 to 2% weight percent of the solution with 10% weight percent of the polymer (the polymer concentration was 40% weight percent of the solution) as adsorbent, the treatment time was 24 h to reach the equilibrium with mild magnetic mixing at temperature range from 30 to 50 degrees Celsius.

And finally using equilibrium data, various kinetic models were applied to the adsorption process, and thermodynamic parameters were determined. The pH of polymer solution is not critical; advantageously the pH resulting from the polymerization that is about 4-9 is retained throughout the process (Nuber et al., 1989).

The NVP concentration was determined mainly by gas chromatography using GC-950 chromatograph. The Gas chromatograph was equipped with a 3mmx2m Carbon Wax 20M column and a flame ionization detector. Chromatographic data were collected and analyzed by N-2000 chromatographic data system. The gas chromatography operating conditions were as follows:

Temperature conditions:
- Column, 180^{o} C;
-Injector port, 240^{o} C
-Detector, 240^{o} C.

Gas flows:
-Nitrogen (ultra pure), 30ml/min;
-Hydrogen, 30ml/min, and
-Air, 250ml/min.

GC sample preparation

PVP solution requires some preparative operations prior to the injection in GC. This was done as follows:

5.0 ml of aqueous solution was pipetted into a separator funnel containing 0.5 ml 0.1 N NaOH and exactly 5.0 ml of dichloromethane. The mixture was shaken vigorously by hand for 5 minutes and the emulsion allowed breaking so as to obtain clear dichloromethane phase. 10 µL of the organic phase were injected into the gas chromatograph. The chromatograms were run until a broad peak was eluted at about 3.7-4.1 min.

The amount of NVP adsorbed was calculated as follows:

$$q_t = \frac{(C_o - C_t)V}{m} \tag{1}$$

At equilibrium $q_t = q_e$ and $C_t = C_e$; therefore

$$q_e = \frac{\left(C_o - C_e\right)V}{m} \tag{2}$$

The percentage removal of NVP was determined by the following relation:

$$\mathrm{Re}moval\% = \frac{C_o - C_t}{C_o} x100 \tag{3}$$

Where q_t and q_e are amount adsorbed at time t and at equilibrium respectively.

C_o and C_t are the initial and time t liquid-phase concentrations of NVP respectively.

V is the volume of the solution and m is the mass of the adsorbent.

3. Results And Discussion

3.1. Effect of contact time

The concentration of NVP remaining in the solution was plotted as a function of the contact time for the resin. Figures 3.1 - 3.4 present the effect of contact time on adsorption of NVP, the plots indicate that the NVP removal increases rapidly in the beginning and slows down in the end. High adsorption rates of NVP are observed at the onset; and then plateau values are gradually reached. The initial faster rate of NVP adsorption may be explained by the large number of adsorption sites available for adsorption.

For the initial bare surface, the sticking probability is large, and consequently adsorption proceeded with a high rate. The slower adsorption rate at the end is probably due to the saturation of active sites. The removal increases with time and will attain equilibrium (Gode, 2003, Anirudhan, et al., 2008, Abburi, 2003, Lee, 2000).

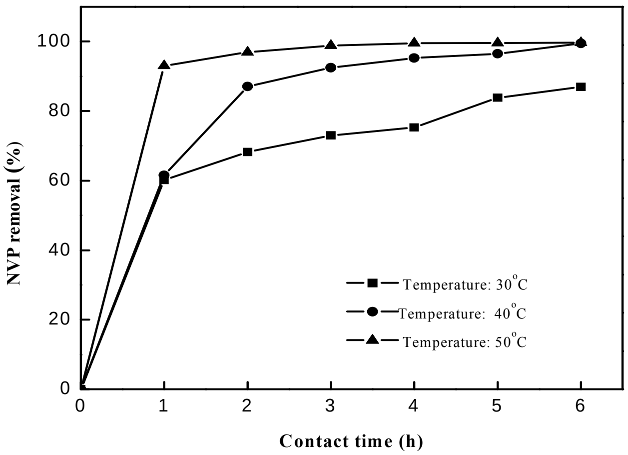


Figure 3.1 : Effect of contact time (adsorbent: activated carbon, PVP content: 20 %, NVP initial content: 0.1 %, adsorbent dose: 10 % weight percent of PVP)

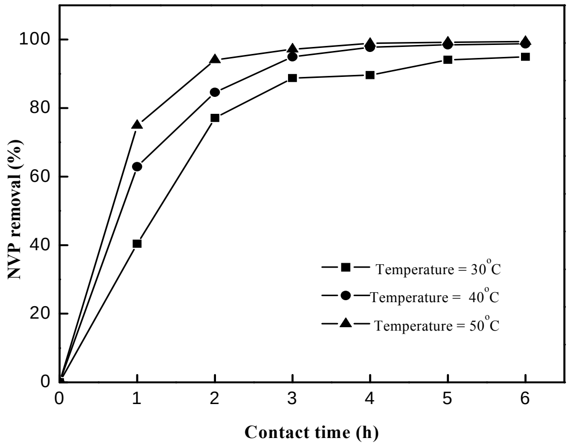


Figure 3.2 : Effect of contact time (adsorbent: resin, PVP content: 20 %, NVP initial content: 0.18 %, adsorbent dose: 10 % weight percent of PVP)

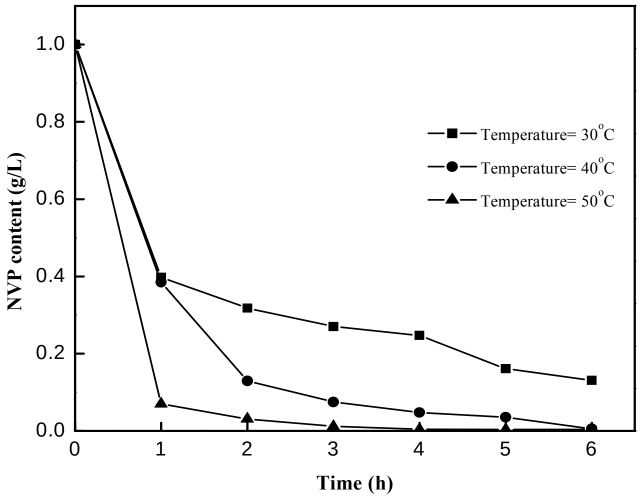


Figure 3.3 : Variation of NVP content with contact time (adsorbent: activated carbon, PVP content: 20 %, NVP initial content: 0.1 %, adsorbent dose: 10 % weight percent of PVP)

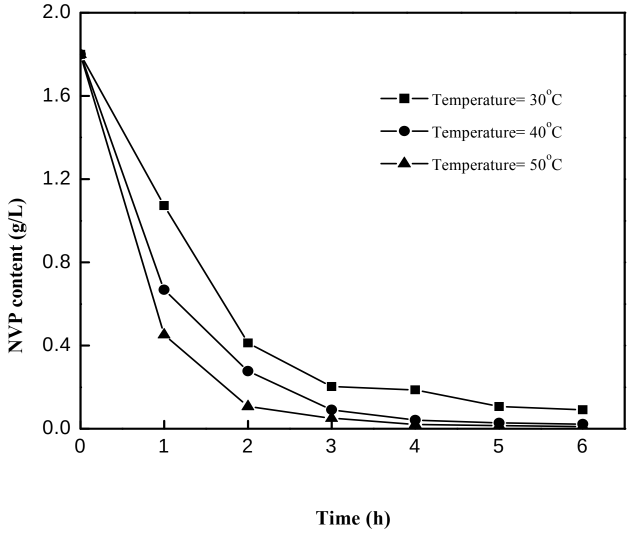


Figure 3.4 : Variation of NVP content with contact time (adsorbent: resin, PVP content: 20 %, NVP initial content: 0.18 %, adsorbent dose: 10 % weight percent of PVP)

3.2. Effect of adsorbent dosage

The adsorbent dosage is an important parameter because this determines the capacity of an adsorbent for a given initial concentration of the adsorbate.

The effect of variation of resin dosage on the removal of NVP by activated carbon and HD-8 strongly ion-exchange resin at different temperatures is shown figures 3a and 3b. Adsorbent dosage was varied from 1 to 20% weight percent with respect to polymer concentration for 6 h.

It is apparent that the equilibrium concentration in solution phase decreases with increasing resin doses for a given initial NVP concentration. Since the adsorptive fraction removed from the aqueous phase increases as the adsorbent dosage is increased in the batch vessel with a fixed initial NVP concentration, the curves approach asymptotic values as adsorbent dose increases. This trend is clearly observed when the adsorbent dose concentration is more than 5% weight percent of polymer weight. It is obvious that an increase in the adsorbent amount results in a decrease in the contact time required to reach equilibrium because for a fixed initial NVP concentration, increasing adsorbent dose provides greater surface area and adsorption sites of the adsorbent (Gode et al., 2001, Juang et al., 1999, Manohar, et al., 2006).

It was noticed that uptake per unit mass of the adsorbent was higher when its concentration was lower. Such performance on the adsorbent may be attributed to the fact that some of the adsorption sites remain unsaturated during the adsorption process. However, the results also showed that the percentage adsorption increased with increasing concentration of the resin because of the increase in the number of reaction sites available to the adsorptive (Juang, et al., 1999, Manohar, et al., 2006, Ku, et al., 2004, Anasthas, et al., 1999, Rangaraj et al., 2002).

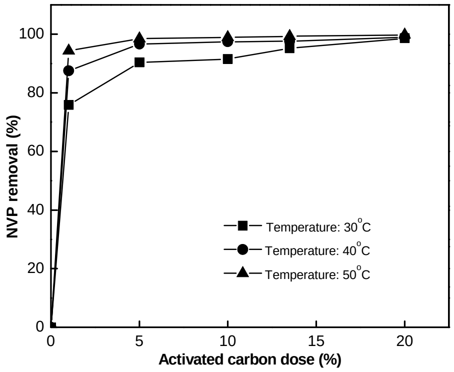


Figure 3.5 : Effect of adsorbent dosage (adsorbent: activated carbon, PVP content: 20 %, NVP initial content: 0.1 %)

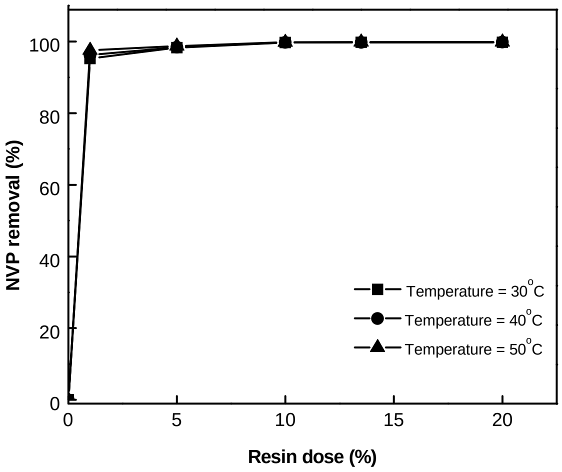


Figure 3.6: Effect of adsorbent dosage (adsorbent: resin, PVP content: 20 %, NVP initial content: 0.18 %)

3.3. Effect of temperature

The effect of temperature was investigated in the temperature range of 30 to 50°C with different adsorbent dosages; Figures 3.5 and 3.6 show the trend of NVP removal with increasing temperature. As it can be seen NVP adsorption on both adsorbents increased with increase of the temperature within the range studied. This increase may be attributed to endothermic nature of the interactions (Malik, 2003, Al-Ghouti, et al., 2005, Anirudhan, et al., 2008).

3.4. Effect of initial NVP content

It is clear from the figure 4 that NVP equilibrium concentration increases with the increasing initial NVP concentration; at the beginning the increase is slow and becomes faster as NVP initial concentration increases. This can be attributed to the decrease of the ratio of adsorbent active sites to adsorbate concentration which diminishes as adsorbate concentration increases (Zheng, et al. 2008, Kim, et al., 2002).

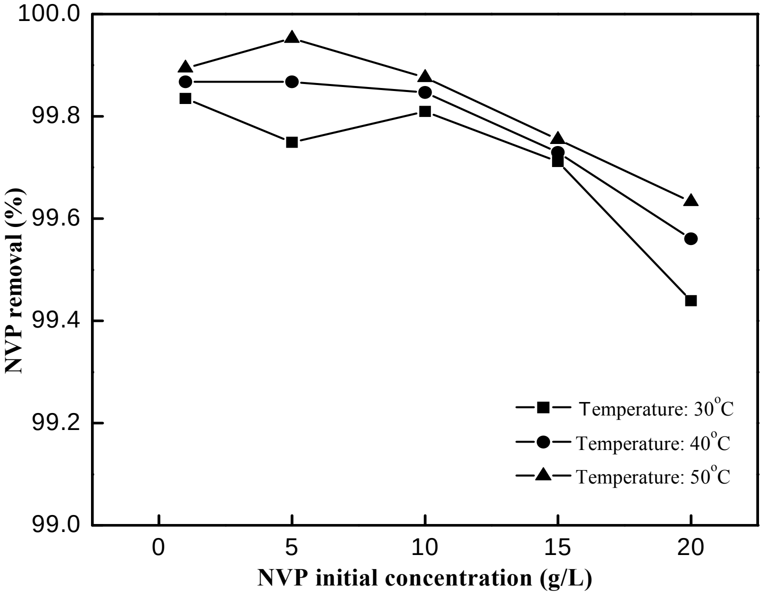


Figure 3.7: Effect of NVP concentration (adsorbent: resin, PVP content: 20 %, adsorbent dose: 10 % weight percent of PVP)

3.5. Effect of PVP concentration

At a constant initial concentration of NVP, NVP removal decreases with increase of PVP concentration up to a constant value as it is seen in Figure 3.8. This may be attributed to the fact that the increase in PVP concentration enhances the viscosity of the adsorptive solution which makes adsorption process harder because the adsorptive solution does not move easily on the adsorbent sites. For a better adsorption of NVP from PVP solution, the upper limit of PVP concentration in the solution to be treated is determined by viscosity, which in turn depends on the molecular weight. For example, the concentration may be from 20 to 40 % by weight for a K-value of 15-60, while a concentration of about 20-30% is preferred for a K-90 PVP (Nuber et al., 1989, Marilyn, J. et al., 1993, Liu et al., 1998).

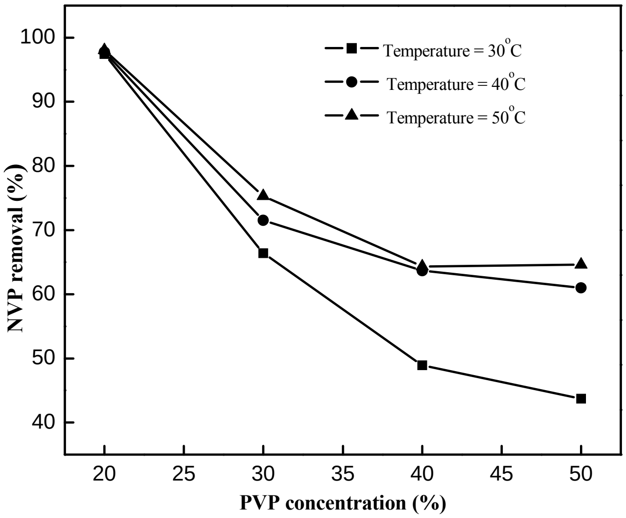


Figure 3.8. : Effect of PVP concentration (adsorbent: resin, NVP initial content: 0.1 %, adsorbent dose: 10 % weight percent of PVP)

3.6. Adsorption isotherms

The amount of material adsorbed is determined as a function of the concentration at a constant temperature that could be explained in adsorption isotherms. Equations that are often used to describe the experimental isotherm data were developed by Freundlich and Langmuir.

The Freundlich adsorption isotherm is mathematically expressed as

$$q_e = K_f C_e^{1/n} \tag{4}$$

Taking natural logarithm and rearranging:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{5}$$

Where q_e is the amount of adsorbate adsorbed per unit weight of resin at equilibrium, *C*e is the equilibrium concentration of adsorbate in solution, and K_f and *n* are empirical constants.The coefficients K_f and n can be estimated from slopes and by substituting values from a line fitted to a graph of log q_e versus log C_e. The method of least squares can be used to get a statistical fit. The Langmuir equation is expressed here as:

$$\Gamma = \frac{\Gamma_{\max} KC}{1 + KC} \tag{6}$$

The last linear regression commonly used is the Langmuir linear regression proposed by Langmuir himself in 1918:

$$\frac{C}{\Gamma} = \frac{C}{\Gamma_{\max}} + \frac{1}{K\Gamma_{\max}} \qquad (7)$$

Where K = Langmuir equilibrium constant, C = aqueous concentration (or gaseous partial pressure), Γ = amount adsorbed, and Γ_{max} = maximum amount adsorbed as C increases.

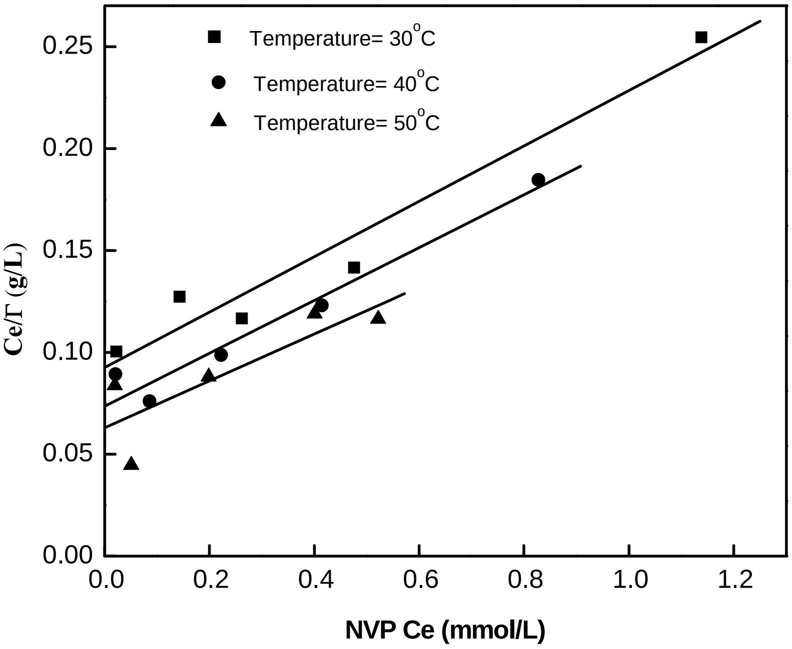


Figure 3.9 : Langmuir isotherm (adsorbent: activated carbon, PVP content: 40 %, NVP initial content: 0.1-2 %, adsorbent dose: 10 % weight percent of PVP)

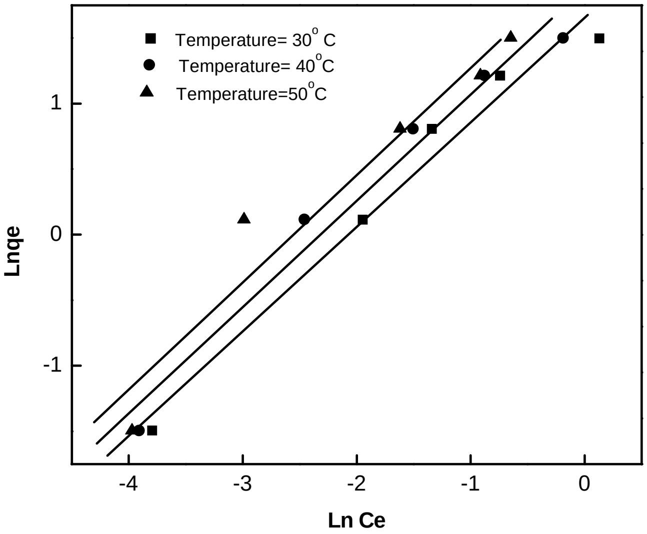


Figure 3.10 : Freundlich isotherm (adsorbent: activated carbon, PVP content: 40 %, NVP initial content: 0.1-2 %, adsorbent dose: 10 % weight percent of PVP)

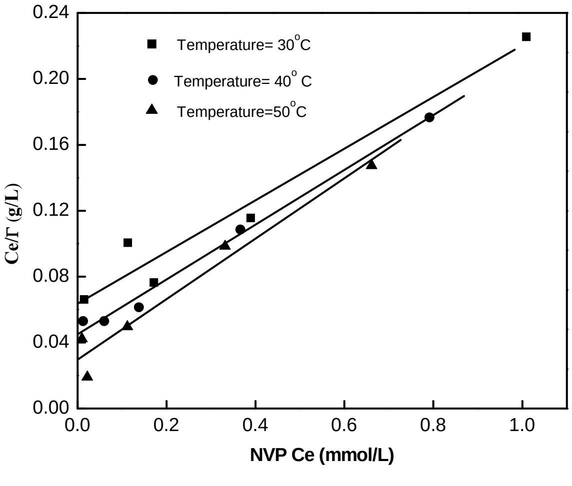


Figure 3.11 : Langmuir isotherm (adsorbent: resin, PVP content: 40 %, NVP initial content: 0.1-2 %, adsorbent dose: 10 % weight percent of PVP)

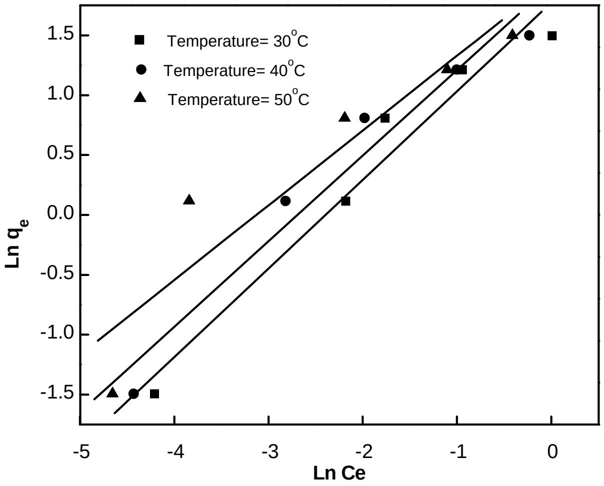


Figure 3.12 : Freundlich isotherm (adsorbent: resin, PVP content: 40 %, NVP initial content: 0.1-2 %, adsorbent dose: 10 % weight percent of PVP)

Langmuir isotherm and Freundlich isotherm are plotted in figures 3.9 - 3.12 at different temperatures for both adsorbents. The purpose of these isotherms is to relate the adsorbate concentration in the bulk and the adsorbed amount at the interface. Isotherm studies provide information about the capacity of the adsorbent or the amount required to remove a unit mass of pollutant from adsorptive solution. The information is necessary for adsorption modelling, adsorption optimization and predicting sorption capacity.

The values of all the isotherm constants were calculated from the slope and intercepts of the plots using the least squares method and are summarized in Table3. As seen from the Table3, for the activated carbon, Freundlich isotherm shows a better mathematical fitness than Langmuir, whereas for the adsorption onto ion-exchange resin, the Langmuir equation represents the adsorption better than Freundlich equation especially at 40°C where the R^2 value was almost higher than 0.99 indicating a very good mathematical fitness (Kiniburgh, et al. 1983, Altin, et al. 1998).

Table 3: Isotherm constants

		Langmuir constants			Freundlich constants		
Adsorbent	**Temperature (oC)**	**Γ_{max} (mmol /g)**	**K (L/mmol)**	**Correlation coefficient**	**n**	**K_f (mmol/ g)**	**Correlation coefficient**
Resin	30	6.40	2.50	0.9591	1.35	5.90	0.9581
	40	6.01	3.70	0.992	1.40	6.87	0.9538
	50	5.45	6.17	0.9617	1.60	7.06	0.8773
Carbon	30	7.35	1.47	0.9543	1.25	5.23	0.9728
	40	7.71	1.76	0.9603	1.23	6.56	0.9699
	50	8.70	1.83	0.7026	1.22	8.07	0.9376

3.7. Kinetic modelling of the adsorption of NVP

There are several kinetic models in the literature to examine the controlling mechanism of adsorption process such as chemical reaction, diffusion control and mass transfer. Each model has its own limitations and is derived according to certain conditions. The NVP adsorption process was analyzed by using pseudo-first-order, pseudo-second- order and intra-particle diffusion models to test experimental data.

1. Pseudo first-order model

The pseudo first-order equation is generally expressed as follows (Ho, et al. 1999, McKay, 1999, Aksu, and Tezer 2000, Aksu, 2001, Özacar and Sengil, 2003)

$$\frac{dq_t}{dt} = k_1\left(q_e - q_t\right) \tag{8}$$

After integration and applying the boundary conditions, for qt = 0 at t = 0 and qt = qt at
t = t, the integrated form of Eq. (8) becomes:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303}t \tag{9}$$

Where q_e and q_t are the amounts of NVP adsorbed at equilibrium and at time t (mg/g), respectively, and k_1 is the rate constant of pseudo first-order sorption (1/min).

2. Pseudo second-order model

If the rate of sorption is a second-order mechanism, the pseudo second-order chemisorption kinetic rate equation is expressed as (Ho, et al. 1999, McKay, 1999, Aksu, and Tezer 2000, Aksu, 2001, Özacar and Sengil, 2003)

$$\frac{dq_t}{dt} = k_2\left(q_e - q_t\right)^2 \tag{10}$$

Integrating this equation for the boundary conditions, gives:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \qquad (11)$$

Which is the integrated law for a second-order reaction, where q_e is the amount of NVP adsorbed at equilibrium (mg/g), k_2 is the rate constant of pseudo second- order adsorption (g/mg min). Eq.11 can be rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{1}{q_e} t \qquad (12)$$

And

$$h = k_2 q_e^{\,2}$$

Where h is the initial sorption rate (mg/g min).

3. Intraparticle diffusion model

In the intraparticle model, the relationship between the adsorption capacity at time t, q_t, and $t^{1/2}$ can be expressed as follows (Wu, et al. 2001, Annadurai, 2002, Özacar, 2003):

$$q_t = k_{\mathrm{int}} t^{1/2} + C_{\mathrm{int}} \qquad (13)$$

Where k_{int} is the intraparticle diffusion rate constant (mg/g min$^{1/2}$), t is the contact time (min) and C_{int} is a constant that gives idea about the thickness of the boundary layer (mg/g).

Table 4. Kinetic modelling parameters

			Pseudo-first-order model			Pseudo-second-order model				Intraparticle diff. model		
Adsorbent	**Temper. (^oC)**	**q_e, exp. (mg/g)**	**q_e, calc. (mg/g)**	**k_1 (1/min)**	**R^2**	**q_e, calc. (mg/g)**	**k_2(g/mg min)**	**h (mg/gmin)**	**R^2**	**k_{int} (mg/g min$^{1/2}$)**	**C_{int} (mg/g)**	**R^2**
Acidic resin	30	46.9587	29.5596	0.0071	0.9045	56.1797	0.8148	0.6667	0.9744	2.007	9.733	0.7974
	40	46.9669	21.7170	0.0094	0.9094	51.2820	1.7030	1.4084	0.9973	1.38	22.42	0.8203
	50	46.9736	11.4551	0.0085	0.8591	48.7804	3.7532	2.770	0.9989	0.875	31.46	0.7224
Activated Carbon	30	24.9374	12.7673	0.0036	0.9642	23.9808	0.0008	0.5016	0.9892	0.5871	10.435	0.9642
	40	24.9443	21.3599	0.0133	0.9003	27.6243	0.0011	0.6963	0.9975	0.7546	11.624	0.9003
	50	24.9477	3.1732	0.0138	0.9427	25.3164	0.0082	5.1466	1.0000	0.1438	22.47	0.9427

The variation of NVP quantity adsorbed onto unit mass of two adsorbents with contact time, the rate constants, predicted equilibrium uptakes and the corresponding correlation coefficients for the two adsorbents were studied and results are presented in table 4 and Figures 4.1 – 4.6. As it can be seen, the values of R^2 of pseudo second-order are located between 0.97 and 1.00 this makes them the highest of all three models used. They are followed by those of pseudo first-order model and intraparticle diffusion model respectively. The initial adsorption capacity h increased with increasing temperature for both adsorbents.

In the first three hours, the pseudo-first-order kinetics fits and thereafter the data deviated greatly from linearity. This means that the initial stages of this process are rapid but slows down as contact time increases, this behaviour makes the pseudo-first-model makes the pseudo-first-model kinetics inappropriate on the entire range of time of the process (Poots, et al., 1978).

A close examination of the correlation coefficients and predicted equilibrium uptakes *q*e,cal values from the pseudo-second-order kinetic model shows a better constancy with the experimental results.

Intraparticle diffusion model showed a linear form when q_t was plotted against $t^{1/2}$ only at the initial part whereas the following part was curved and does not pass through the origin. The linear portion corresponds to intra-particle diffusion and curved portion is attributed to bulk diffusion. If it passes through origin, intra-particle diffusion is the only rate controlling step (Kannan and Sundaram, 2001. When the plots do not pass through the origin, it indicates some degree of boundary layer control (McKay, et al. 1985) and this further show that intra-particle diffusion is not the only rate limiting step but other kinetic models may also control the rate of adsorption, all of which may be operating simultaneously (Asfour, et al. 1985).

Figure. 9a and 9b show a comparison between experimental and modelled effect of time using various kinetic models for the two adsorbents used for NVP with an initial concentration of 1g /L and 1.8g/L for the solution treated by activated carbon and ion-exchange resin respectively at 50°C. The pseudo-second-order model gives the best fit all over the time of the adsorption process. This suggests that the adsorption systems studied belong to the pseudo-second-order kinetic model, based on the assumption that the rate limiting step may be chemisorption involving electrostatic forces through sharing or exchange of electrons between the adsorbent and the adsorbate.

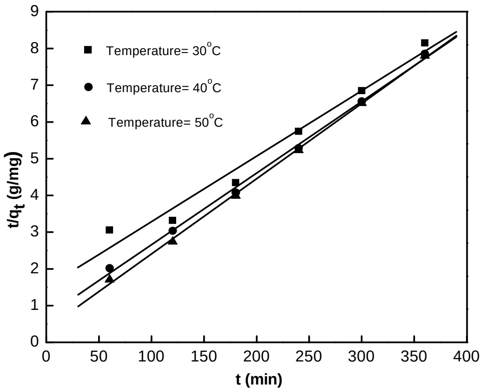


Figure 4.1: Pseudo-second-order model of NVP adsorption onto strongly acidic ion exchanger resin (Initial NVP content: 0.18 % PVP content: 40 %, adsorbent dose: 10 % weight percent of PVP).

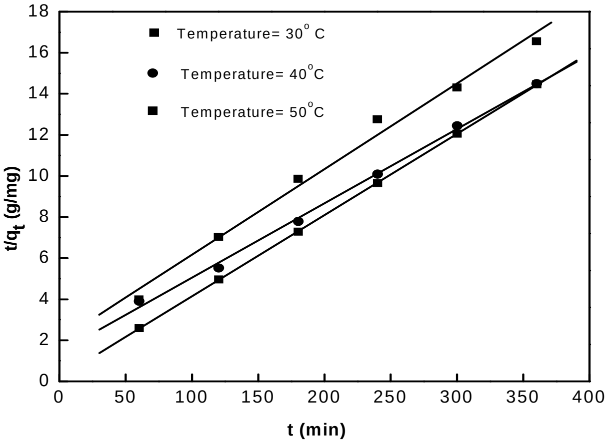


Figure 4.2: Pseudo-second-order model of NVP adsorption onto activated carbon (Initial NVP content: 0.1 % PVP content: 40 %, adsorbent dose: 10 % weight percent of PVP)

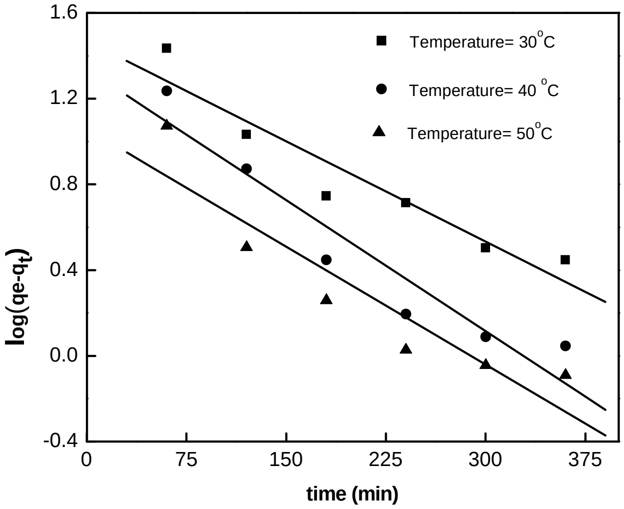


Figure 4.3: Pseudo-first-order model of NVP adsorption onto strongly acidic ion exchanger resin (Initial NVP content: 0.18 % PVP content: 40 %, adsorbent dose: 10 % weight percent of PVP)

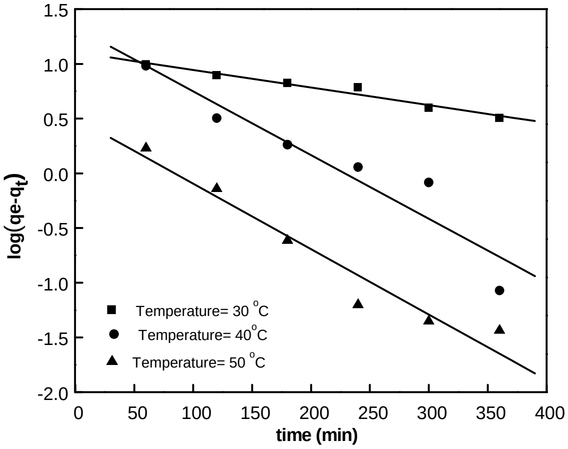


Figure 4.4 Pseudo-first-order model of NVP adsorption onto activated carbon (Initial NVP content: 0.1 % PVP content: 40 %, adsorbent dose: 10 % weight percent of PVP)

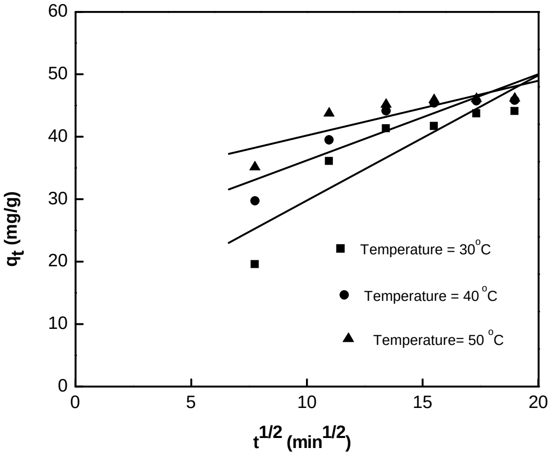


Figure 4.5 Intraparticle diffusion model of NVP adsorption onto strongly acidic ion-exchange resin (Initial NVP content: 0.18 % PVP content: 40 %, adsorbent dose: 10 % weight percent of PVP)

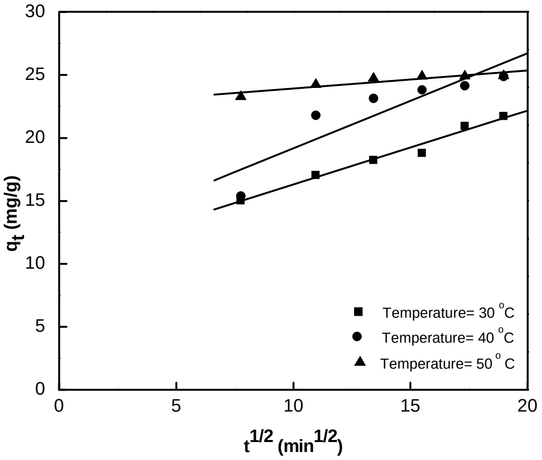


Figure 4.6: Intraparticle diffusion model of NVP adsorption onto activated carbon (Initial NVP content: 0.1 % PVP content: 40 %, adsorbent dose: 10 % weight percent of PVP).

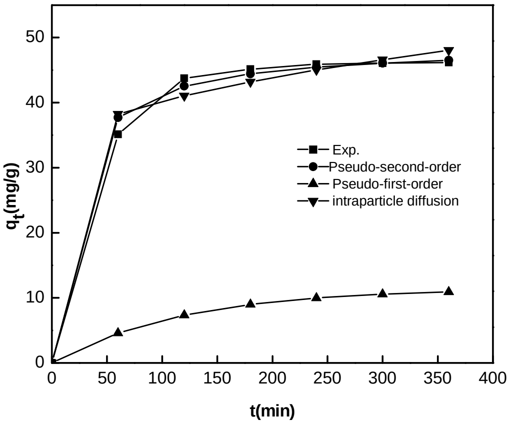


Figure 4.7: Experimental and modeled effect of time on adsorption of NVP onto ion-exchange resin (Initial NVP content: 1.8 g/L, PVP concentration: 40 %, resin dose: 10 % weight percent of PVP).

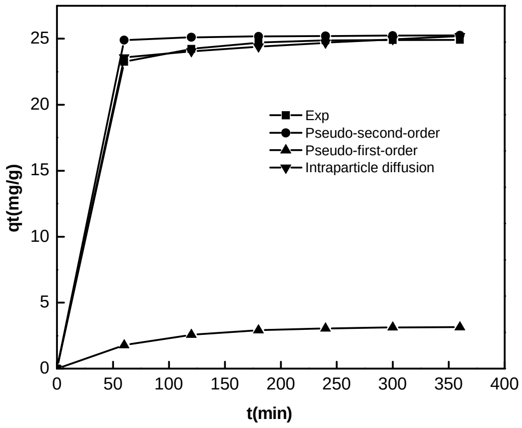


Figure 4.8: Experimental and modeled effect of time on adsorption of NVP onto activated carbon (Initial NVP content: 1g/L, PVP concentration: 40 %, Activated carbon dose: 10 % weight percent of PVP).

3.8. Thermodynamic studies

Thermodynamic parameters such as free energy change, enthalpy change and entropy change give information about the feasibility and spontaneity of the adsorption process, the activation energy helps to know the controlling mechanism of the process. These parameters were determined from the following equations:

$$K_d = \frac{C_a}{C_e} \tag{14}$$

$$\Delta G^o = -RT\ln(K_d) \tag{15}$$

$$\log(K_d) = -\frac{\Delta H^o}{2.303RT} + \frac{\Delta S^o}{2.303R} \tag{16}$$

$$\ln k_2 = \ln k_o - \frac{E_a}{RT} \tag{17}$$

Where R is the gas constant, K_d is the distribution coefficient for the adsorption, C_e is the equilibrium concentration in solution (mg/L) and C_a is the solid-phase concentration at equilibrium (mg/L), T is the solution temperature (K), $\triangle S^o$ the entropy of adsorption (kJ/mol K), $\triangle H^o$ the enthalpy of adsorption (kJ/mol), $\triangle G^o$ the free energy of adsorption (kJ/mol), k_2 the pseudo- second order constant (mg/g min), k_o the rate constant of adsorption (mg/g min) and E_a the activation energy of adsorption (kJ/mol).

LnK$_d$ versus 1/*T* was plotted in figure10 from this plot thermodynamic parameters were determined using eq.15-18.

Table 5. Thermodynamic parameters

Adsorbent	**$\triangle G^o$ (kJ/mol)**			**$\triangle H^o$ (kJ/mol)**	**$\triangle S^o$ (kJ/mol)**	**Ea (kJ/mol)**
	303K	313K	323K			
Resin	-7.01	-7.49	-7.99	18.19	0.11	62.09
Carbon	-6.55	-6.90	-7.19	7.34	0.074	93.93

Table 5 presents the thermodynamic parameters for NVP adsorption on both adsorbents. The negative values of $\triangle G^o$ indicate the feasibility and spontaneity of the adsorption process. The positive values of $\triangle H^o$ confirm the endothermic nature of the overall adsorption process. The enhancement of adsorption at higher temperature may be due to the increase in the diffusion rate of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution (Asfour, et al. 1985).

The positive value of $\triangle S^o$ suggests increased randomness at the solid-solution interface with some structural changes in the adsorbate and the adsorbent and an affinity of the adsorbent. Similar results were observed for adsorption of Acid Green 25 on activated palm ash (Hameed et al., 2007).

Lower activation energy values (<42 kJ/mol) indicate diffusion control processes and the higher activation energy values (>42 kJ/mol) indicate chemically controlled processes. This is because the temperature dependence of the pore diffusivity is relatively weak. Here, the diffusion process refers to the movement of the solute to an external surface of adsorbent and not diffusivity of material along micropore wall surfaces in a particle (Scheckel and Sparks 2001).

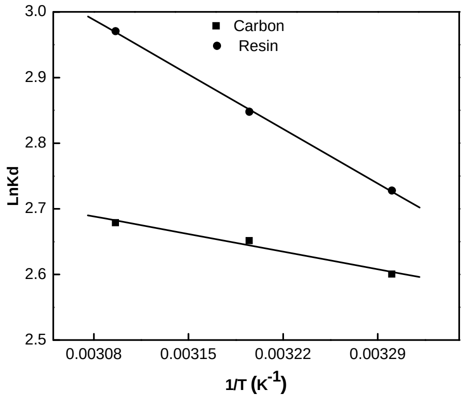


Figure 10 : The plot of lnKd versus 1/T for adsorption of NVP on carbon and resin at various temperatures.

3. CONCLUSION

The results of this study show that activated carbon and strongly acid resin can be adequately used to remove NVP from PVP aqueous solution because they have suitable adsorption capacities. Contact time, adsorbent dose, temperature, NVP initial concentration and PVP concentration were found to have important effects on NVP equilibrium concentration. Strongly acidic resin showed a better performance than activated carbon. Experimental adsorption data of activated carbon fitted better the Freundlich model whereas the data of NVP adsorption onto strongly acidic resin were found to follow Langmuir model.

The adsorption process obeys the pseudo-second-order process. The thermodynamic parameters determination is very important to predict the effect of temperature changes on the NVP equilibrium concentration. The positive values of the activation energy suggested that the rise in the solution temperature favors NVP adsorption process. The negative values of $\triangle G^o$ indicate spontaneous adsorption of NVP onto both adsorbents. The positive values of $\triangle H^o$ confirm the endothermic nature of the overall adsorption process. The positive value of $\triangle S^o$ suggests increased randomness at the solid-solution interface. The results of this study are very important for the optimization of this purification process.

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