

4.4 Effect of Particle size

Adsorbent particle size has a significant influence on the kinetics of sorption due to change in number of adsorption sites. A series of experiments were performed to optimize the adsorption conditions for the removal of Ni(II) from aqueous solutions using TTCNS and TAINS. The dependence of adsorption of Ni (II) onto two different adsorbents are shown in figures 4.19 and 4.20, the corresponding amounts adsorbed being depicted in tables 4.1 and 4.2

The experimental results for the adsorption of Ni(II) at five different particle sizes of TTCNS viz., 0.18mm-0.71mm indicated that the decrease in particle size has a favourable effect on Ni(II) removal by the adsorbent. This is because adsorption being a surface phenomenon, smaller adsorbent surface offers larger surface area for metal binding²¹⁷. The smooth steep maximum curve obtained for 0.42 mm particle size (Fig 4.19) shows the enhancement in the amount adsorbed with respect to time compared to other particle sizes employed. Thus, adsorbent with 0.42 mm particle size was found to be optimum showing a higher percentage removal (Table 4.1) for the employed adsorbate concentration. When the particle size was further decreased, the percentage removal did not register pronounced effect which shall be due to the agglomeration of the adsorbent at finer particle sizes, depending upon the nature of the adsorbent.

The removal of Ni(II) ions at different particle sizes of TAINS (0.18mm- 0.71mm) showed that the capacity of nickel adsorption at the equilibrium increased with the decrease in particle size. The percentage adsorption was high for the particle size of 0.18 mm (Table 4.2). The relatively higher adsorption with smaller adsorbent particle may be attributed to the fact that smaller particles yield large surface areas and indicate that Ni(II) adsorption had occurred through a surface mechanism. It was also noticed that there is a tendency for a smaller particle to produce shorter time to equilibration²¹⁸.

From the results of the parameter study, it is obvious that TTCNS with particle size of 0.42 mm and TAINS with particle size of 0.18 mm possessed the maximum Ni(II) removal compared to the other four sizes mentioned. Hence, the forthcoming discussions corresponding to other variable parameters are restricted with 0.42mm and 0.18m m particle sizes of TTCNS and TAINS respectively for the removal of Ni(II) ion. Particle size determination had been carried out in chapter-III, based on the microscopic studies. Thence, the microscopic view of the chosen particle sizes viz., 0.42 mm of TTCNS and 0.18 mm of TAINS are given in figures 4.17 and 4.18.

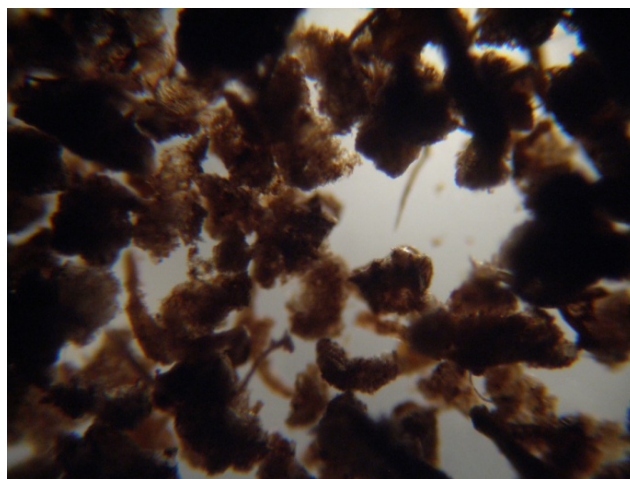


Figure 4.17 Microscopic views of TTCNS (0.42 mm)

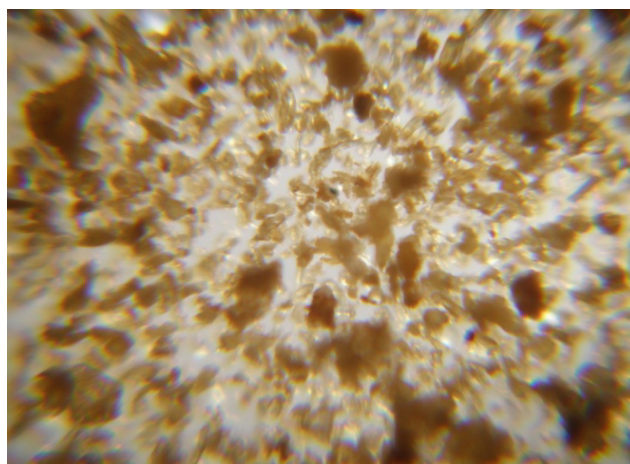


Figure 4.18 Microscopic views of TAINS (0.18 mm)

Table 4.1 Effect of Particle size (TTCNS)

Time (min)	Amount Adsorbed (mg/g)					Percentage Removal
	0.18 mm	0.24 mm	0.30 mm	0.42 mm	0.71 mm	0.42 mm
0	0	0	0	0	0	0
2	0.6	9.6	16.4	28.4	10.3	12.9
4	8.8	25.4	43.0	44.4	22.0	30.4
6	32.6	36.6	58.0	67.2	38.8	55.5
8	32.8	37.9	58.2	67.4	39.0	55.5
10	33.1	37.9	58.8	67.4	39.2	55.7
12	33.4	40.0	59.0	67.8	39.4	55.8
14	33.8	40.1	59.4	67.8	39.4	55.8

Metal ion concentration: 11 ppm; Adsorbent dose: 50 mg; pH: 3.4; Temperature: 303K.

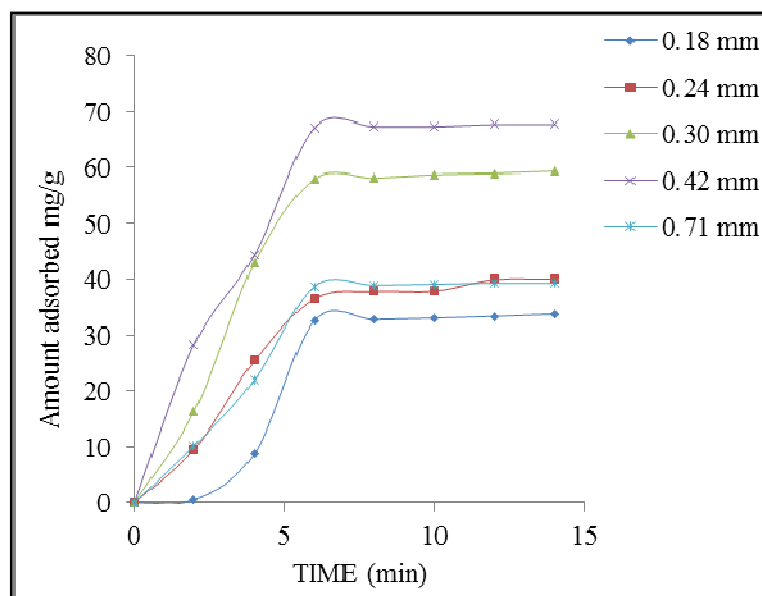
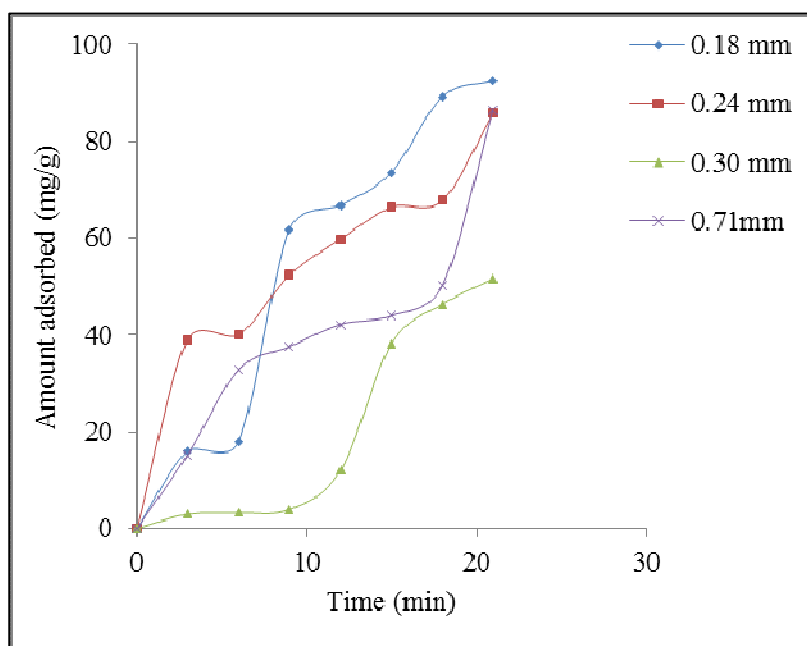
**Figure 4.19 Effect of Particle size (TTCNS)**

Table 4.2 Effect of Particle size (TAINS)

Time (min)	Amount Adsorbed (mg/g)				Percentage Removal
	0.18 mm	0.24 mm	0.30 mm	0.71 mm	0.18 mm
0	0	0	0	0	0
3	16.0	39.0	3.0	15.2	7.3
6	18.0	40.0	3.3	32.8	8.2
9	61.8	52.4	4.0	37.6	28.1
12	66.8	59.8	12.0	42.2	30.4
15	73.6	66.4	38.2	44.0	33.5
18	89.2	67.8	46.4	51.6	40.5
21	92.6	85.8	51.6	86.4	42.1

Metal ion concentration: 13 ppm; Adsorbent dose: 150 mg; pH: 7.1; Temperature: 303K.

**Figure 4.20 Effect of Particle size (TAINS)**

4.5 Effect of Contact time and Initial concentration

The contact time for the maximum adsorption of Ni(II) ions (3-13 ppm) by the sorbents were investigated at varying agitation periods a viz., (2-14 min: 2 min interval) (Tables 4.3 and 4.4) and the corresponding curves are represented in figures 4.21 and 4.22 respectively.

The amount adsorbed (mg/g) by TTCNS was 40.80, 48.40, 49.20, 54.80, 67.40 and 35.40 at an initial Ni(II) concentration of 3, 5, 7, 9, 11 and 13 ppm respectively (table 4.3). From the table, it is evident, 8 minutes is the minimum equilibrium time at which 11ppm of Ni(II) registered maximum removal. Similar observations were reported for other low-cost adsorbents²¹⁹. The amount adsorbed declined from 67.40 mg/g to 65.30 mg/g at an increasing initial concentration of 13 ppm. This may be due to the saturation of the sorption sites on the adsorbent as the concentration of the metal ions increased²²⁰.

From the table 4.4, it is evident that a minimum equilibrium time of 21 minutes was required for maximum removal of 11ppm of Ni(II) concentration. All the time profile curves are single, smooth and continuous leading to saturation, suggesting the possible monolayer coverage of metal ions on the surface of the adsorbent²²¹. The enhancement in the initial concentration of metal ions decreased the percentage removal. The data show that the metal uptake rises and the percentage adsorption of Ni(II) declines with increase in metal ion concentration. This is due to the increase in the driving force i.e. concentration gradient. At lower concentrations, almost all Ni(II) ions present in solution can interact with the binding sites and thus percentage adsorption could be higher than those at higher Ni(II) environments²²².

Table 4.3 Effect of Contact time and Initial concentration (TTCNS)

Time(min)	Amount adsorbed (mg/g)					
	3 ppm	5 ppm	7 ppm	9 ppm	11 ppm	13 ppm
2	29.4	11.0	34.2	19.6	28.4	29.3
4	37.0	33.8	42.0	48.0	44.4	40.2
6	40.4	47.8	48.6	54.0	67.2	59.0
8	40.6	48.0	49.0	54.2	67.4	65.3
10	40.8	48.4	49.2	54.8	67.4	65.3
12	41.2	48.6	49.8	54.8	67.8	65.9
14	41.4	48.6	50.0	55.0	67.8	65.9

Particle size: 0.42 mm; Adsorbent dose: 50 mg; pH: 3.4; Temperature: 303K

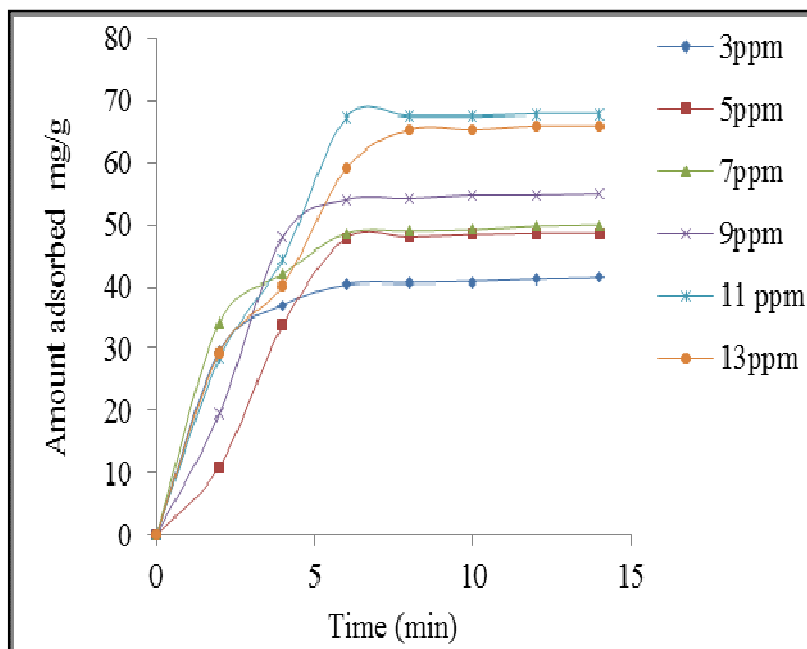
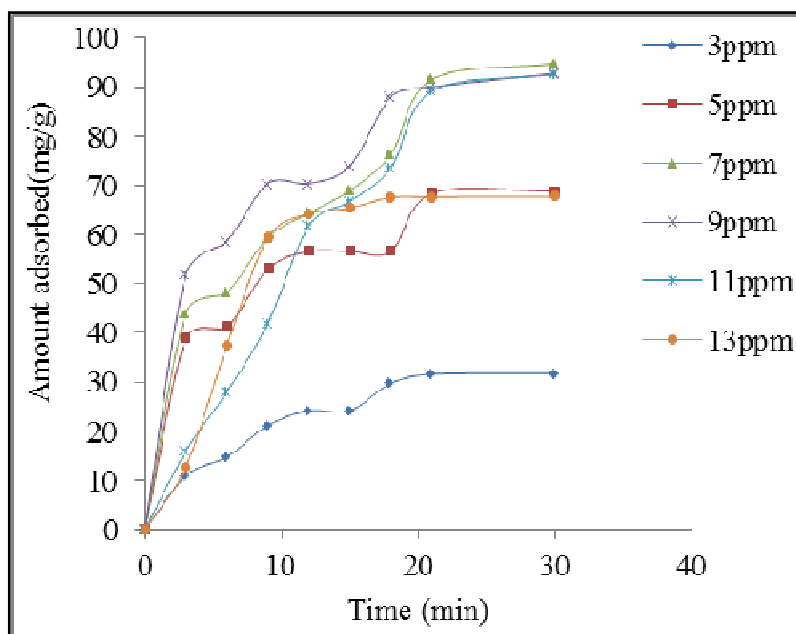
**Figure 4.21 Effect of Contact time and Initial concentration (TTCNS)**

Table 4.4 Effect of Contact time and Initial concentration (TAINS)

Time(min)	Amount adsorbed (mg/g)					
	3 ppm	5 ppm	7 ppm	9 ppm	11 ppm	13 ppm
3	11.0	38.8	44.0	51.8	16.0	12.8
6	14.8	41.2	48.2	58.6	28.0	37.4
9	21.2	53	59.4	70.4	42.0	59.4
12	24.2	56.6	64.4	70.4	61.8	64.2
15	24.2	56.6	69.0	74.0	66.8	65.4
18	29.8	56.6	76.4	88.0	73.6	67.6
21	31.6	68.4	91.6	90.0	89.2	67.7
30	31.8	68.8	94.8	92.8	92.6	67.8

Particle size: 0.18 mm; Adsorbent dose: 150 mg; pH: 7.1; Temperature: 303K

**Figure 4.22 Effect of Contact time and Initial concentration (TAINS)**

4.6 Effect of Dosage

Adsorbent dose seems to have a great influence in sorption process. It involves the attachment of the material to be adsorbed onto adsorbent at available adsorption sites²²³. Dose of adsorbent added into the solution determine the number of binding sites available for adsorption. The effect of varied doses of TTCNS is depicted in figure 4.23 and the corresponding values are given in table 4.5. The smooth curves obtained as evident from the figure.4.23 indicated that Ni(II) removal increased with adsorbent doses for the given initial concentration, because higher dosages provide greater surface area and increased pore volume for greater adsorption^{217,220,224, 225}. The amount of metal ion adsorbed at an optimum contact time of 8 minutes, varied from 22.2 mg/g to 67.4 mg/g (table 4.5) for the TTCNS dosage of 20 mg to 50 mg. This may be attributed to the fact that for a fixed initial solute concentration, increasing adsorbent doses provide greater surface area. Further dosage, did not register appreciable changes in adsorption percentage. Therefore, 50 mg adsorbent dosage was fixed as optimum for further studies, beyond which the system did not register appreciable change in th amount adsorbed.

The effect of adsorbent dose on Ni(II) uptake was investigated by varying the TAINS dose (50-200mg; 50 mg interval) and the results are tabulated in table 4.6. After a certain dose of adsorbent, maximum adsorption is obtained and hence the ratio of the amount of ions bound to the adsorbent and the amount of free ions remain constant even with the further addition of dosage of the adsorbent²²⁶. The experimental results showed that the amount of Ni(II) adsorbed (mg/g) is proportional to the dosage variation upto 150 mg (fig 4.24). Thus, 150 mg was optimized for further experiments carried out employing TAINS. Similar results on adsorbent dose were reported for the removal of Ni(II) by various low-cost adsorbents such as tea waste²²⁷, *Carica papaya*²²⁷ and tamarind seeds²²⁸

Table 4.5 Effect of Adsorbent dose (TTCNS)

Time (min)	Amount adsorbed mg/g				
	20 mg	30 mg	40 mg	50 mg	60 mg
0	0	0	0	0	0
2	06.0	18.9	25.2	28.4	31.4
4	16.0	25.1	36.4	44.4	41.5
6	22.0	26.1	45.0	67.2	63.8
8	22.2	26.3	45.0	67.4	64.4
10	22.6	27.8	45.2	67.4	66.4
12	22.6	27.9	45.6	67.8	67.2
14	23.0	28.2	45.8	67.8	67.2

Initial metal ion concentration 11 ppm; pH: 3.4; Temperature: 303K

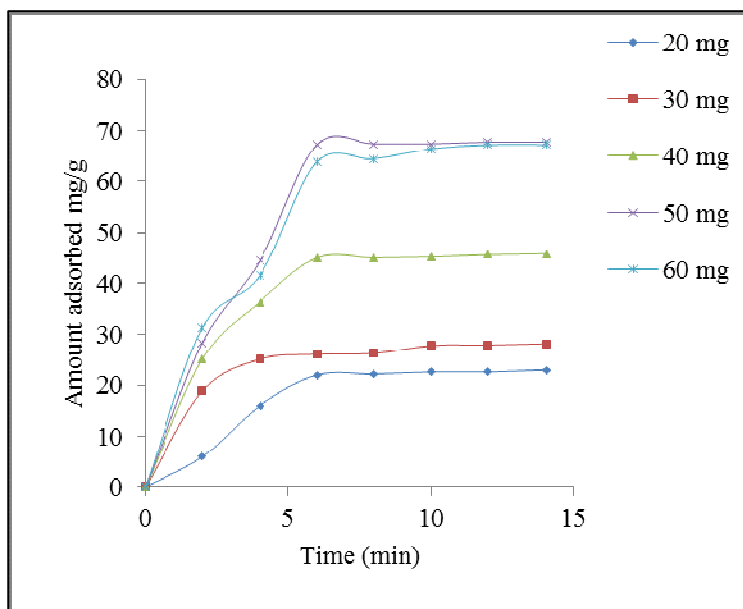
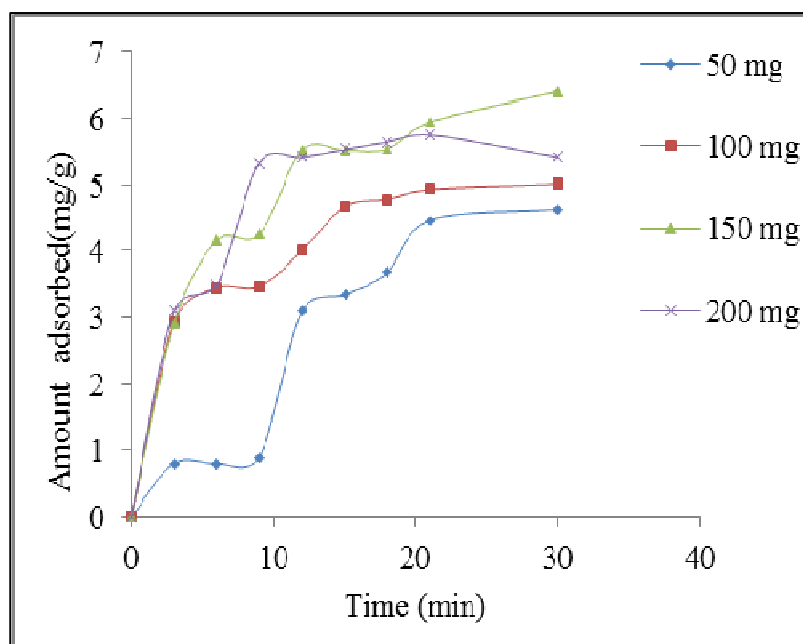
**Figure 4.23 Effect of Adsorbent dose (TTCNS)**

Table 4.6 Effect of Adsorbent dose (TAINS)

Time (min)	Amount Adsorbed (mg/g)			
	50 mg	100 mg	150 mg	200 mg
0	0	0	0	0
3	0.80	2.93	2.90	3.09
6	0.80	3.45	4.15	3.49
9	0.90	3.47	4.25	5.32
12	3.09	4.00	5.51	5.40
15	3.34	4.67	5.51	5.52
18	3.68	4.78	5.53	5.64
21	4.46	4.93	5.94	5.75
30	4.63	5.01	6.40	5.40

Initial metal ion concentration: 11 ppm; pH: 7.1; Temperature: 303K

**Figure 4.24 Effect of Adsorbent dose (TAINS)**

4.7 Effect of pH

4.7.1 pH studies for Ni(II) onto TTCNS

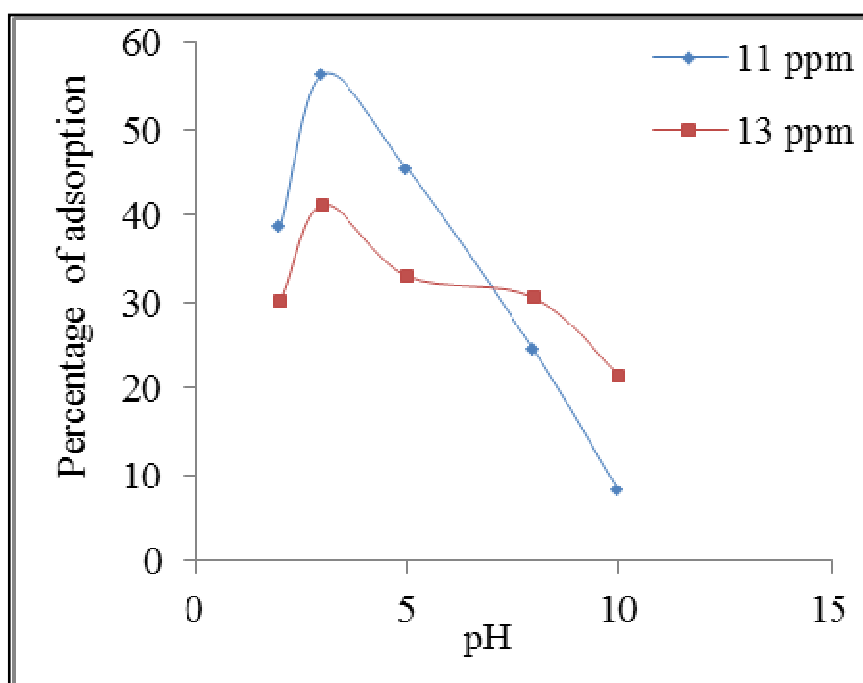
The pH of the aqueous solution is one of the most important parameters controlling uptake of heavy metals from wastewaters and aqueous solutions. The acidity of the medium affects the competition ability of hydrogen ions with metal ions towards the active sites on the adsorption surface. It also influences ionization of functional groups on the adsorbent surface and chemical speciation of metal ions.

The effect of pH on the adsorption of Ni(II) onto TTCNS for an initial concentration of 11 and 13 ppm is given in table 4.7. The influence of pH on the adsorption of Ni (II) ions onto TTCNS was studied by varying the initial pH from 2 to 10 and the results are depicted in figure 4.25. It is apparent from the results, that the adsorption was very low between the pH 2 to 3. The steep curve indicates that the percentage adsorption was minimum below the optimal pH 3.4 (fig 4.25) which shall be explained as at a low pH, due to high concentration and mobility of H^+ ions, the hydrogen ions preferentially get adsorbed onto the sorbent sites²³⁰. For this reason, the optimal pH value was fixed to be 3.4. At this pH, the maximum metal removal by TTCNS was determined as 56.36% and 41.25% for the respective concentrations of Ni(II). Above pH >5, the Ni (II) ions got precipitated due to hydroxide ion formation. Madhava Rao et al.,²³¹ reported similar trend in the removal of Pb(II) ions utilizing agricultural wastes.

Table 4.7 Effect of pH (TTCNS)

Percentage of adsorption at varying pH values					
Metal ion concn.(ppm)	2	3	5	8	10
11	38.85	56.36	45.45	24.45	8.18
13	30.24	41.25	33.08	30.61	21.50

Adsorbent dose: 50mg; Agitation time: 8 min; Temperature: 303K

**Figure 4.25 Effect of pH (TTCNS)**

4.7.2 pH studies for Ni(II) onto TAINS

The effect of pH on the adsorption of Ni (II) -TAINS system was studied by varying the initial pH from 3 to 10, the results being listed in table 4.8 and the plot in figure 4.26. It is obvious from the figure that the percentage removal increased at increasing pH environments and maximum removal was observed at pH 7.1. Above these values, the removal was found to decrease above pH 9.0. So the studies were restricted upto pH 7.1.

As pH approaches to 7, the competition of hydrogen ions becomes negligible and more Ni(II) ions are bound to the adsorbent. The maximum removal of Ni(II) is found to be 48.9 % and 47.7% for 11ppm and 13ppm respectively. The reason can be attributed to the higher electronegative characteristics (polar groups like $-\text{NH}_2$, $-\text{COOH}$, $-\text{OH}$ etc) of the adsorbent material. The ingredients contribute an electro negativity of 35.1%. S.A.Bhale Rao et al.,²³² reported similar effect in favour of neutral pH.

Table 4.8 Effect of pH (TAINS)

Percentage of adsorption at varying pH values					
Metal ion concn.(ppm)	2	3	5	8	10
11	20.88	27.20	48.90	24.45	28.09
13	22.01	29.41	47.70	31.10	23.45

Adsorbent dose: 150mg; Agitation time: 21 min; Temperature: 303K

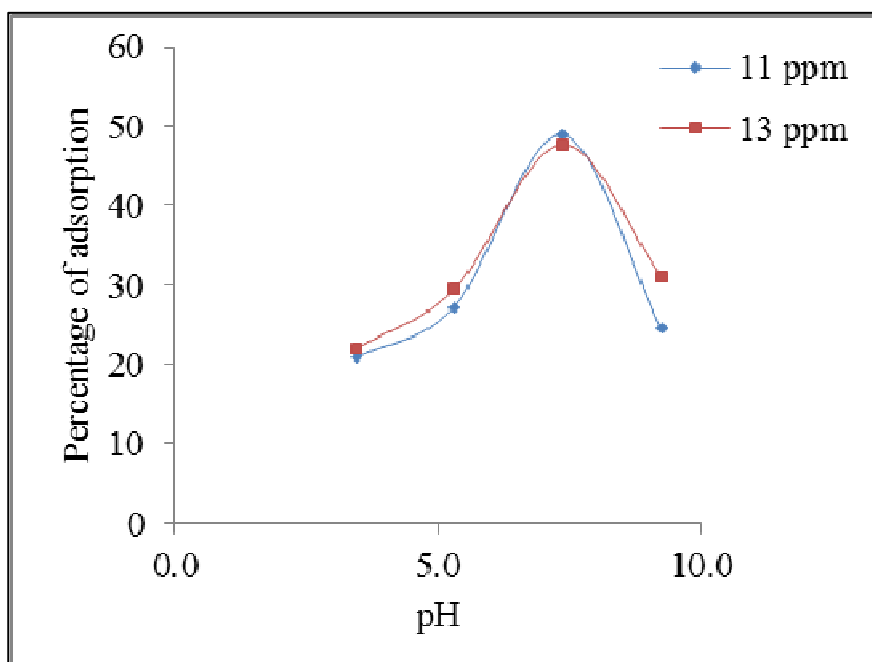


Figure 4.26 Effect of pH (TAINS)

4.8 Effect of Cations

The influence of cations such as sodium, potassium and magnesium on the Ni (II)-TTCNS and Ni (II)-TAINS systems were carried out at varied concentrations of the cations. The corresponding plots are represented in figures 4.27 and 4.28 and the values in tables 4.9 and 4.10 respectively. It is evident from the results that the adsorption decreased with increase in the concentration of interfering metal ions. Ni(II) removal by both TTCNS and TAINS were reduced by K^+ ions to a greater extent than Na^+ and Mg^{2+} ions. This can be explained in terms of ionic radii of the respective metal ions. Ionic radii²³³ of Na^+ and Mg^{2+} are $1.02A^0$ and $0.72A^0$ while that of K^+ is $1.38A^0$. Smaller the size of the ion, greater is the degree of hydration. So the hydrated ionic radius of $Mg^{2+} > Na^+ > K^+$. For the ions of same valence, the extent of exchange reaction increases with decreasing hydrated radius. This is so because, ions with smaller hydrated radii decrease the swelling pressure within the sorbent and increase the affinity of the sorbent for such ions. The effect of diverse ions on heavy metal ions have been reported by Shubha et al.²³⁴

4.9 Effect of Anions

The influence of chloride, sulphate and nitrate ions in trapping Ni(II) are depicted in figures 4.27 and 4.28 and the values are listed in tables 4.9 and 4.10 respectively. The experiments were carried out at different concentrations of anions ranging from 11 to 100 mg/L. The percentage removal decreased with increase in the concentration of anions in a varying manner. The inhibition of chloride ion on the percentage removal of Ni (II) is found to be higher compared to nitrate and sulphate ions. This may be due to the formation of chloro complexes of Ni(II) namely $NiCl$, $NiCl_2$, $NiCl_3^-$ which have low sorption capacity and the formation of stable hydroxo chloro complex $Ni(OH)Cl$ by the hydrolysis of $NiCl_2$, all of which are not adsorbed to the same extent²³⁵ as Ni^{2+} . Moreover, the formations of complexes reduce the availability of free Ni(II) ions for the sorbents' surface, hence a decrease is observed. The presence of nitrate and sulphate anions do not affect the removal efficiency of Ni(II) by

TAINS to a large extent, but the removal efficiency of Ni(II) by TTCNS is decreased at increasing concentrations of these ions.

Table 4.9 Effect of Cations and Anions (TTCNS)

Conc. of ions (ppm)	% adsorption			% adsorption		
	Mg ²⁺	Na ⁺	K ⁺	NO ₃ ⁻	Cl ⁻	SO ₄ ²⁻
0	50.0	50.0	50.0	50.0	50.0	50.0
11	32.3	45.8	48.0	45.2	46.4	37.4
25	22.9	31.4	36.3	35.0	24.7	32.1
50	20.2	34.0	26.5	15.6	23.7	25.6
75	19.9	20.1	16.5	12.2	20.5	11.3
100	17.4	18.0	10.5	8.0	3.5	6.9

Concentration of metal ion: 11 mg/L; Adsorbent dose: 50 mg; pH: 3.4; Temperature: 303K

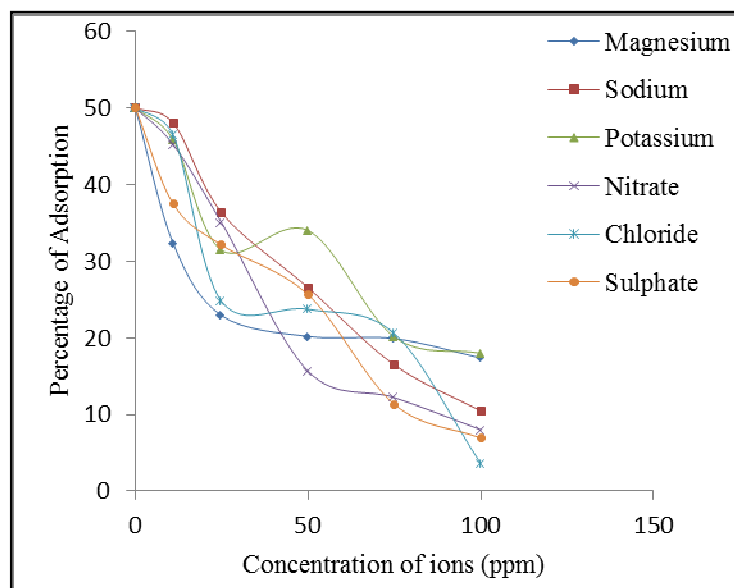
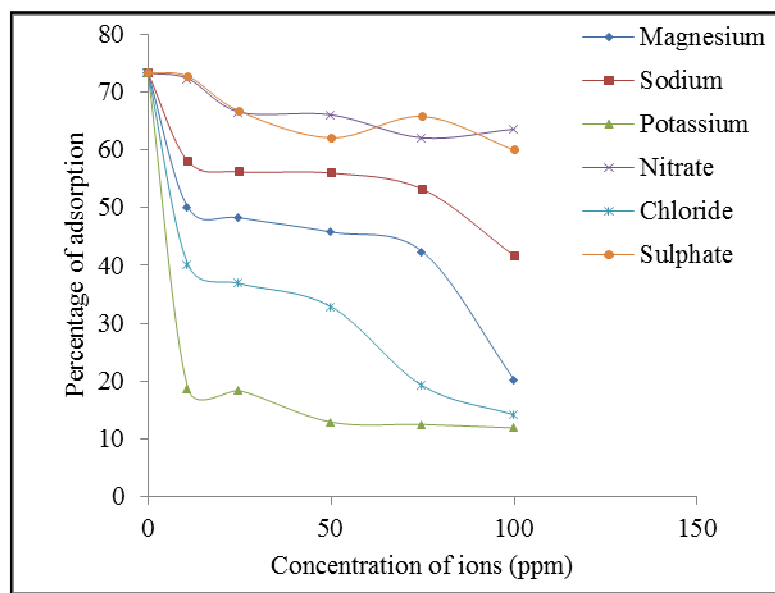


Figure 4.27 Effect of Cations and Anions (TTCNS)

Table 4.10 Effect of Cations and Anions (TAINS)

Conc. of ions (ppm)	% adsorption			% adsorption		
	Mg ²⁺	Na ⁺	K ⁺	NO ₃ ⁻	Cl ⁻	SO ₄ ²⁻
0	73.3	73.3	73.3	73.3	73.3	73.3
11	50.0	58.0	18.6	72.3	40.1	72.7
25	48.3	56.2	18.4	66.5	36.9	66.7
50	45.8	56.0	12.9	66.1	32.9	62.1
75	42.4	53.2	12.5	62.1	19.2	65.8
100	20.3	41.7	11.9	63.6	14.2	60.0

Concentration of metal ion: 11 mg/L Adsorbent dose: 150 mg pH: 7.1 Temperature: 303K

**Figure 4.28 Effect of Cations and Anions (TAINS)**

4.10 Effect of Co-ions

Study of the influence of co-ions on the removal of a specific metal ion becomes relevant when selective adsorption of metal ions occurs from the effluent systems. The percentage removal of Ni(II) by TTCNS and TAINS in the absence and presence of co-ions are depicted in figures 4.29 and 4.30. The results revealed that Ni(II) removal was very slightly affected by 6 to 8 % in the presence of Cr(VI) ions. Speciation diagram of Cr(VI) shows that between pH 1 and 6, Cr(VI) is mainly existing as HCrO_4^- ions²³⁶. The surface of the adsorbent is less protonated around pH 3-6 where maximum adsorption of Ni(II) had occurred. The decrease in electrostatic interaction between the adsorbent surface and HCrO_4^- ions may be one of the reasons for the non-inhibiting nature of Cr(VI). The increase in hydrated ionic radii due to extensive hydration of Cr(VI) retards itself from being trapped onto the sorbent surface. This may be the other reason for the minimal inhibiting effect of Cr(VI) on Ni(II) removal²³⁷ by TTCNS and TAINS. The presence of Co(II) decreased the removal of Ni(II) by TTCNS and TAINS from 50.0% to 13.6% (fig 4.29) and from 68.1 % to 8.1 % (fig 4.30) respectively.

The influence of co-ions, is slightly more for Ni(II) removal by TAINS than for Ni(II) removal by TTCNS. This may be explained on the basis of the slightly higher electronegativity characteristics of TAINS as compared to TTCNS²³⁷. The presence of few polar groups in the phytochemical composition of TAINS creates little availability for the divalent metal ions to involve in weak electrostatic interaction.

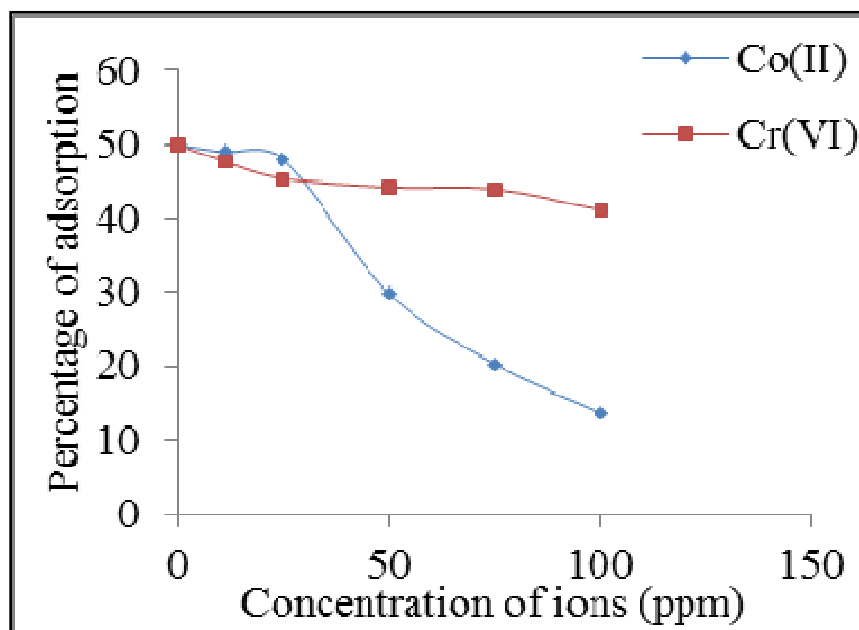


Figure 4.29 Effect of Co-ions (TTCNS)

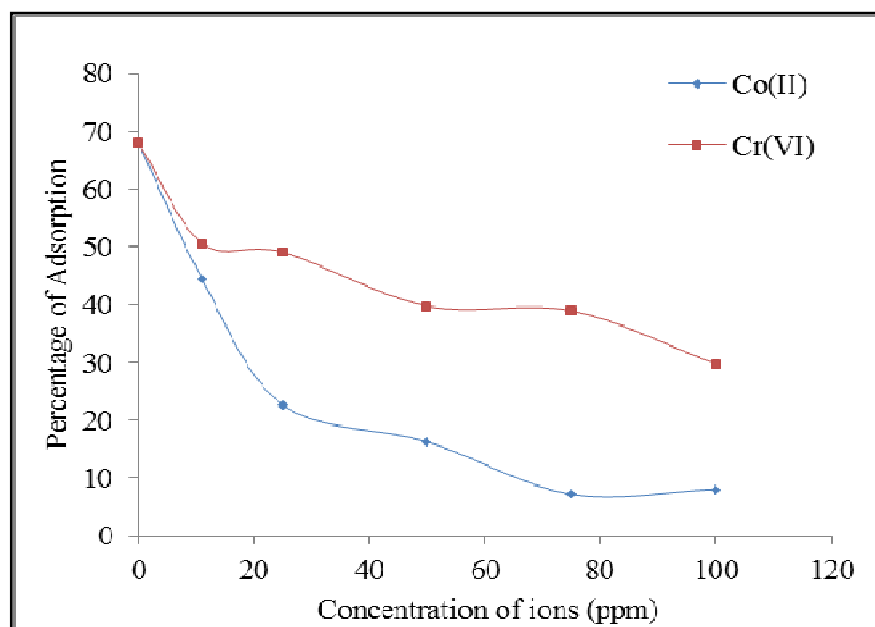


Figure 4.30 Effect of Co-ions (TAINS)

4.11 Effect of Temperature

To determine the effect of temperature on the adsorption study of Ni(II) using TTCNS and TAINS, experiments were conducted at 293, 303, 313 and 323 K. It was

observed that the adsorption capacities of Ni(II) increased with temperature. As a typical case, the effects of temperature on Ni(II) sorption by TTCNS and TAINS are illustrated in figures 4.31 and 4.32 and corresponding data in tables 4.11 and 4.12. The enhancement of adsorption capacity at higher temperature may be attributed to the desolvation of adsorbing species, increase in the number of active sites available for adsorption onto the adsorbent, enlargement of pore size of the adsorbent or due to decrease in the boundary layer thickness surrounding the sorbent, so that the mass transfer resistance of adsorbate in the boundary layer is retarded²³⁸

Table 4.11 Effect of Temperature (TTCNS)

Conc. of ions (ppm)	Percentage Removal				
	293K	303 K	313 K	323 K	333 K
3	61.3	65.1	81	82.2	83.4
5	39.8	41.3	51.0	61.0	64.7
7	28.2	48.1	86.7	85.2	88.1
9	14.0	34.0	84.4	86.8	87.4
11	15.2	73.0	87.1	83.0	84.9

Adsorbent dose: 50 mg; pH: 3.4; Agitation time: 8 min

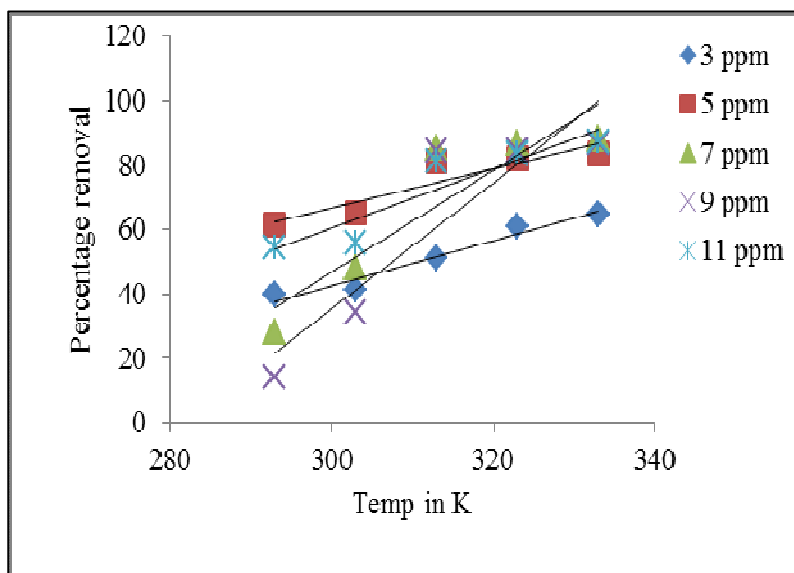


Figure 4.31 Effect of Temperature (TTCNS)

Table 4.12 Effect of Temperature (TAINS)

Conc. of ions (ppm)	Percentage Removal				
	293K	303 K	313 K	323 K	333 K
3	10.7	30.3	33.3	34.3	51.3
5	27.9	44.1	69.4	71.4	73.2
7	35.5	44.3	67.6	72.8	74.2
9	30.7	42.8	70.4	73.7	73.7
11	18.1	30.0	68.5	71.4	71.4

Adsorbent dose: 150 mg; pH: 7.1; Agitation time: 21 min

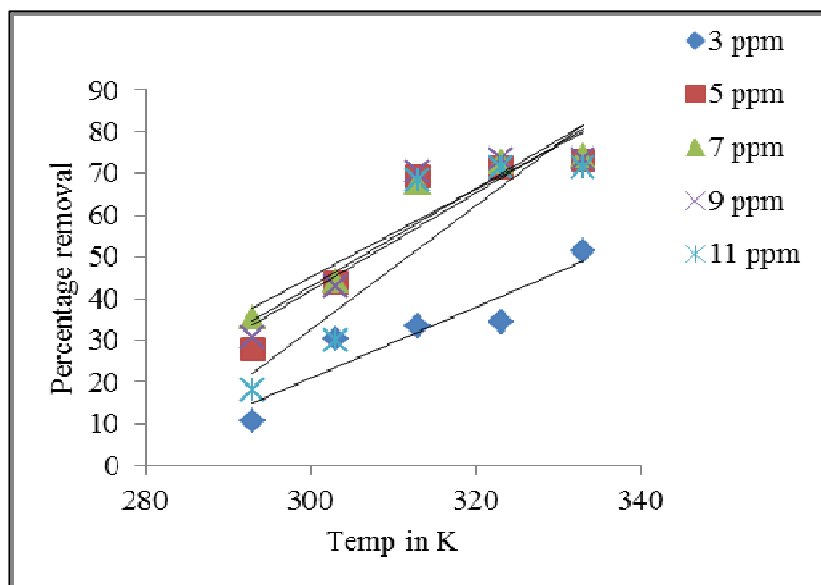


Figure 4.32 Effect of Temperature (TAINS)

4.12 Desorption

A successful desorption process requires the proper selection of the eluents which strongly depend on the type of sorbent and the mechanism of sorption. The selected eluent must be effective, harmless for the sorbent, non-polluting and cheap. For such purposes, dilute solution of mineral acids such as HCl and HNO₃ are used to desorb²³⁹ metal ions. The effects of HCl strengths on the desorption of Ni(II) from TTCNS and TAINS were investigated and the plots are shown in figures 4.33 and 4.44. The percentage of desorption increased from 75.75 to 90.12 with the increasing strengths of HCl for Ni(II)-TTCNS system and from 29.37 to 83.20 for Ni(II)-TAINS system. This indicates that higher concentrations of HCl are more efficient in releasing Ni(II) ions. In acidic conditions, Ni(II) cations are displaced by protons from the binding sites.

As a typical case, it is obvious from figure 4.44 that desorption percentage increased when the HCl strength increased from 0.05 to 0.40 M. The recovery of Ni(II) by HCl is due to a combination of H⁺ attack, which promotes displacement of metal from the binding sites. The maximum desorption shown by Ni(II) from TTCNS and TAINS are 90.12% and 83.20%

respectively. Such partial desorption for divalent metal ions had been reported by earlier workers^{240, 241}. Complete desorption will indicate ion exchange mechanism in the adsorption process. In the present study, the incomplete desorption attained in both cases indicates that in addition to ion exchange mechanism, surface complexation may have been involved in the adsorption.

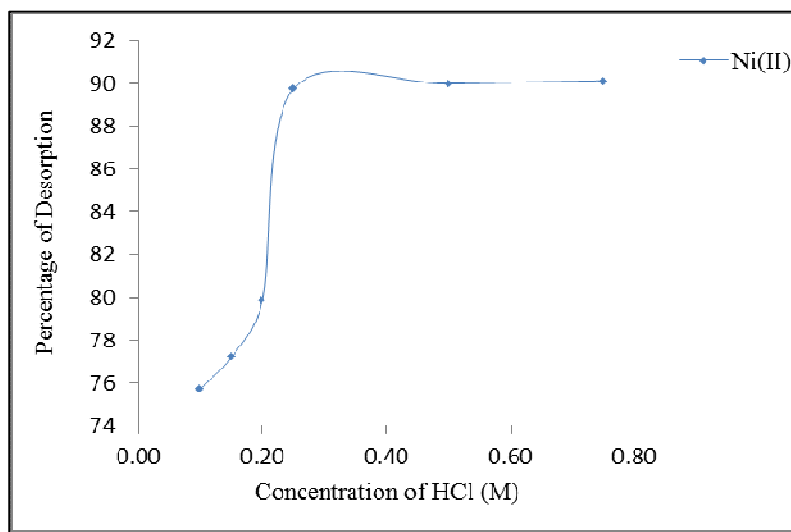


Fig 4.33 Desorption of Ni(II) [TTCNS]

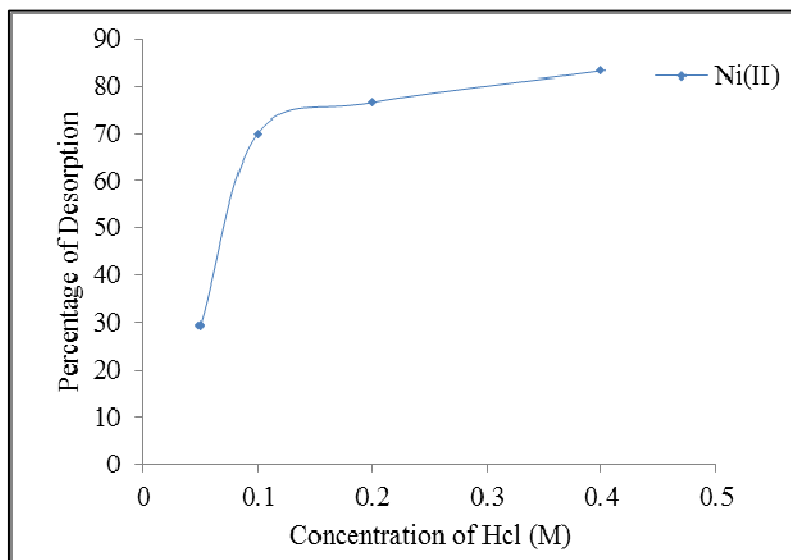


Fig 4.34 Desorption of Ni(II) [TAINS]

4.13 Regeneration of TTCNS and TAINS

To test the suitability and stability of the sorbent, 11 ppm of Ni(II) loaded TTCNS and loaded TAINS each of 200 mg was subjected to successive adsorption and desorption cycles with 0.75 M and 0.40 M HCl as the desorbing agent for Ni (II)

The adsorption and desorption cycles are shown in figures 4.35 and 4.36. The amounts of Ni(II) adsorbed onto TTCNS and TAINS were 10.28, 9.52, 8.96 mg/g and 10.25, 8.43, 7.95 mg/g in the first, second and third cycles. The corresponding desorbed amounts were 9.55, 8.27, 7.12 mg/g and 8.22, 7.46 and 7.25 mg/g for the respective systems. The desorption efficiencies were found to be 86.30% and 86.54% for Ni(II)-TTCNS and TAINS systems respectively as per the equation (9). The partial desorption may be due to the fact that a portion of adsorbed metals are not recoverable by regeneration. It can be inferred that the metals are bound through strong interactions and as a result, the sorption efficiency is reduced.

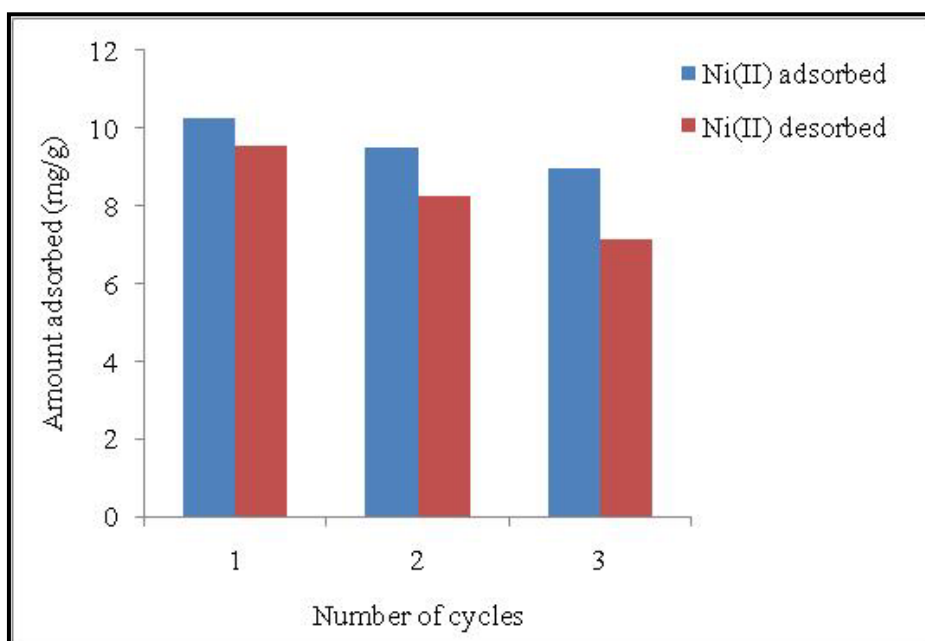


Fig 4.35 Regeneration [Ni(II)-TTCNS]

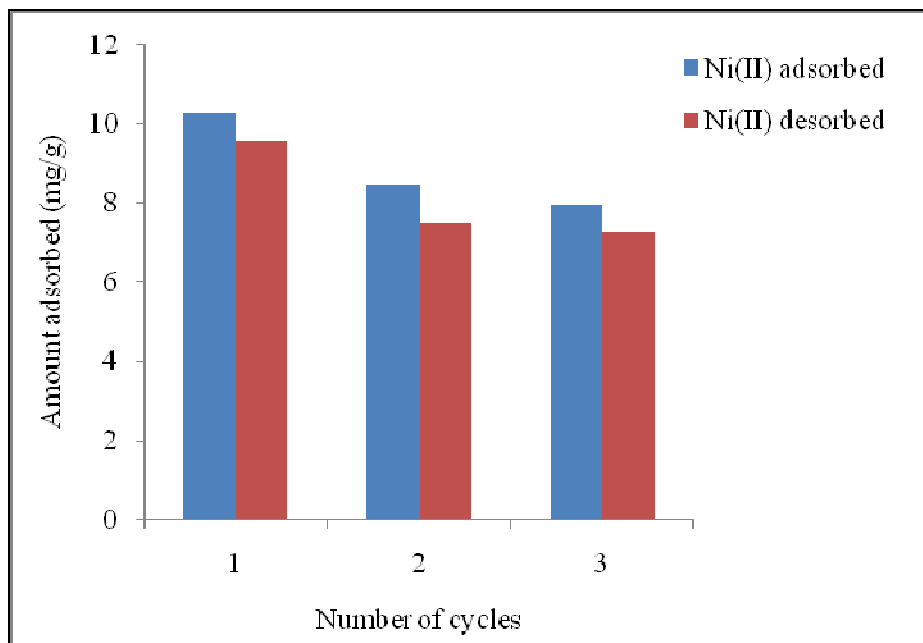


Fig 4.36 Regeneration [Ni(II)-TAINS]

4.14 Adsorption Isotherm

The equilibrium study on adsorption has provided sufficient information on the capacity of the adsorbent. An adsorption isotherm is characterized by certain constant values that express the surface properties and affinity of the sorbent²⁴². It can also be used to compare the adsorptive capacities of the various adsorbents. The adsorption isotherms for Ni(II) removal were carried out using adsorbent dosages of 50 mg TTCNS and 150 mg TAINS respectively for metal ion concentrations between 3 to 11 mg/L. The linear fit of the Langmuir, Freundlich, Tempkin and Dubinin-Kaganer- Radushkevich isotherm models are depicted in respective figures and the corresponding isothermal constants are tabulated in table 4.18.

4.14.1 Langmuir isotherm model

The mostly used Langmuir model assumes that²⁴³

- i. Sorption occurs at specific homogeneous adsorption sites each of which can hold only one molecule.
- ii. The adsorption is limited to monolayer
- iii. All adsorption sites are energetically equivalent and there is no interaction or migration between the adsorbed ions on the surface of adsorbent

Langmuir Isotherm model can be written as follows²⁴⁴

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m} \quad \dots (10)$$

where q_e is the equilibrium metal ion concentration on the sorbent (mg/g), C_e is the equilibrium metal ion concentration in solution (mg/L), q_m is the maximum monolayer adsorption capacity of the sorbent (mg/g) and b is the Langmuir sorption constant (L/mg) related to the free energy of sorption. The Langmuir constants q_m and b were determined from the linear plot of C_e/q_e versus C_e , which has a slope of $1/q_m$ and intercept of $1/bq_m$. Higher the value of b , higher is the affinity of adsorbent for the metal to be sorbed²⁴⁵.

Separation factor (R_L)

The linearity of the Langmuir isotherm can be used to predict whether a sorption system is favourable or unfavourable. It assumes that a monomolecular layer is formed when adsorption takes place and that there is no interaction between molecules adsorbed on adjacent binding sites. Accordingly, the essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless parameter called the separation factor or equilibrium parameter R_L , which is defined by the following relationship¹⁸⁴

$$R_L = \frac{1}{(1 + b C_i)} \quad \dots (11)$$

where, C_i is the initial metal ion concentration (mg/L). The parameter R_L indicates the shape of the isotherm and the nature of the sorption process²⁴⁶ shall be

$R_L > 1$ Unfavourable isotherm $R_L = 1$ Linear isotherm

$R_L = 0$ Irreversible isotherm $0 < R_L < 1$ Favourable isotherm

The Langmuir isotherm data for the Ni(II)-TTCNS and Ni(II)-TAINS systems are given in table 4.13 and the plots in figures 4.37, 4.38. The correlation coefficients (R^2) for the metal with two adsorbents are approximately 0.99. The R_L values for Ni(II)-TTCNS system are between 0.08 and 0.26 and for Ni(II)-TAINS system are between 0.13 and 0.40 (Table 4.14) indicating favorable adsorption.

Table 4.13 Equilibrium concentrations - Langmuir isotherm

Conc. of metal ion (ppm)	Ni(II) -TTCNS		Ni(II) -TAINS	
	C_e	C_e/q_e	C_e	C_e/q_e
3	0.08	0.0019	1.79	0.0285
5	2.57	0.0528	2.17	0.0383
7	4.61	0.0964	4.73	0.0739
9	6.30	0.1136	5.48	0.0778
11	7.64	0.1166	7.91	0.1279
13	7.95	0.1184	8.54	0.1293

Adsorbent dose: 50mg (TTCNS), 150mg (TAINS) Temperature: 303K

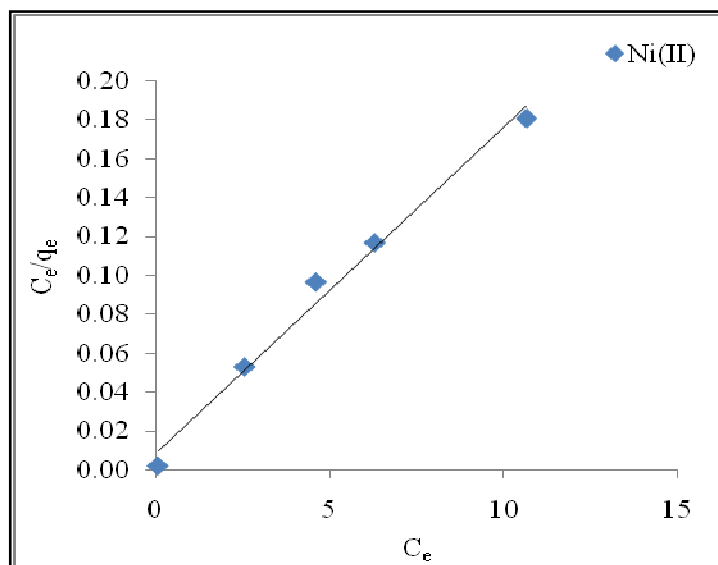


Figure 4.37 Langmuir isotherm model [Ni(II)-TTCNS]

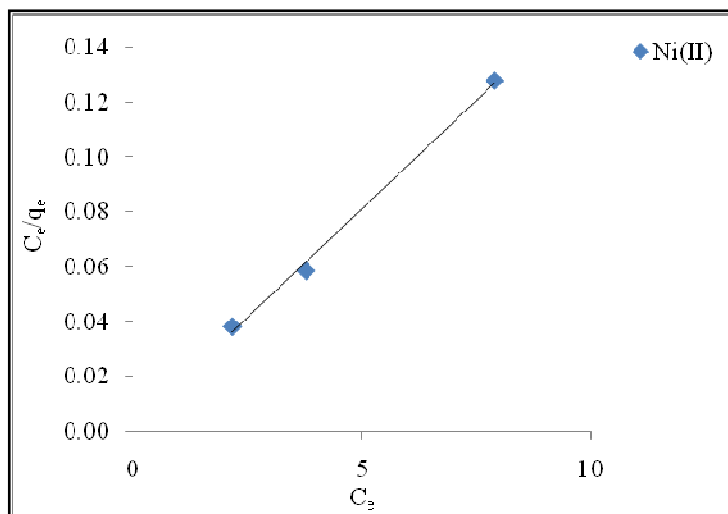


Figure 4.38 Langmuir isotherm model [Ni(II)-TAINS]

Table 4.14 Equilibrium parameter (R_L)

Conc. of metal ion (ppm)	Ni(II)-TTCNS	Ni(II)-TAINS
3	0.40	0.26
5	0.29	0.18
7	0.22	0.13
9	0.18	0.11
11	0.15	0.09
13	0.13	0.08

4.14.2 Freundlich isotherm model

The Freundlich isotherm is the most widely used non-linear sorption model. This model proposes a multilayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interaction between adsorbed molecules. The empirical form of this model is represented as²⁴⁵

$$q_e = K_F C_e^{1/n} \quad \dots (12)$$

where, K_F and $1/n$ are the Freundlich's constants related to the adsorption capacity (mg/g) and adsorption intensity of the adsorbent respectively, which vary with the heterogeneity of the adsorbent.

The Freundlich equation is expressed linearly as

$$\log q_e = \log K_F + 1/n \log C_e \quad \dots (13)$$

The values of K_F and $1/n$ were obtained from the intercept and slope of a plot of $\log q_e$ versus $\log C_e$. The adsorption is favourable for the n values in the range $1-10^{247}$. The larger the K_F and smaller the $1/n$ values, greater is the adsorption capacity and adsorption

intensity of the adsorbent for the metal ions²⁴⁸. A smaller value of $1/n$ indicates better adsorption and formation of relatively strong bond between the adsorbate and the adsorbent²⁴⁹. The Freundlich isotherm data for Ni(II) with two adsorbents are listed in table 4.15 and the linear plots are illustrated in figures 4.39 and 4.40.

Table 4.15 Equilibrium concentrations - Freundlich isotherm

Conc. of metal ion (ppm)	Ni(II)-TTCNS		Ni(II)-TAINS	
	log C_e	log q_e	log C_e	log q_e
3	-1.0970	1.6060	0.2528	1.3838
5	0.4099	1.6860	0.3384	1.7528
7	0.6637	1.6790	0.5774	1.8088
9	0.6900	1.7320	0.7387	1.8475
11	0.7993	2.0860	0.8987	1.7909
13	0.8015	2.5431	0.6748	2.2180

Adsorbent dose : 50mg (TTCNS), 150mg (TAINS) Temperature: 303K

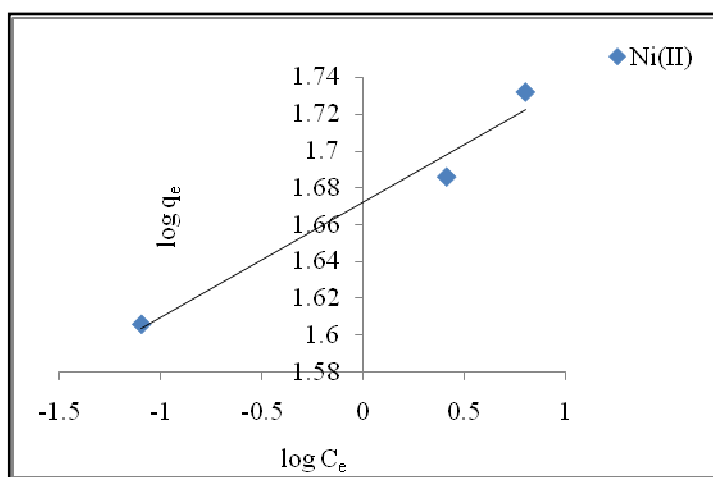


Figure 4.39 Freundlich isotherm model [Ni(II)-TTCNS]

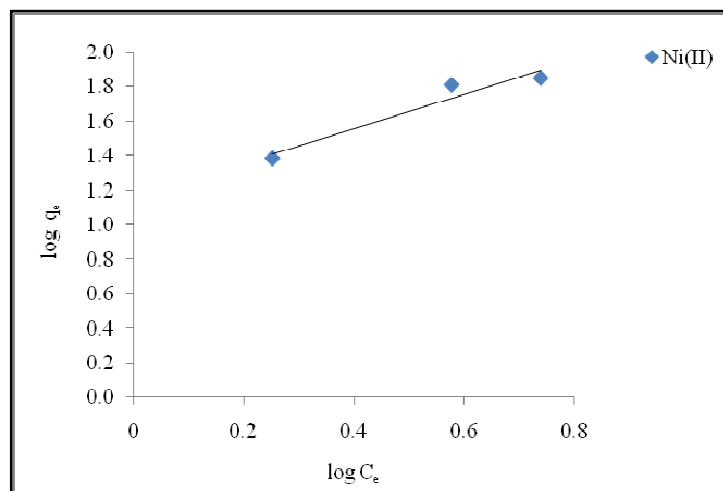


Figure 4.40 Freundlich isotherm model [Ni(II)-TAINS]

The K_F and n values are in the order as Ni(II)-TTCNS > Ni(II)-TAINS. The n values (table 4.18) for metal adsorption with two adsorbents 1.594 and 1.947 indicate that the adsorption of Ni(II) onto these two adsorbents was favourable at the performed experimental condition. However, correlation coefficient, which is a measure of how well the predicted values from a forecast model shall fit with the real time data, implies that the Langmuir model fit in well for the Ni(II)-TTCNS & TAINS systems under study when compared to Freundlich model. Similar research findings were observed for the removal of Ni(II) from aqueous solutions^{220,250}.

4.14.3 Tempkin isotherm model

Tempkin isotherm equation contains a factor that explicitly takes into account adsorbent-adsorbate interactions. It assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate-adsorbate repulsions and the adsorption is a uniform distribution of maximum binding energy²⁵¹. The linearized form of isotherm is²⁵²

$$q_e = B_T \ln A_T + B_T \ln C_e \quad \dots (14)$$

where, $B_T = RT/b_T$, T is the absolute temperature in Kelvin and R is the universal gas constant, 8.314 J/mol K . The constant b_T is related to the heat of sorption. The constant A_T is the equilibrium binding constant corresponding to the maximum binding energy. The Tempkin constants A_T and b_T were obtained from the intercept and slope of the linear plots of q_e vs $\ln C_e$ as shown in figure 4.41, 4.42 and the equilibrium data in table 4.16. The constants are tabulated in table 4.18. Ni(II)-TTCNS and TAINS systems recorded a correlation coefficient value approximating to 0.96 which indicates the best fit of the model for these systems under study. P.Senthil Kumar et al.,²⁵³ had reported similar observations in the equilibrium and kinetic studies of Ni(II) adsorption using Bael leaf powder.

Table 4.16 Equilibrium concentrations - Tempkin isotherm

Conc. of metal ion (ppm)	Ni(II)-TTCNS		Ni(II)-TAINS	
	$\ln C_e$	q_e	$\ln C_e$	q_e
3	-2.526	40.4	0.532	24.2
5	0.944	48.6	0.778	56.6
7	1.529	47.8	1.33	61.8
9	1.841	54.0	1.701	64.4
11	2.033	59.0	2.068	70.4
13	2.366	67.2	1.554	165.4

Adsorbent dose : 50mg (TTCNS) 150mg (TNSS) Temperature: 303K

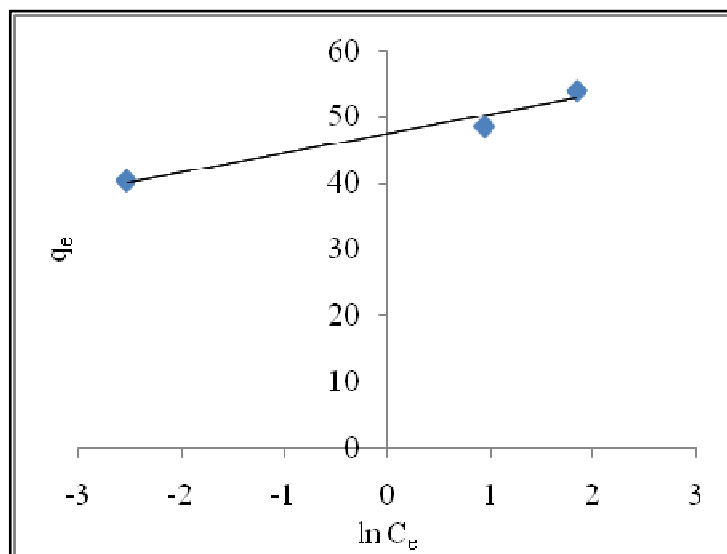


Figure 4.41 Tempkin isotherm model [Ni(II)-TTCNS]

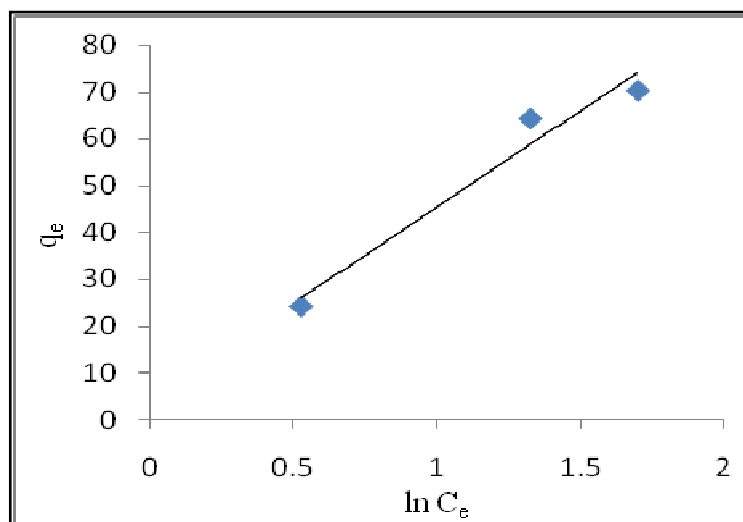


Figure 4.42 Tempkin isotherm model [Ni(II)-TAINS]

4.14.4 Dubinin--Kaganer-Radushkevich (DKR) isotherm model

This model is more general than the Langmuir model, since it does not assume a homogeneous surface or a constant sorption potential. This model which assumes a

monolayer adsorption permits to evaluate the maximal adsorption capacity and distinguish between physical and chemical adsorption of metal ions²⁵⁴.

The linear form of the DKR isotherm equation is²⁵⁵

$$\ln q_e = \ln q_s - \beta_{DR} \varepsilon^2 \quad \dots (15)$$

where, q_e is the amount of metal ions adsorbed per unit weight of the adsorbent (mol/g), q_s is the theoretical saturation sorption capacity (mol/g), β_{DR} is a constant related to mean free energy of sorption per mole of the sorbate (mol^2/J^2) and ε corresponds to Polanyi potential, which is equal to $RT \ln (1+1/C_e)$, where R is the gas constant expressed in J/mol K units and T (K) is the absolute temperature. The values of q_s and β_{DR} were obtained from the linear plot of $\ln q_e$ versus ε^2 .

The constant β_{DR} gives an idea about the mean free energy E (kJ/mol) of sorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated using the relationship.

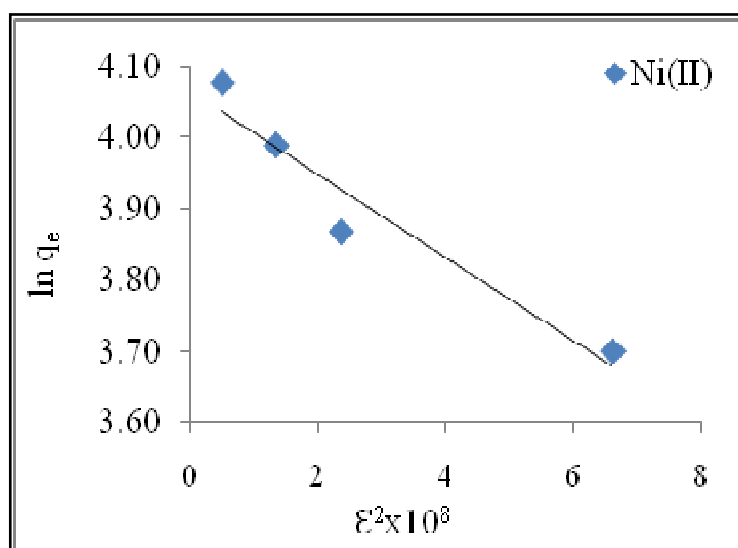
$$E = \frac{1}{(2 \beta_{DR})^{1/2}} \quad \dots (16)$$

This parameter gives information about sorption mechanism which may be chemical ion exchange or physical sorption. If the magnitude of E is between 8 and 16 kJ/mol, the sorption process follows chemical ion exchange, and for the values of $E < 8$ kJ/mol, the sorption process is of physical nature²⁵⁶. The DKR isotherm model fits well with the equilibrium data as shown in table 4.17, figures 4.43, 4.44 and the correlation coefficients reported in table 4.18. The E value obtained from the Dubinin-Radushkevich constant K are $15.82 \text{ kJ mol}^{-1}$ and 9.1 kJ mol^{-1} respectively for TTCNS and TAINS sorbents employed, which is in the energy range of an ion-exchange reaction i.e., $8\text{-}16 \text{ kJ mol}^{-1}$. The results suggested that the adsorption process of Ni(II) by both adsorbents are chemical in nature. Sakthi et al.,²⁵⁷ reported similar trend in the adsorptive removal of Pb(II) using *Bombax ceiba* sawdust.

Table 4.17 Equilibrium concentrations - DKR isotherm

Conc. of metal ion (mg/L)	Ni(II)-TTCNS		Ni(II)-TAINS	
	$\varepsilon^2 \times 10^8$	$\ln q_e$	$\varepsilon^2 \times 10^8$	$\ln q_e$
3	4.156	3.195	2.36	-1.43
5	0.700	3.883	1.68	-1.07
7	0.200	3.867	1.33	-0.80
9	0.100	3.989	1.09	-0.61
11	0.009	4.208	0.94	-0.45
13	0.004	4.077	0.40	-0.21

Adsorbent dose: 50mg (TTCNS), 150mg (TAINS) Temperature: 303K

**Figure 4.43 DKR isotherm model [Ni(II)-TTCNS]**

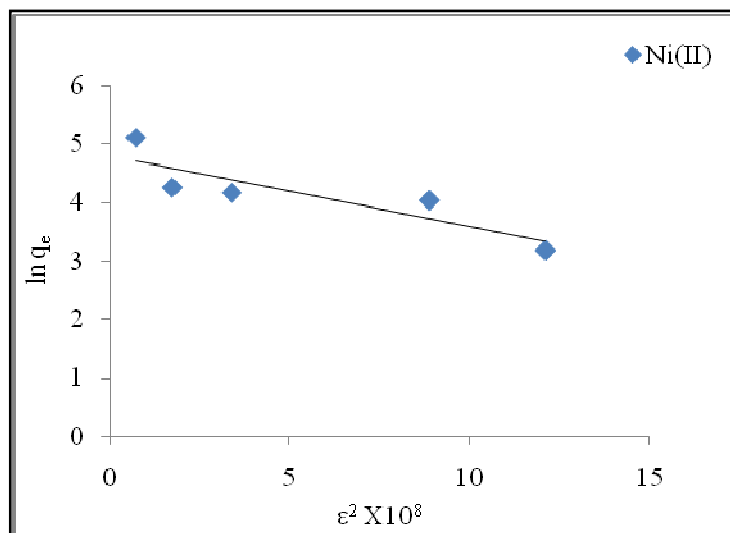


Figure 4.44 DKR isotherm model [Ni(II) -TAINS]

4.14.5 Comparison of isotherm models

The values of R^2 are regarded as a measure of goodness of fit of experimental data on the isotherm models. All the isotherm models fit well for the removal of Ni(II) by TTCNS and TAINS. The Langmuir model is valid for modelling monolayer adsorption onto homogeneous surface with constant adsorption energy. The Freundlich equation points a heterogeneous surface and considers that molecules attached to a surface site will have an effect on the neighboring sites. The DKR isotherm does not assume homogeneous surface or constant adsorption energy.

It is well known that the Langmuir isotherm corresponds to a dominant ion exchange mechanism while the Freundlich isotherm show adsorption complexation taking place in the adsorption process¹³¹. These observations indicate that the adsorption of Ni(II) ion onto TTCNS and TAINS may involve the ion exchange and surface complexation mechanism²⁵⁸.

Table 4.18 Isotherm constants

Isotherm parameters	Ni(II)-TTCNS	Ni(II)-TAINS
Langmuir isotherm		
q_m (mg/g)	62.50	63.29
b (L/g)	0.5000	0.9302
R^2	0.9870	0.9967
Freundlich isotherm		
K_F (mg/g)	47.02	54.26
n	1.594	1.9478
R^2	0.9702	0.9356
Tempkin isotherm		
A_T (L/g)	1.585	1.1019
b_T	35.54	54.66
R^2	0.9990	0.9967
DKR isotherm		
q_s (mg/g)	62.46	58.10
E (kJ/mol)	15.82	9.10
R^2	0.9986	0.9103

4.15 Adsorption Kinetics

The efficiency of the adsorbent is evaluated by studying adsorption kinetics. Adsorption kinetics describes the solute uptake rate which in turn controls the residence time and hence the size of the adsorption experiment. The kinetic data were analysed using pseudo-first-order rate expression of Lagergren model²⁵⁹ and the pseudo-second-order kinetic rate expression of Ho and Mc Kay²⁶⁰.

4.15.1 Pseudo-first-order model

The model is based on the assumption that the rate of sorption is proportional to the number of unoccupied sites.

The rate constant of adsorption is determined from the pseudo-first-order equation of Lagergren which is generally expressed as

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad \dots (17)$$

where, q_e and q_t are the adsorption capacity at equilibrium and at time t , respectively (mg/g) and k_1 is the rate constant for pseudo-first-order adsorption (min^{-1}). After integration, by applying the conditions that $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the equation (17) becomes

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad \dots (18)$$

The kinetic data for pseudo-first-order model are given in tables 4.19 and 4.20 for Ni(II)-TTCNS and Ni(II)-TAINS systems respectively. The linear plots of $\log(q_e - q_t)$ vs t for pseudo-first-order model for the metal ion with the two adsorbents are shown in figures 4.45 and 4.46 respectively. The slopes and intercepts of plots of $\log(q_e - q_t)$ versus t were used to determine the first-order rate constant k_1 and equilibrium adsorption capacity q_e .

Table 4.19 Effect of concentration-Kinetics [Ni(II)-TTCNS]

Time (min)	3 (ppm)		5 (ppm)		7 (ppm)		9 (ppm)		11 (ppm)	
	$\log(q_e - q_t)$	t/q_t	$\log(q_e - q_t)$	t/q_t	$\log(q_e - q_t)$	t/q_t	$\log(q_e - q_t)$	t/q_t	$\log(q_e - q_t)$	t/q_t
2	1.0790	0.0675	1.2418	0.0584	1.588	0.1818	1.5587	0.0833	1.9760	0.0704
4	0.6627	0.1081	0.9344	0.0952	1.2041	0.1183	0.892	0.1020	1.7510	0.0900
6	0.0791	0.1485	0.3010	0.1234	0.3010	0.1255	0.2552	0.1111	0.0791	0.0892
8	0.0000	0.1970	0.2041	0.1632	0.2552	0.1666	0.2041	0.1476	0.0000	0.1186
10	-0.096	0.2450	0.1461	0.2032	0.1461	0.2066		0.1824	-0.2218	0.1483
12	-0.397	0.2912	-0.096	0.2409	0.0791	0.2469		0.2189	-0.2218	0.1769
14	-0.698	0.3381	-0.221	0.2800	0.0791			0.2554	-0.3970	0.2064
30		0.7211		0.5928		0.6024		0.5376		0.4424

Adsorbent dose: 50 mg; pH: 3.4; Temperature: 303K

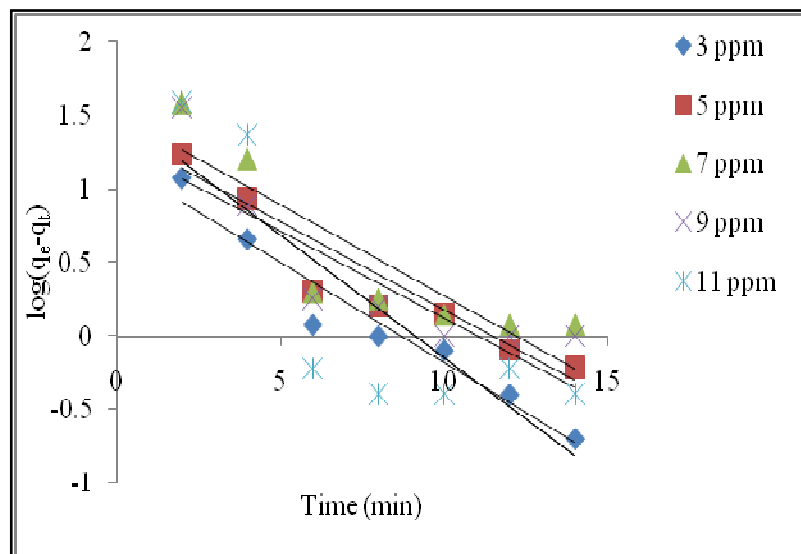


Figure 4.45 Pseudo-first-order kinetics [Ni(II)-TTCNS]

Table 4.20 Effect of concentration-Kinetics [Ni(II)-TAINS]

Time (min)	3 (ppm)		5 (ppm)		7 (ppm)		9 (ppm)		11 (ppm)	
	log (q _e -q _t)	t/q _t	log (q _e -q _t)	t/q _t	log (q _e -q _t)	t/q _t	log (q _e -q _t)	t/q _t	log (q _e -q _t)	t/q _t
3	0.8020	0.8196	1.0000	0.2320	1.2280	0.2046	1.1350	0.1738	1.4070	0.5628
6	0.7050	1.2170	0.9637	0.4369	1.1914	0.3735	1.0560	0.3072	1.4070	0.5825
9	0.4683	1.2740	0.7218	0.5096	1.0718	0.4545	0.8733	0.3836	1.3955	0.6738
12	0.2878	1.4880	0.6089	0.6360	1.0060	0.5591	0.7972	0.5115	1.0111	0.7337
15	0.2878	1.8610	0.6089	0.7950	0.9344	0.6521	0.2041	0.6082	0.9344	0.7063
18	0.8020	1.8120	0.6089	0.9540	0.7881	0.7069	1.1350	0.6137	0.8014	1.2570
21				0.9210		0.6878		0.7000	0.0569	1.5000

Adsorbent dose: 150 mg; pH: 7.1; Temperature: 303K

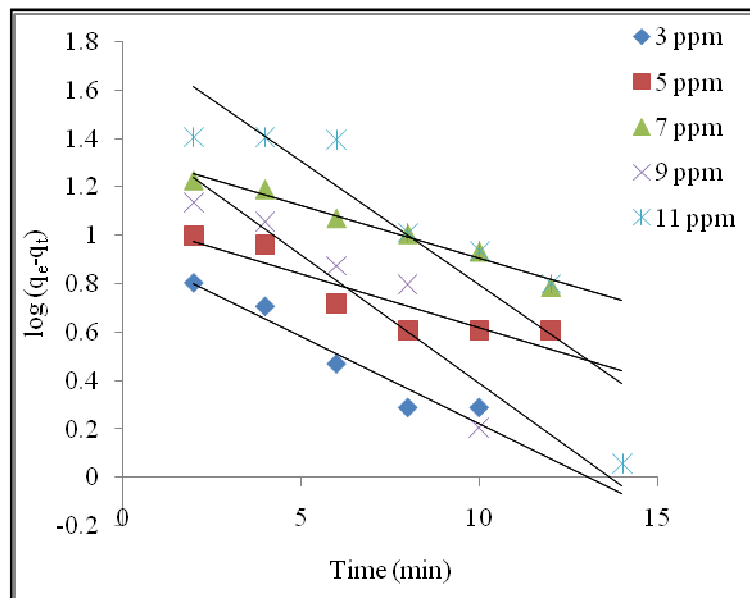


Figure 4.46 Pseudo-first-order Kinetics [Ni(II)-TAINS]

4.15.2. Pseudo-second-order model

The model is based on the assumption that the rate of sorption is proportional to the square of the number of unoccupied sites. The pseudo-second-order adsorption kinetic rate equation is expressed as

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad \dots (19)$$

where, k_2 is the rate constant for pseudo-second-order adsorption (g/mg min). After integration by applying the conditions that $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the equation (19) becomes

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \quad \dots (20)$$

Equation (20) is the integrated rate law for pseudo-second-order reaction and it can be rearranged to a linear form

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \dots (21)$$

The slopes and intercepts of plots of t/q_t versus t were used to calculate the q_e and pseudo-second-order rate constant k_2 .

The kinetic data for pseudo-second-order model is also incorporated in tables 4.19 and 4.20 for both the systems. The linear plots of t/q_t vs t for pseudo-second-order model are shown in figures 4.47 and 4.48 respectively as this model is more suitable to the studies. The calculated kinetic parameters, the sum of error squares (SSE) and the correlation coefficients are shown in table 4.21 for Ni(II)-TTCNS and Ni(II)-TAINS systems. A relatively high value of correlation coefficients and low value of SSE^{261} are considered for the evaluation of the best fit model.

The sum of squares of errors is given by

$$SSE = \sqrt{\frac{\sum (q_{e,exp} - q_{e,cal})^2}{N}} \quad \dots (22)$$

where, the subscripts “exp” and “cal” are the experimental and calculated data respectively and N is the number of data points.

The observed correlation coefficient values against calculated values for pseudo-second-order model are relatively higher and hence the equilibrium sorption capacities determined using this model are in good agreement with the experimentally determined equilibrium sorption capacities. Therefore the values of SSE are less for pseudo-second-order model. From the observations recorded, it is concluded that the pseudo-second-order adsorption model is more suitable to describe the adsorption kinetics of all the three systems under investigation.

The second order rate constant k_2 was found to decrease with increase in initial concentrations of Ni(II). Similar trend was observed for the removal of Ni(II) by P Senthil Kumar et al.,²⁵³ There are many factors which can contribute to this sorbate concentration effect on the rate of adsorption. The first reason may be increase in the metal ion concentration in solution may diminish the diffusion of metal ions through the boundary layer to enhance the diffusion in the solid. The second cause can be due to the progressive

decrease in covalent interactions, relative to electrostatic interaction of the sites with lower affinity for the metal ions with an increase of initial metal ion concentration²⁶².

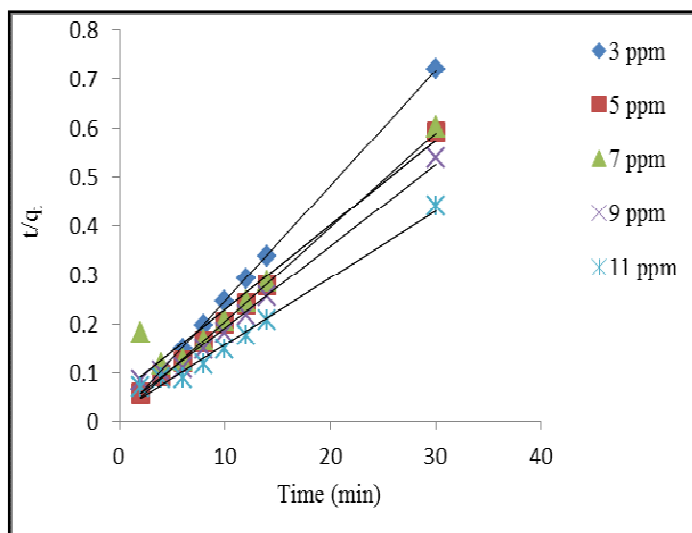


Figure 4.47 Pseudo-second-order Kinetics [Ni(II)-TTCNS]

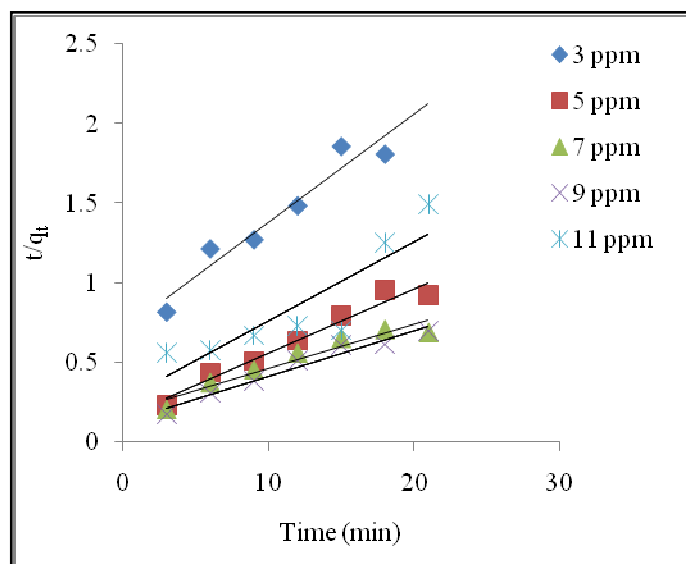


Figure 4.48 Pseudo-second-order Kinetics of [Ni(II)-TAINS]

Table 4.21 Pseudo-first-order and Pseudo-second-order kinetic constants

Conc. of metal ions (mg/L)	q_e (exp.) (mg/g)	Pseudo-first-order kinetics				Pseudo-second-order kinetics			
		q_e (cal.) (mg/g)	$k_1 \times 10^{-3}$ (min^{-1})	R^2	SSE	q_e (cal.) (mg/g)	$k_2 \times 10^{-4}$ (g/mg min)	R^2	SSE
Ni(II)-TTCNS									
3	41.60	15.10	0.313	0.9410	10.01	43.47	4.81	0.9990	0.71
5	49.80	20.04	0.271	0.9020	3.67	52.63	2.77	0.9990	1.07
7	50.6	207.96	0.741	0.9485	59.47	58.82	0.51	0.9300	3.10
9	55.80	160.32	0.750	0.9998	35.29	62.50	1.06	0.9910	2.53
11	123.20	291.74	0.467	0.9951	63.70	76.92	0.84	0.9860	17.49
Ni(II)-TAINS									
3	10.53	8.78	16.65	0.9339	0.66	16.18	5.24	0.9550	2.13
5	22.93	19.81	20.42	0.9578	1.17	21.83	1.85	0.9880	0.42
7	31.60	21.88	9.99	0.9758	3.67	29.32	0.91	0.9816	0.86
9	30.93	18.38	13.77	0.9700	4.74	35.71	0.62	0.9772	1.80
11	30.86	63.60	19.25	0.9533	12.37	18.41	1.13	0.9138	4.70

4.15.3 Elovich model

Elovich equation was also used to correlate experimental data. The Elovich equation has been applied satisfactorily to systems in which the adsorbing surface is heterogeneous. The Elovich equation is expressed as²²⁹

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad \dots (23)$$

where α (mg/g min) is the initial adsorption rate and β (g/mg) represents the adsorption constant related to the extent of the surface coverage. Equation (23) is simplified by assuming $\alpha \beta \gg t$ and by applying boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$. The modified equation is as below

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad \dots (24)$$

The plots for Ni(II)-TTCNS and Ni(II)-TAINS systems are depicted in figures 4.49 and 4.50 respectively. The Elovich constants α and β were obtained from the intercept and slope of the linear plot of q_t vs $\ln t$. The Elovich constants α , β and the correlation coefficients are reported in table 4.22. According to Cheung et al.,²⁶³ the constant α which is related to adsorption rate increases with the concentration of the solution and the constant β related to the extent of surface coverage decreases with increase in concentration which shall be due to the non availability of sorption surfaces for the sorbates. Such observations were reported for the removal of Ni(II) onto *Camella cinsensis*.²⁶⁴

Analysis of the results of the present study reveals that, the constant β was found to decrease at increasing concentration environments for all the systems.

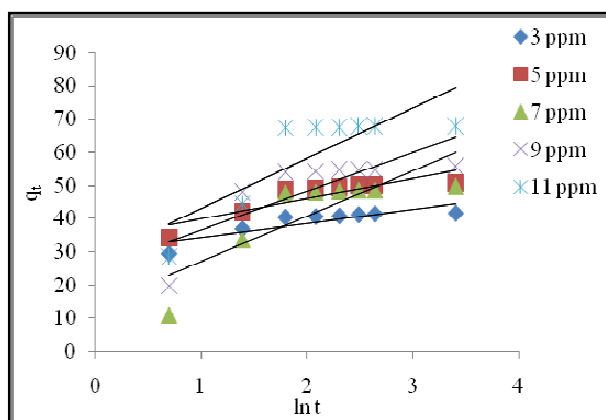


Figure 4.49 Elovich model [Ni(II)-TTCNS]

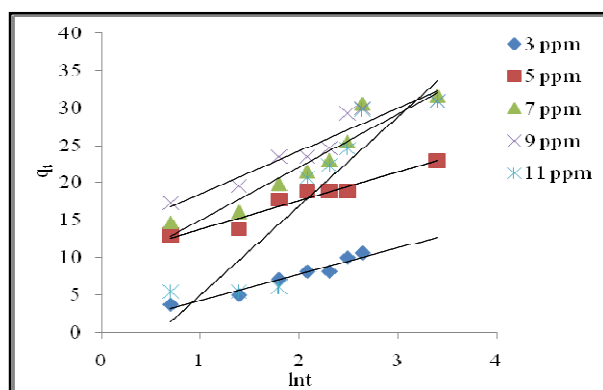


Figure 4.50 Elovich model [Ni(II)-TAINS]

Table 4.22 Elovich constants

Conc. of metal ions (mg/L)	Ni(II)-TTCNS			Ni(II)-TAINS		
	α	β	R^2	α	β	R^2
3	3.39	0.8538	0.9090	3.62	0.2816	0.9283
5	237	0.1113	0.9122	50.65	0.2598	0.9606
7	2291	0.0513	0.9120	21.50	0.1400	0.9838
9	3826	0.0510	0.9353	53.27	0.1740	0.9852
11	59.84	0.0456	0.9420	6.66	0.0835	0.9924

α : (mg/g min), β :(g/mg)

4.15.4 Intraparticle diffusion model

In order to gain insight into the mechanisms and rate controlling steps affecting the kinetics of adsorption, the kinetic experimental results were fitted to the Weber and Morris intraparticle diffusion model and Boyd's model. Adsorption of any metal ions from aqueous phase onto solid phase is a multi-step process involving transport of metal ions from aqueous phase to the surface of the solid particles (bulk diffusion) and then, diffusion of metal ions via the boundary layer to the surface of the solid particles (film diffusion), followed by transport of metal ions from the solid particle surfaces to its interior pores (pore diffusion or intra particle diffusion), which is likely to be a slow process, which may be the rate determining step in many adsorption process⁴⁵. The possibility of intraparticle diffusion is explored by using Weber and Morris equation as described by Mehmet Emin Argun et al.,¹⁸⁸

$$q_t = K_i t^{1/2} + C \quad \dots (25)$$

where, K_i ($\text{mg/g min}^{1/2}$) is the of intraparticle diffusion rate constant and C (mg/g) is related to the thickness of the boundary layer. K_i and C values are calculated from the slope and intercept of q_t versus $t^{1/2}$ plots respectively.

According to previous studies the intraparticle diffusion plot may represent multilinearity, representing the different stages in adsorption^{169, 228}. All the plots have the same general features of an initial curved portion followed by a linear portion and a plateau. The initial curved portion is attributed to rapid external diffusion or boundary layer diffusion and surface adsorption. The linear portion represents a gradual adsorption stage due to the intraparticle diffusion while the plateau to the equilibrium, where the intraparticle diffusion starts to decrease due to the low concentration of adsorbate in solution phase as well as fewer available adsorption sites²²⁸. The plot of q_t versus $t^{1/2}$ should be linear if the intraparticle diffusion is involved in the adsorption process and if these lines pass through the origin, then the intraparticle diffusion is the rate controlling step²⁶⁵.

The plot of q_t versus $t^{1/2}$ are linear for Ni(II) TTCNS and Ni(II)-TAINS as evident from figures 4.51 and 4.52. Based on the plot, it is obvious that the sorption process of Ni(II) ions had occurred in two phases. Masood Alam et al., reported similar observations in the removal of Ni(II) and Zn(II) from aqueous solutions²⁶⁶. The initial portion of the plot indicates an film diffusion whereas the second linear portion is due to intraparticle or pore diffusion. An extrapolation of the second linear portions of the plots back to the axis provides the intercepts, which gives an estimation of the thickness of the boundary layer, (i.e.) the larger the intercept value, greater is the boundary layer effect²⁵⁸. The slope of the second linear portion of the plot has been identified as intraparticle diffusion rate constant K_i . The K_i , C and R^2 values are shown in the table 4.23. The K_i and C values increased with initial concentration²⁶⁷.

The results indicate that metal ions diffuse quickly in the sorbent at the beginning of the sorption process, and then intraparticle diffusion slows down and is stabilized. The deviation of straight lines from the origin indicates that intraparticle transport is not the rate limiting step²⁶⁸.

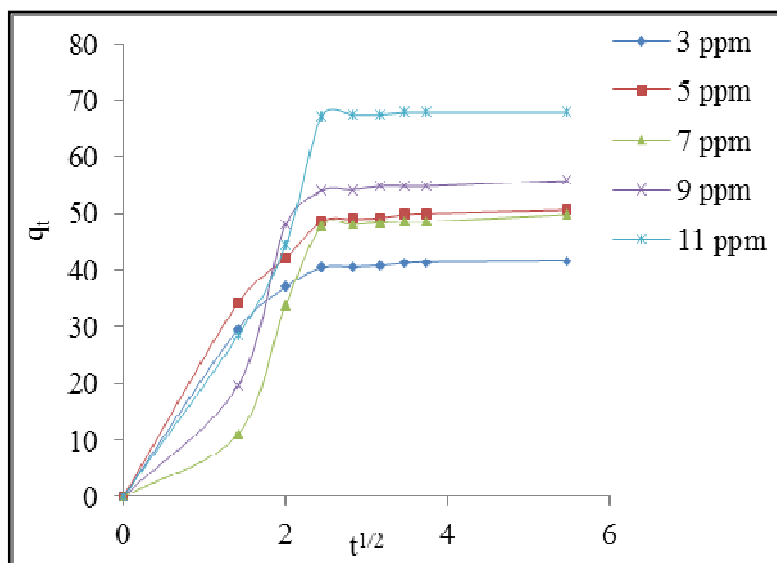


Figure 4.51 Intraparticle diffusion model [Ni(II)-TTCNS]

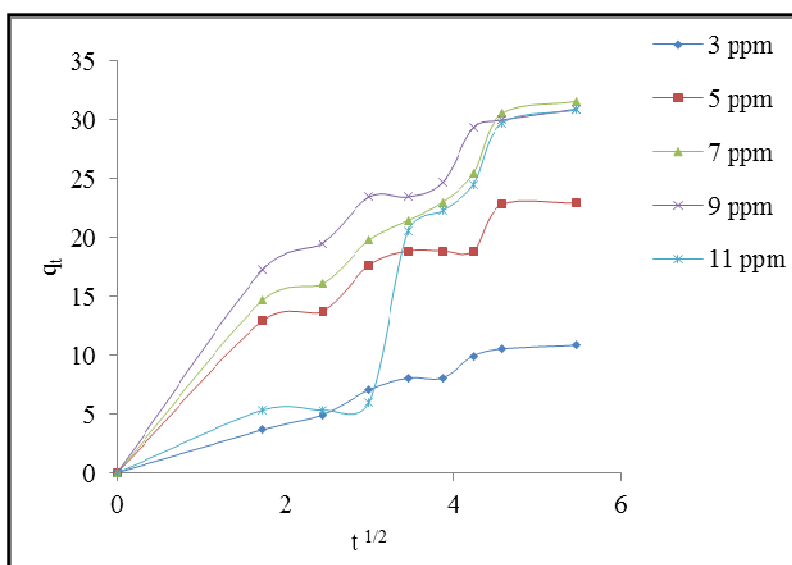


Figure 4.52 Intraparticle diffusion model [Ni(II)-TAINS]

Table 4.23 Intraparticle diffusion model constants at different concentrations

Conc. of metal ions (mg/L)	Ni(II)-TTCNS			Ni(II)-TAINS		
	K_i (mg/g min ^{1/2})	C	R ²	K_i (mg/g min ^{1/2})	C	R ²
3	12.65	0.7523	0.9772	2.428	0.2816	0.9739
5	14.30	1.8431	0.9571	2.874	0.2598	0.9056
7	15.01	2.9883	0.9330	21.5	4.998	0.9521
9	16.89	1.0235	0.9764	53.271	3.995	0.9361
11	35.08	0.1898	0.9814	6.663	8.469	0.8728

4.15.5 Comparison of kinetic models

Of all the models envisaged, the pseudo-second-order model provides the best correlation for the two systems, as evident from tables 4.21, 4.22 and 4.23. Though pseudo-first-order model has appreciable correlation coefficient values, the experimental and calculated q_e values are significantly different. Correlation coefficient values (R^2) for Elovich model substantiates the better fit of the model for both the systems compared to intraparticle diffusion model. However these models are found to have lower correlation coefficient values against the best fit of Pseudo second order model. Hence, this suggests that the adsorption systems studied belong to the pseudo-second-order kinetic model.

4.16 Adsorption Dynamics

Temperature dependence of the sorption process is related with several thermodynamic parameters including the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°), which are used to decide whether the sorption is a spontaneous process or not. The thermodynamic parameters were calculated from the following equations²⁶⁹

$$\Delta G^\circ = -RT \ln K_c \quad \dots (26)$$

where, K_c is the thermodynamic equilibrium constant for the adsorption, calculated using the equation $K_c = C_A/C_e$, C_A is the amount of metal ion adsorbed on the adsorbent at equilibrium (mg/g), C_e is the equilibrium concentration of metal ion in the solution (mg/L), R , the gas constant and T , the temperature (K). The change in enthalpy and entropy of adsorption were calculated using Vant Hoff's equation:

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad \dots (27)$$

Vant Hoff's plot for Ni(II) by the two adsorbents are shown in figures 4.53 and 4.54. Values of ΔH° and ΔS° were calculated from the slopes and intercepts of the plot of $\ln K_c$ vs $1/T$. The thermodynamic parameters are tabulated in table 4.24. The positive values of ΔH° for both the systems confirm the endothermic nature of adsorption. This behaviour indicates that higher temperatures are more preferred for higher sorption which has been reported in earlier studies^{130, 270}.

Table 4.24 Thermodynamic constants

Temp. K	Ni(II)-TTCNS			Ni(II)-TAINS		
	$-\Delta G$ kJ/mol	ΔH kJ/mol	ΔS J/mol K	$-\Delta G \times 10^{-3}$ kJ/mol	ΔH kJ/mol	ΔS J/mol K
293	0.4530			0.1125		
303	0.5794	16.40	136.34	0.1163	23.15	81.36
313	0.3765			0.2027		
323	0.4132			0.2274		
333	0.5147			0.4180		

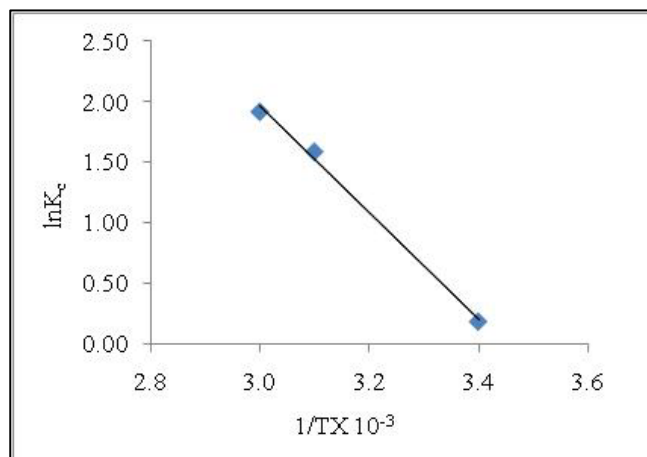


Figure 4.53 Vant Hoff's plot [Ni(II)-TTCNS]

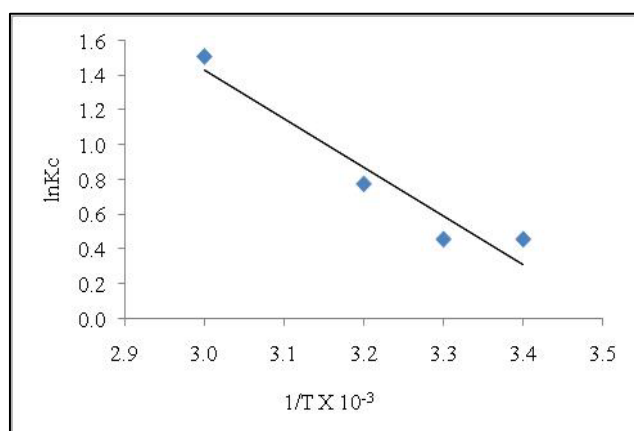


Figure 4.54 Vant Hoff's plot [Ni(II)-TAINS]

When the temperature was increased from 293K- 313K, the magnitude of free energy change shifted to a high negative value suggesting that the adsorption was rapid, spontaneous and spontaneity increases with temperature^{268,271}. The positive values of ΔS° show the increased randomness at the solid-solution interface during the adsorption of Ni(II) on TTCNS and TAINS^{167,270}.

4.19 Effect of TTCNS and TAINS dosage on industrial effluent containing nickel

The industrial effluent sample collected from chemical industry, Salem, Tamilnadu was employed for the study. Batch adsorption studies were carried out at different dosages of TTCNS and TAINS with optimum contact time. The experimental data and the

corresponding graph are shown in table 4.25 and figure 4.55. A rise in percentage removal of Ni(II) from effluent was observed as the adsorbents' dose increased from 50 mg to 500mg. 450 mg of TTCNS dosage was sufficient to remove 54% of the metal from the effluent laden, as compared to 44% in case of the same dose of TAINS. This proves the relative ability of TTCNS over TAINS.

Table 4.25 Effect of TTCNS and TAINS on industrial effluent

Weight of adsorbent (mg)	Percentage removal of Ni(II) from effluent	
	TTCNS	TAINS
50	34.89	28.33
100	39.20	29.79
150	40.70	30.38
200	42.09	33.00
250	44.87	35.64
300	46.63	36.55
350	50.35	38.50
400	51.18	39.30
450	54.32	44.08
500	54.53	46.10

Particle size: 0.42mm TTCNS, 0.18mm TAINS

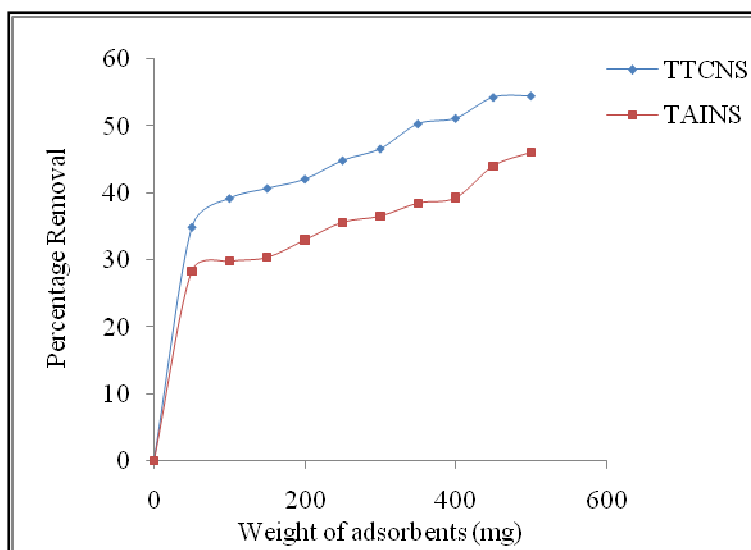


Figure 4.55 Effect of TTCNS and TAINS on effluent containing nickel