5.3 Effect of Particle size

The influences of the adsorbents' particle size for Co(II) removal were investigated using five different particle sizes (18mm, 0.24mm, 0.30mm, 0.42mm and 0.71mm). The batch experiments were carried out using 11ppm of Co(II) concentration for TTCNS and TAINS at dosages of 100 mg and 150 mg, at pH values of 4.04 and 6.30 respectively. The effect of particle sizes on the uptake rate of Co(II) are given in tables 5.1, 5.2 and their respective plots (Amount adsorbed vs. Time) are illustrated in figures 5.7, 5.8.

Smaller the particle size, higher the surface area per unit weight of the adsorbent[227]. Amongst the experimentally verified particle sizes, the percentage removal was found to increase appreciably for 0.42mm of TTCNS and 0.18 mm of TAINS. This may be due to the increase in number of binding sites at high surface area[243]. Similar results have been reported on *Tamarindus indica* seeds[239]. In view of the good experimental results obtained for 0.42 mm TTCNS and 0.18 mm TAINS particle sizes, it was decided to limit the discussions of further experiments under these dimensions.

Table 5.1 Effect of Particle size (TTCNS)

Time (min)	Amount Adsorbed (mg/g)				
	0.18 mm	0.24 mm	0.30 mm	0.42 mm	0.71mm
0	0	0	0	0	0
2	64.1	47.2	35.9	85.7	13.1
4	69.0	50.8	52.5	85.7	28.6
6	76.2	65.3	70.4	88.3	48.0
8	76.2	67.7	75.5	98.5	53.0
10	78.6	69.0	80.6	100.5	68.0
12	78.6	71.4	83.2	106.1	73.4
14	81.0	71.4	83.2	108.7	78.8
16	80.5	71.1	83.1	108.2	78.0
18	80.1	69.8	82.9	108.0	77.6

Metal ion concentration:11 ppm; Adsorbent dose:100 mg; pH:4.04; Temperature:303K.

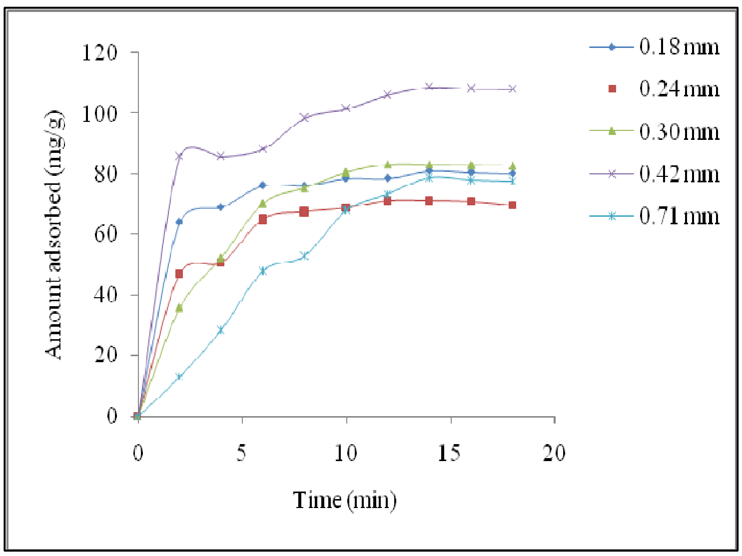

Figure 5.7 Effect of Particle size (TTCNS)

Table 5.2 Effect of Particle size (TAINS)

Time (min)	Amount Adsorbed (mg/g)				
	0.18 mm	0.24 mm	0.30 mm	0.42 mm	0.71 mm
0	0	0	0	0	0
3	55.00	41.66	30.00	18.53	7.46
6	57.80	43.00	30.73	20.33	8.73
9	59.20	45.26	33.00	20.33	9.66
12	63.20	46.13	33.86	21.66	10.53
15	79.20	47.46	35.26	22.53	11.40
18	80.60	47.93	36.13	23.46	11.80
21	82.25	47.93	36.93	23.86	12.26
24	82.12	47.85	36.25	22.52	12.10
27	82.04	47.14	36.05	22.32	12.05

Metal ion concentration:11 ppm; Adsorbent dose:150 mg; pH:6.30; Temperature:303K.

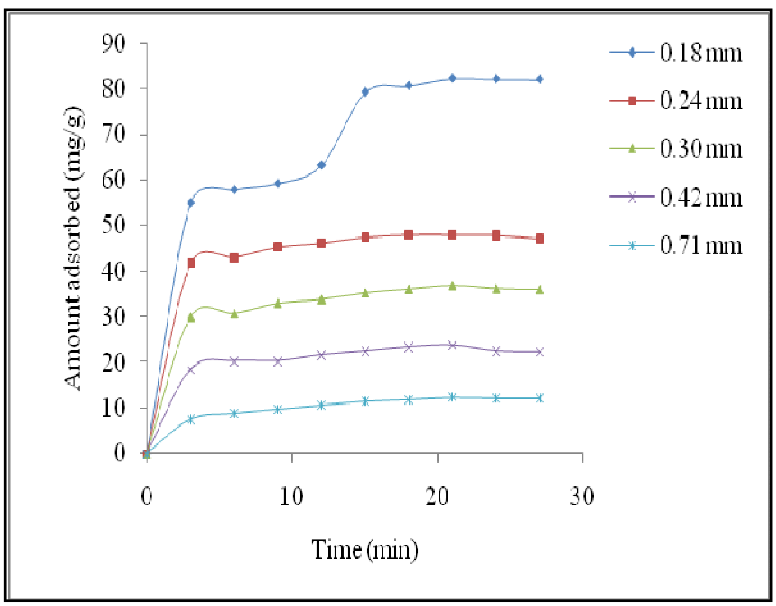

Figure 5.8 Effect of Particle Size (TAINS)

5.4 Effect of Contact time and Initial concentration

The effect of time course profiles for the adsorption of Co(II) ions varied concentrations ranging from (3-13ppm: 2ppm interval) at varying time intervals (2-14 minutes: 2 minutes interval) are shown in figures 5.9 and 5.10 and the corresponding data in tables 5.3 and 5.4. In both the systems, the initial sorption rate was very rapid and thereafter adsorption was gradual while reaching the equilibrium.

The amount of Co(II) adsorbed onto TTCNS after attaining equilibrium was found to be 27.8, 67.6, 85.4, 87.8, 102.3 and 96.5mg/g respectively (Table 5.3) at initial concentrations of 3, 5, 7, 9, 11and 13 ppm. Percentage sorption of Co(II) has lowered at a higher concentration of 13 ppm. Such behaviour can be attributed to the unchanging number of available active sites on the adsorbent, since the amount of adsorbent is kept constant [274]. Similar results have been observed in the case of Co(II)-TAINS system, as obvious from the table 5.4.

The equilibrium time, being independent of initial concentrations were found to be 20 and 15 minutes for Co(II)-TTCNS and TAINS systems respectively. Such concentration independent equilibrium time had been reported by B.Krishna et al.,[159]**.** In view of the observed data, a contact time of 10 and 15 minutes for the respective systems and an initial concentration of 11ppm for both the systems have been fixed.

Table 5.3 Effect of Contact time and Initial concentration (TTCNS)

Time(min)	Amount adsorbed (mg/g)					
	3 ppm	5ppm	7ppm	9ppm	11ppm	13 ppm
2	1.0	17.4	37.5	32.8	71.6	57.0
4	5.8	38.2	58.3	64.4	72.8	69.8
6	8.6	53.6	60.4	65.6	77.6	71.2
8	26.8	62.4	75.0	67.8	97.6	96.4
10	27.8	67.6	85.4	87.8	102.3	96.5
12	37.2	69.2	89.6	87.6	102.9	96.8
14	37.1	69.0	89.1	87.5	102.8	96.7

Particle size: 0.42 mm; Adsorbent dose: 100mg; pH: 4.04; Temperature: 303K

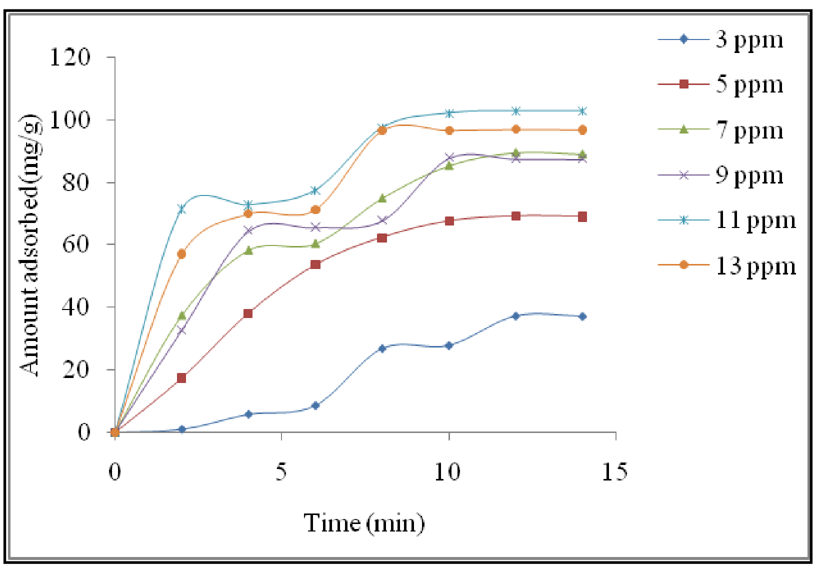

Figure 5.9 Effect of Contact time and Initial concentration (TTCNS)

Table 5.4 Effect of Contact time and Initial concentration (TAINS)

Time(min)	Amount adsorbed mg/g					
	3 ppm	5ppm	7ppm	9ppm	11ppm	13ppm
3	7.4	4.4	21.0	12.8	55.0	22.0
6	9.4	6.4	25.0	31.0	57.8	34.0
9	10.0	9.6	36.8	52.2	59.2	37.6
12	10.6	10.6	40.6	62.0	63.2	42.0
15	11.4	12.8	43.2	66.2	79.2	43.8
18	11.4	12.8	43.2	67.6	80.6	44.8
21	13.2	14.8	43.2	67.6	82.0	43.6
30	13.99	14.9	43.2	67.6	82.1	43.1

Particle size: 0.18 mm: Adsorbent dose: 150 mg; pH: 6.30; Temperature: 303K

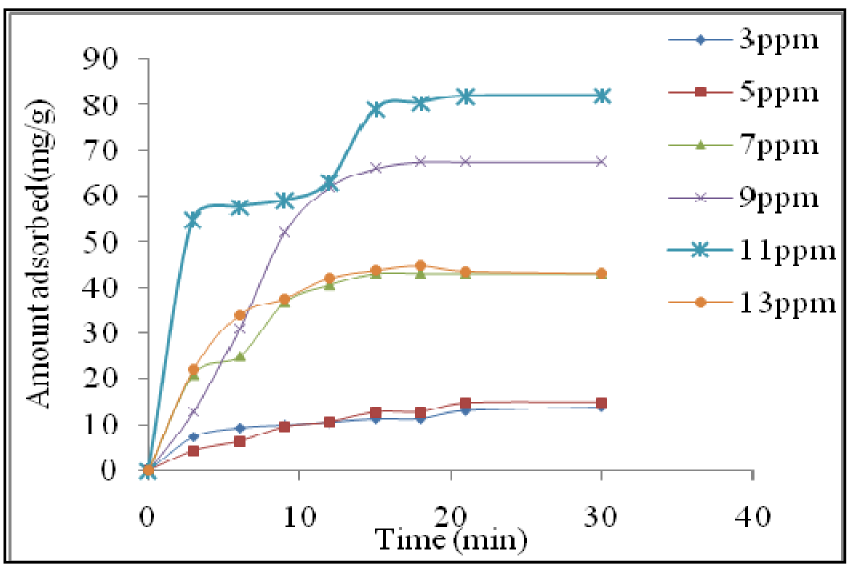

Figure 5.10 Effect of Contact time and Initial concentration (TAINS)

5.5 Effect of Dosage

The influences of adsorbent doses (50-200mg: 50mg interval) of TTCNS and TAINS are presented in tables 5.5 and 5.6. The adsorption percentage registered a maximum at a dose of 100mg and 150mg of TTCNS and TAINS correspondingly, thereafter a decline was observed. With increasing adsorbent dosage, more surface area is available for adsorption due to increase in active sites on the adsorbent and thus making easier penetration of metal ions to the sorption sites[137]. The decrease beyond these optimum doses of 100mg and 150 mg of the respective adsorbents can be attributed to the fact that the saturation of adsorption sites through the adsorption reaction might occur.

Table 5.5 Effect of Adsorbent dose (TTCNS)

Time (min)	Amount adsorbed mg/g			
	50 mg	100mg	150 mg	200 mg
2	17.95	52.40	85.70	20.00
4	20.85	86.60	85.70	35.50
6	26.10	88.40	88.30	37.00
8	28.95	97.40	98.50	38.06
10	31.85	104.60	101.50	40.20
12	31.85	126.40	106.17	40.80
14	31.92	126.40	108.73	40.91

Initial metal ion concentration 11 ppm; pH: 4.04; Temperature: 303K

Table 5.6 Effect of adsorbent dose (TAINS)

Time (min)	Amount adsorbed mg/g			
	50 mg	100 mg	150 mg	200 mg
3	8.00	29.30	29.00	30.90
6	8.00	34.5	41.50	34.90
9	9.00	34.70	42.50	53.20
12	30.90	40.00	55.10	54.00
15	33.40	46.70	55.10	55.20
18	36.80	47.80	55.30	56.40
21	44.60	49.30	59.40	57.50
30	46.30	50.10	64.00	54.00

Initial metal ion concentration 11 ppm; pH: 6.30; Temperature: 303K

5.6 Effect of pH

The effect of pH was studied at varying pH environments (3, 5, 7, 9 & 11ppm) and the results are depicted in figures 5.11 and 5.12. Maximum adsorption was recorded at pH 4.04 and 6.03 for Co(II)-TTCNS and Co(II)-TAINS systems. Above this pH values, the percentage adsorption decreased. This can be due to the precipitation of insoluble metal hydroxides at alkaline pH ranges[267].

As a specific mention to TTCNS material, the decline in sorption below pH 4 may be due to the increased positive charge density on the sites of adsorbent surface, which might have inhibited the approach of Co^{2+} ions towards the sorption sites, whereas in contrast, the higher sorption observed i.e., 89.8% against pH 4.04 (Table 5.7) shall be explained in terms of zero-point charge. The pH_{ZPC} of TTCNS is 6.2, at which the adsorbent is neutral. The adsorption of cobalt below pH_{ZPC} may be due to the exchange process H^+ and Co^{2+} as explained by Alka Shukla et al.,[275] Hence the experiments pertaining to the upcoming systems were carried out at the above mentioned pHs.

Table 5.7 Effect of pH (TTCNS)

Percentage of adsorption at varying pH values					
Metal ion concn.(ppm)	3	5	7	9	11
11	35.8	89.81	54.13	52.47	47.30
13	21.60	37.80	30.12	23.30	22.40

Adsorbent dose: 100mg; Agitation time: 10min; Temperature: 303K

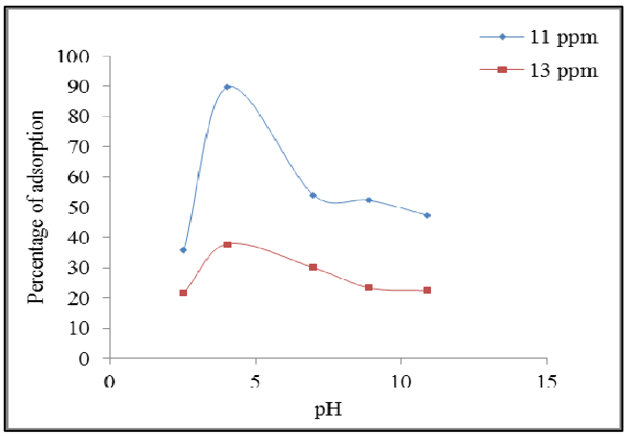

Figure 5.11 Effect of pH (TTCNS)

Table 5.8 Effect of pH (TAINS)

Percentage of adsorption at varying pH values					
Metal ion concn.(ppm)	3	5	7	9	11
11	36.27	48.45	69.96	23.81	11.63
13	31.52	42.15	53.33	19.90	10.25

Adsorbent dose: 150 mg; Agitation time: 15 min; Temperature: 303K

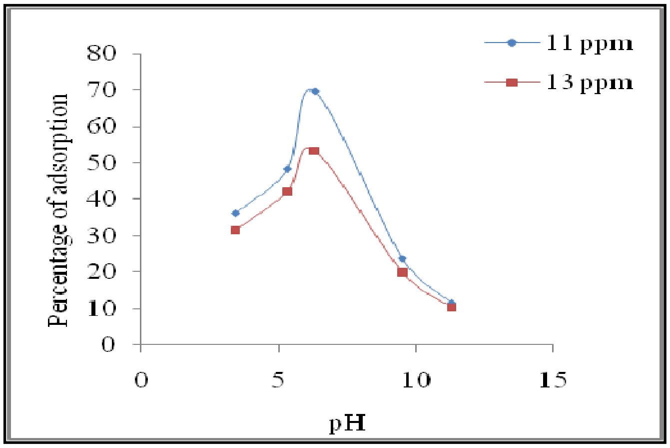

Figure 5.12 Effect of pH (TAINS)

5.7 Effect of Cations

The effect of cations on the percentage removal of Co(II) by TTCNS and TAINS were investigated and the results are depicted in tables 5.9 and 5.10 respectively. The results indicate that, as the concentration of these cations were increased from 11 to 100 ppm, the removal of Co(II) by TTCNS decreased. It is evident from the tables, that the influence of Mg^{2+}, Na^{+}, and K^{+} ions in the removal of Co(II) by TTCNS and TAINS was observed to be enhanced at higher concentrations of the interfering ions. The effect of Mg^{2+} was much more apparent than those of Na^{+} and K^{+} in Co(II) removal. This is in agreement with other studies that showed stronger inhibition with high valence ions than that of lower ones[276].

5.8 Effect of Anions

The effect of anions on the uptake of Co(II) onto TTCNS and TAINS are shown as percentage of adsorption in tables 5.9 and 5.10. The tabulated results indicate that amongst NO_3^-, Cl^- and SO_4^{2-}, chloride ions registered greater inhibition on the adsorption, compared to the other two ions. This can be attributed to the fact that the chloride ions are competing for the adsorption sites of Co(II). Similar trends were reported using polymer grafted *Cassia grandis* seed[241].

Table 5.9 Effect of Cations and Anions (TTCNS)

Conc. of ions(ppm)	% adsorption			% adsorption		
	Mg^{2+}	Na^{+}	K^{+}	NO_3^{-}	Cl^{-}	SO_4^{2-}
0	72.6	72.6	72.6	72.6	72.6	72.6
11	42.3	69.5	55.8	51.1	40.8	66.2
25	28.1	60.6	54.7	40.4	21.3	41.8
50	21.2	41.2	51.7	31.2	14.3	40.0
75	13.6	19.4	37.9	28.4	12.3	37.5
100	12.5	17.5	32.1	21.2	3.5	37.3

Concentration of metal ion: 11 ppm; Adsorbent dose: 100 mg; pH: 4.04; Temperature: 303K

Table 5.10 Effect of Cations and Anions (TAINS)

Conc. of ions(ppm)	% adsorption			% adsorption		
	Mg^{2+}	Na^{+}	K^{+}	NO_3^{-}	Cl^{-}	SO_4^{2-}
0	51.6	51.6	51.6	51.6	51.6	51.6
11	14.9	22.6	39.0	47.8	21.5	46.2
25	16.5	19.9	40.4	46.0	17.5	44.8
50	17.8	18.0	42.0	44.7	16.5	43.8
75	17.7	25.4	42.8	41.1	11.9	43.5
100	7.2	23.8	37.1	40.1	4.00	43.0

Concentration of metal ion: 11 ppm; Adsorbent dose: 150 mg; pH: 6.30; Temperature: 303K

5.9 Effect of Co-ions

The effect of co-ions on the removal of the adsorbate species (Figures 5.13 and 5.14) shows that the percentage sorption of Co(II) by TTCNS in the presence of Ni(II) ions was reduced to 21% against 72.6% and for TAINS the reduction was upto 18% against 51.6%, at higher Ni^{2+} environments. The reduction experienced in both cases may be due to the fact that the affinity of Co(II) and Ni(II) towards each other is quite appreciable, irrespective of the adsorbent utilized, both the ions are competing with one another for the adsorption sites. The presence of Cr(VI) does not have any antagonistic effect on Co(II) removal by both the adsorbents. This could be explained in terms of different chemical speciation of metal ions, which has a significant effect on the adsorption process, as already discussed in chapter IV.

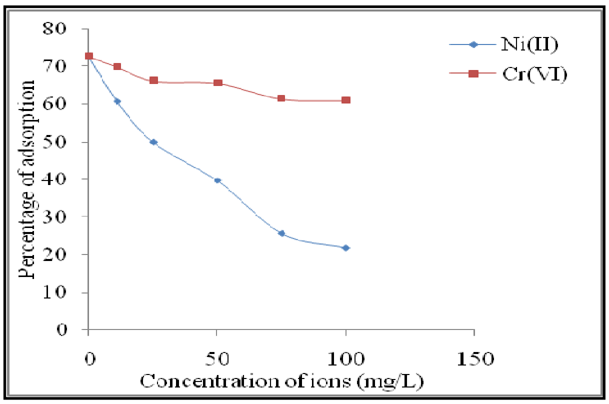

Figure 5.13 Effect of Co-ions (TTCNS)

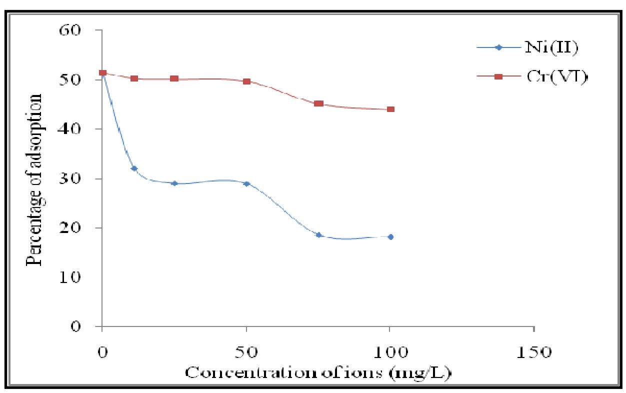

Figure 5.14 Effect of Co-ions (TAINS)

5.10 Effect of Temperature

Temperature has a pronounced effect on the sorption capacity of the adsorbents. The effect of temperature (293K- 333K: 10K intervals) for Co(II)-TTCNS and Co(II)-TAINS systems are illustrated in tables 5.11 and 5.12, where the adsorption percentage was observed to increase from 34.72 to 48.09 and 36.3 to 45.17 respectively at higher temperatures[270,277]. The enhancement of adsorption capacity with temperature may be attributed to the increase in the mobility of ions and/or the activated diffusion, which can cause small pores to widen and provide more surfaces for adsorption[244,272].

Table 5.11 Effect of Temperature (TTCNS)

Conc of ions (ppm)	Percentage Removal				
	293 K	303 K	313 K	323 K	333 K
3	48.09	53.63	55.9	55.90	55.90
5	46.54	48.90	49.63	52.80	53.63
7	44.90	45.72	48.9	50.45	52.00
9	42.54	43.36	45.72	48.9	48.90
11	34.72	41.89	44.18	47.27	48.09
13	33.09	41.81	42.54	43.36	47.24

Adsorbent dose: 100 mg; pH: 4.04; Agitation time: 20 min

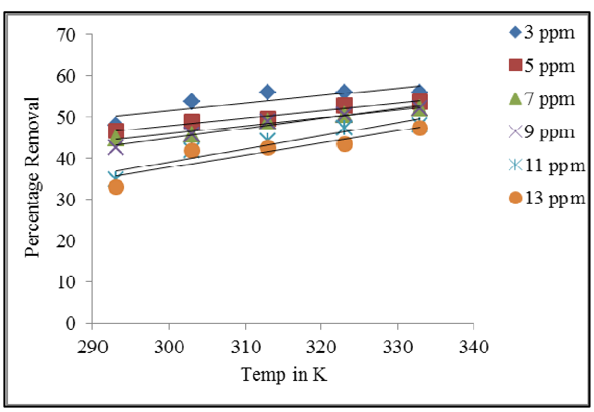

Figure 5.15 Effect of Temperature (TTCNS)

Table 5.12 Effect of temperature (TAINS)

Conc. of ions (ppm)	Percentage Removal				
	293 K	303 K	313 K	323 K	333 K
3	45.17	54.04	54.84	57.26	58.07
5	43.35	44.36	49.20	50.81	54.04
7	41.13	44.36	47.59	50.00	51.61
9	39.52	42.75	45.98	46.78	49.20
11	36.3	40.33	41.13	42.75	45.17

Adsorbent dose: 150 mg; pH: 6.3; Agitation time: 15 min

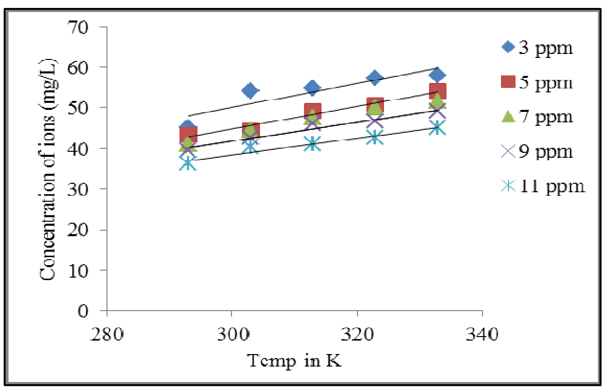

Figure 5.16 Effect of Temperature (TAINS)

5.11 Desorption

The desorption of Co(II) from TTCNS and TAINS were carried out at varying concentrations of HCl and the results are presented in figures 5.17 and 5.18. The percentage of desorption increased from 43.65 to 81.14 for Co(II)-TTCNS system. The percentage of desorption registered a rise from 31.25 to 72.45 for Co(II)-TAINS system. Similar partial desorption had been reported in earlier studies[269]

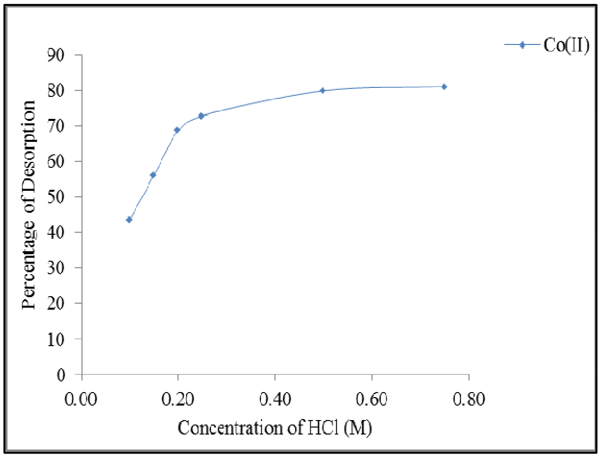

Figure 5.17 Desorption of Co(II) [TTCNS]

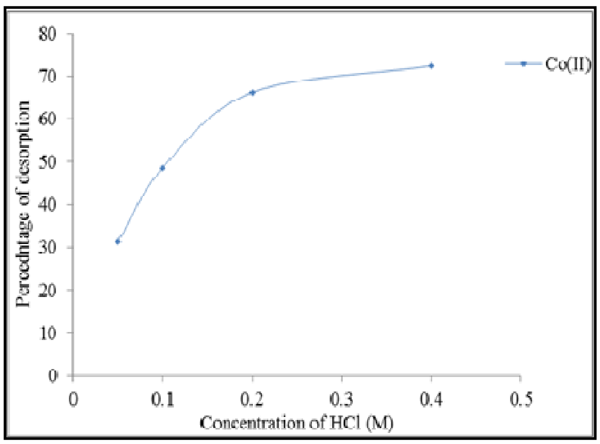

Figure 5.18 Desorption of Co(II) [TAINS]

5.12 Regeneration of TTCNS and TAINS

To make the adsorption process more economical, it is necessary to regenerate the spent adsorbent. To test the reusability of the adsorbent, it was subjected to successive adsorption- desorption cycles with 0.75 M and 0.4 M HCl as the desorbing agent for Co(II)-TTCNS and Co(II)-TAINS system respectively. The adsorption and desorption cycles are shown in figures 5.19 and 5.20 as bar charts. The amount of Co(II) adsorbed from TTCNS was 10.18, 9.84 and 7.32 mg/g in the three successive cycles. The corresponding desorbed amount was 8.65, 7.42 and 6.56 mg/g. Similarly, the amount of Co(II) adsorbed from TAINS was 9.88, 8.24 and 6.55 mg/g. The corresponding desorbed amount was 7.05, 6.55 and 5.42

mg/g. The desorption efficiency was found to be 77.98 % and 65.83 % for the respective adsorbents.

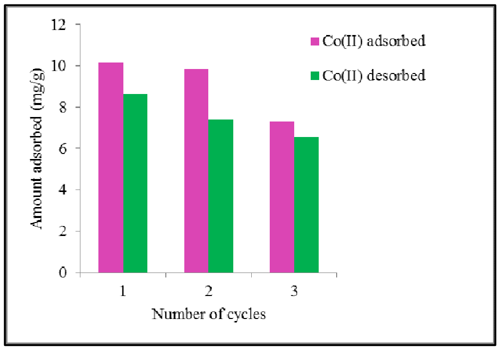

Figure 5.19 Regeneration [Co(II) -TTCNS]

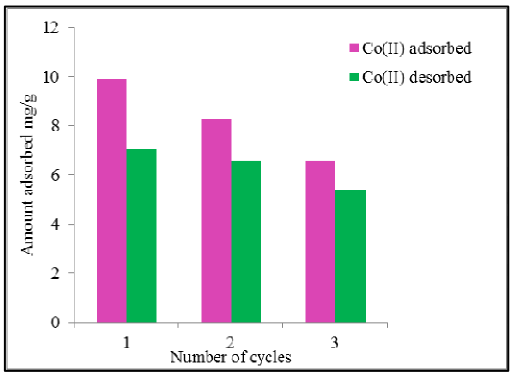

Figure 5.20 Regeneration [Co(II) -TAINS]

5.13 Adsorption Isotherms

A successful representation of the dynamic adsorptive separation of solute from solution onto an adsorbent depends upon a good description of the equilibrium between the two phases. In order to determine the mechanism of Co(II) adsorption on TTCNS and TAINS, the experimental data were applied to Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich isothermal equations. The constant parameters of the isotherm equation for this adsorption process were calculated by regression using linear form of the isotherm equations (Table 5.18).

5.13.1 Langmuir isotherm model

The isothermal data furnished in the table 5.13 are linearised using the Langmuir equation (10) in the plots (5.21 and 5.22) between C_e/q_e versus C_e. The Langmuir constant q_m which is a measure of the monolayer adsorption capacity, was observed as 50.0 and 31.15 mg/g for the employed adsorbents and the Langmuir constant b, (free energy of sorption) was found to be 0.07 and 1.76 respectively, as evident from the table 5.18. The high values of correlation coefficient R^2 for both adsorbents with Co(II) indicate a good agreement between the experimental values and isothermal parameters. The calculated R_L values as per the table 5.14 were between 0.81 and 0.04, which support the statement that R_L values between 0 and 1 is an indicative of favourable adsorption.

Table 5.13 Equilibrium concentrations - Langmuir isotherm

Conc. of metal ion (ppm)	Co(II)-TTCNS		Co(II)-TAINS	
	C_e	C_e/q_e	C_e	C_e/q_e
3	1.12	0.0166	2.43	0.0859
5	1.25	0.0566	4.36	0.0888
7	1.66	0.0619	4.84	0.1120
9	3.88	0.0621	5.69	0.2131
11	5.61	0.0721	7.04	0.2481
13	7.68	0.0827	10.82	0.3406

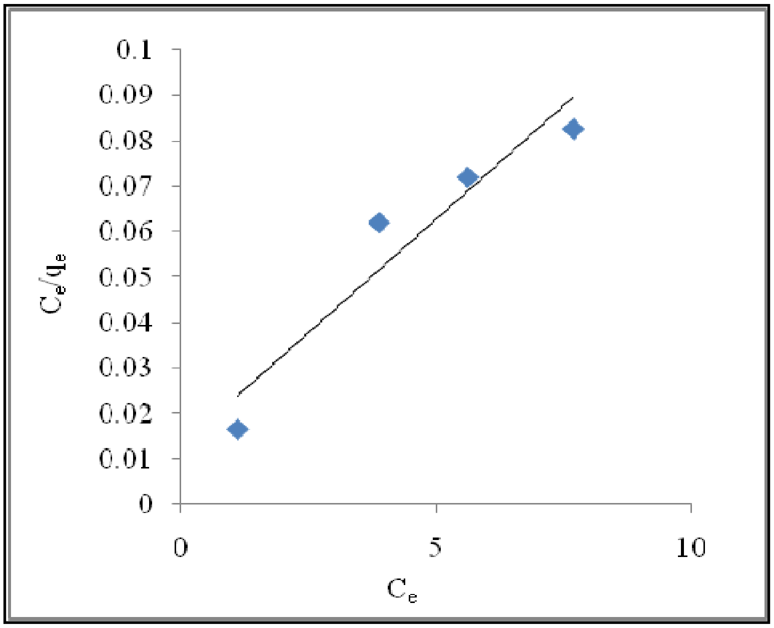

Figure 5.21 Langmuir isotherm model [Co(II)-TTCNS]

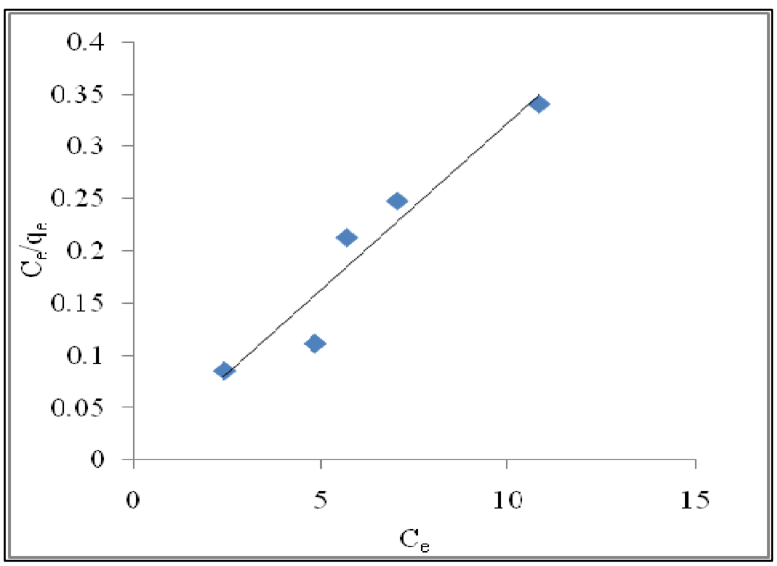

Figure 5.22 Langmuir isotherm model [Co(II)-TAINS]

Table 5.14 Equilibrium parameter (R_L)

Conc. of metal ion (ppm)	Co(II)-TTCNS	Co(II)-TAINS
3	0.81	0.15
5	0.74	0.10
7	0.76	0.07
9	0.61	0.06
11	0.53	0.04

5.13.2 Freundlich isotherm model

The linearity of the Freundlich plots (log q_e versus log C_e ; q_e and C_e values tabulated in table 5.15) for the adsorption of Co(II) onto TTCNS and TAINS depicted in figures 5.23 and 5.24, illustrate that the sorption for the two systems obeyed the isotherm very well. The K_F and n values derived from the intercepts and slopes (Table 5.18) indicate the adsorption capacity and the nature of sorption respectively. The value of 'n' greater than '1' implies favourable nature of adsorption. Similar results are reported for adsorbents like sago waste[278] and acorn waste[279] for metal ion removal.

Table 5.15 Equilibrium concentrations - Freundlich isotherm

Conc. of metal ion (ppm)	Co(II)-TTCNS		Co(II)-TAINS	
	log C_e	log q_e	log C_e	log q_e
3	0.0492	1.4821	0.3586	1.0560
5	0.0969	1.8750	0.6394	1.1070
7	0.2201	1.7951	0.6848	1.6350
9	0.5888	1.8312	0.7551	1.8208
11	0.7489	2.2957	0.8475	1.8987

Adsorbent dose :100mg (TTCNS), 150mg (TAINS) Temperature: 303K

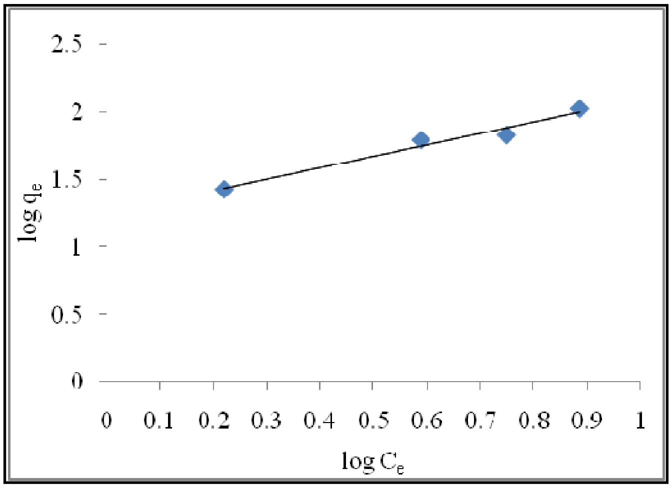

Figure 5.23 Freundlich isotherm model [Co(II)-TTCNS]

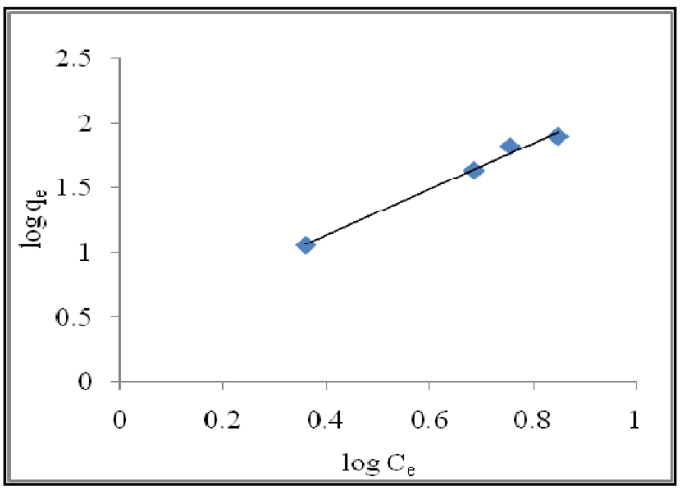

Figure 5.24 Freundlich isotherm model [Co(II)-TAINS]

5.13.3 Tempkin isotherm model

Tempkin isotherm was applied to the adsorption data (table 5.16) under investigation, as per equation (14). Tempkin constants A_T and b_T which are related to the equilibrium binding constant and heat of adsorption are obtained from the linear plot of $\ln C_e$ versus q_e (figure 5.25). The constants and the correlation coefficient values reported in table 5.18, indicate that the isotherm is obeyed by both the systems effectively. Based on this model, the order of heat of adsorption is Co(II)-TTCNS > Co(II)-TAINS. Similar results were documented earlier[280].

Table 5.16 Equilibrium concentrations - Tempkin isotherm

Conc. of metal ion (ppm)	Co(II)-TTCNS		Co(II)-TAINS	
	ln C_e	q_e	ln C_e	q_e
3	0.5069	26.8	0.8880	11.4
5	0.2231	75.0	1.4727	12.8
7	1.3260	62.4	1.5771	43.2
9	1.7248	67.8	1.7390	66.2
11	0.1133	197.6	1.9519	79.2

Adsorbent dose :100mg (TTCNS), 150mg (TAINS) Temperature: 303K

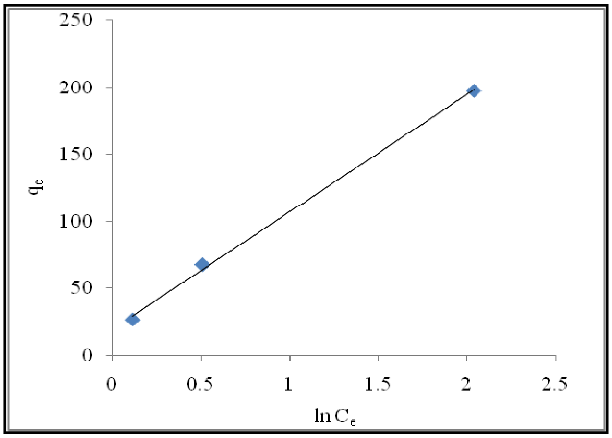

Figure 5.25 Tempkin isotherm model [Co(II)-TTCNS]

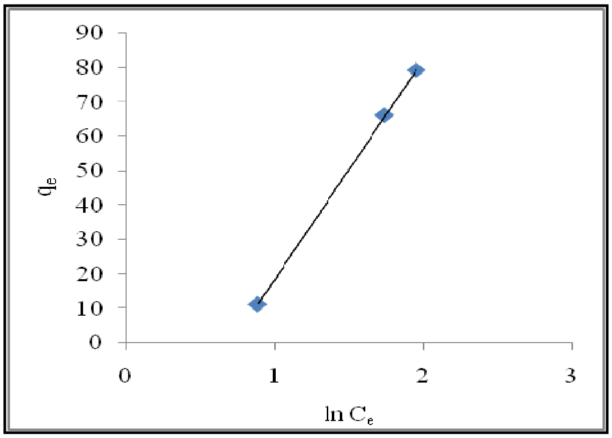

Figure 5.26 Tempkin isotherm model [Co(II)-TAINS]

5.13.4 Dubinin–Kaganer-Radushkevich isotherm model

The equilibrium data were applied to the DKR isotherm model in order to determine the nature of sorption processes as physical or chemical. Figures 5.27 and 5.28 represent the DKR plots for Co(II)-TTCNS and Co(II)-TAINS systems. The values of correlation coefficients shown in table 5.18, indicate that the DKR isotherm fitted well with the experimental data. The mean sorption energy calculated from the slope was 12.84 and 9.37 kJ/mol for the sorption of Co(II) onto TTCNS and TAINS respectively. The results show that the sorption of the the metal ion onto TTCNS and TAINS may be carried out via chemical ion exchange mechanism, as their values lie above 8 KJ/mol. Similar results were reported for various adsorbents[21,191]

Table 5.17 Equilibrium concentrations - DKR isotherm

Conc. of metal ion (ppm)	Co(II)-TTCNS		Co(II)-TAINS	
	ε^2 X10^8	ln q_e	ε^2 X10^8	ln q_e
3	249.94	3.289	72.77	2.432
5	212.09	4.134	26.09	2.549
7	136.47	4.217	21.53	3.768
9	32.27	4.318	15.95	4.193
11	16.51	4.668	10.83	4.372
13	9.19	5.287	4.75	2.381

Adsorbent dose :100mg (TTCNS), 150mg (TAINS) Temperature: 303K

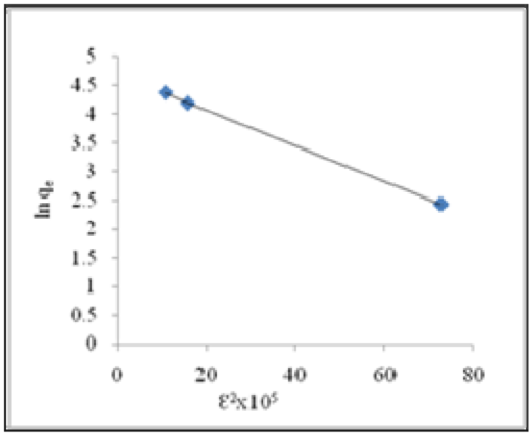

Figure 5.27 DKR isotherm model [Co(II)-TTCNS]

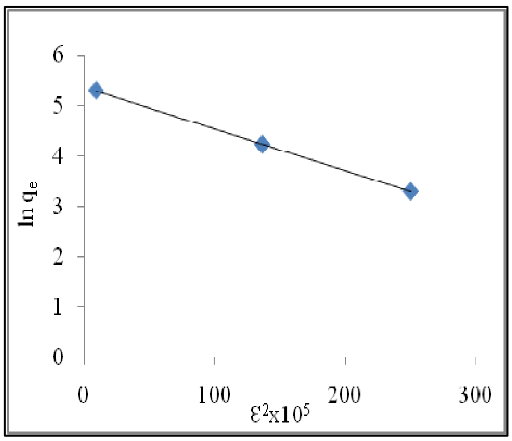

Figure 5.28 DKR isotherm model [Co(II)-TAINS]

5.13.6 Comparison of isotherm models

The equilibrium data fits well to all isotherm models for the two systems studied as indicated by the higher correlation coefficient values in table 5.18. The applicability of Langmuir, Freundlich and DKR isotherm models to the metal ion indicated the homogeneous and heterogeneous distribution of active sites on the surface of TTCNS and TAINS[258]. This implies that, both monolayer sorption and heterogeneous surface conditions exist under the experimental conditions used which involves more than one mechanism[281]

Table 5.18 Isothermal constants [Co(II)]

Isotherm parameters	Co(II)-TTCNS	Co(II)-TAINS
Langmuir isotherm		
q_m (mg/g)	50.0	31.15
b (L/g)	0.07	1.76
R^2	0.9910	0.9214
Freundlich isotherm		
K_F (mg/g)	37.35	27.46
n	1.10	1.37
R^2	0.9955	0.9995
Tempkin isotherm		
A_T (L/g)	1.0625	1.1019
b_T	781.53	41.252
R^2	0.9567	0.9619
DKR isotherm		
q_s (mg/g)	160.6	109.8
E (kJ/mol)	12.82	9.09
R^2	0.9990	0.9990

5.14 Adsorption Kinetics

The kinetics and equilibrium of adsorption are the two major parameters to evaluate adsorption dynamics. The adsorption kinetics were investigated with an aim of obtaining a deep insight into how the amount of adsorbed metal changes with time and the process time required to achieve equilibrium between the aqueous and the solid phase. The kinetics of Co(II) sorption onto TTCNS and TAINS were analyzed using different kinetic models such as pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion models.

5.14.1 Pseudo-first-order model

The pseudo-first-order rate expression of equation (18) used to test the experimental data for Co(II) onto TTCNS and TAINS are tabulated in tables 5.19 and 5.20 respectively. The values of k_1, pseudo-first-order rate constant and q_e calculated obtained by the plot of log (q_e-q_t) versus t are presented in table 5.21 with coefficients of regression and SSE

Table 5.19 Effect of concentration-Kinetics of [Co(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
5	1.281	1.4925	1.4321	0.2666	1.4281	0.5235	1.7671	0.3048	1.3621	0.0582
10	1.222	1.6129	1.2208	0.3428	1.2148	0.5597	1.6304	0.3105	1.3506	0.1157
15	1.1846	1.7857	1.1928	0.4965	0.9395	0.5747	1.6242	0.4573	1.3014	0.2024
20	0.7923	1.7985	0.9190	0.5853	0.6334	0.6410	1.6232	0.4672	1.0080	0.2472
25	0.7558	3.448	0.4899	0.66666	0.2304	0.7396	1.4927	0.5565	0.8859	0.2817
30		3.4883		0.6696		0.867	1.3222	0.5707	0.3729	0.7492

Concentration: 3-11 ppm; Adsorbent dose: 100 mg; pH: 4.04; Temperature: 303K

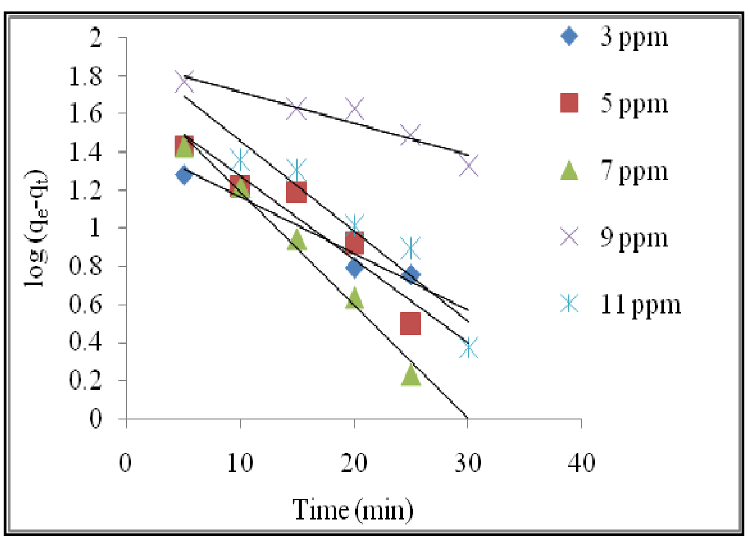

Figure 5.29 Pseudo-first-order Kinetics of Co(II)-TTCNS

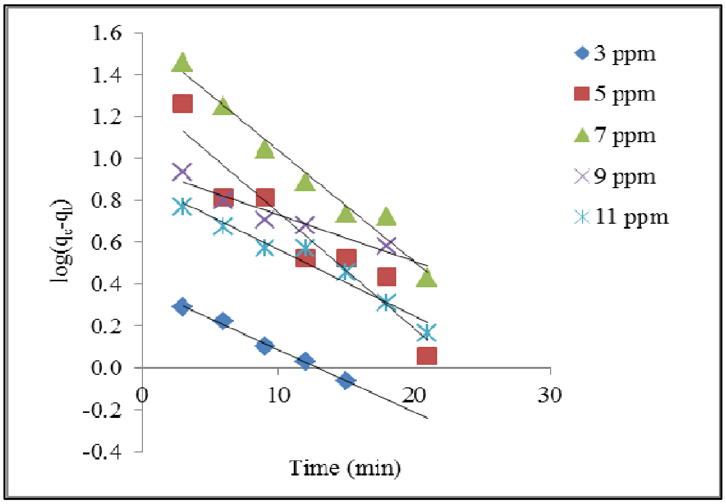

Figure 5.30 Pseudo-first-order Kinetics of Co(II)-TAINS

5.14.2 Pseudo-second-order model

Tables 5.19 and 5.20 correspondingly list out the experimental values for Co(II) TTCNS and TAINS systems. The pseudo-second-order rate constant values obtained from figures 5.31 and 5.32 (t/q_t versus t) are presented in table 5.21. The decrease in K_2 and increase in q_e values with an increase in metal concentration as registered in the present system is supported by other researchers who had employed green algae *Spirogyra* species[270], *Euphorbia rigida*[265] and *Cyanobacterium nostoc*[238]. The increase in q_e with concentration may be due to the more efficient utilization of the sorptive capacities of the adsorbents due to greater driving force (by a higher concentration gradient pressure)[142]. As the increase in the metal concentration reduces the diffusion of metal ions in the boundary layers, K_2 decreases with concentration[282].

Table 5.20 Effect of concentration-Kinetics of [Co(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	0.2878	1.2195	1.259	2.054	1.458	0.4285	0.7032	0.7302	0.1636	0.5628
6	0.1038	1.9169	0.816	2.816	1.250	0.7202	0.6799	0.5808	0.3115	0.5825
9	0.0290	2.7020	0.812	2.812	1.041	0.7340	0.5172	0.5172	0.4561	0.6738
12	-0.0604	3.3990	0.521	3.399	0.887	0.8869	0.5808	0.5808	0.5698	0.7337
15	0.2218	3.9470	0.521	3.521	0.734	1.0410	0.6799	0.6799	0.5681	0.7063
18		3.1570	0.435	3.521	0.720	1.2500	0.7989	0.7989	0.6716	1.2570
21				4.259		1.4580	0.9320	0.9320	0.7692	1.5000

Concentration:3-11 ppm; Adsorbent dose: 150 mg; pH: 6.3; Temperature: 303K

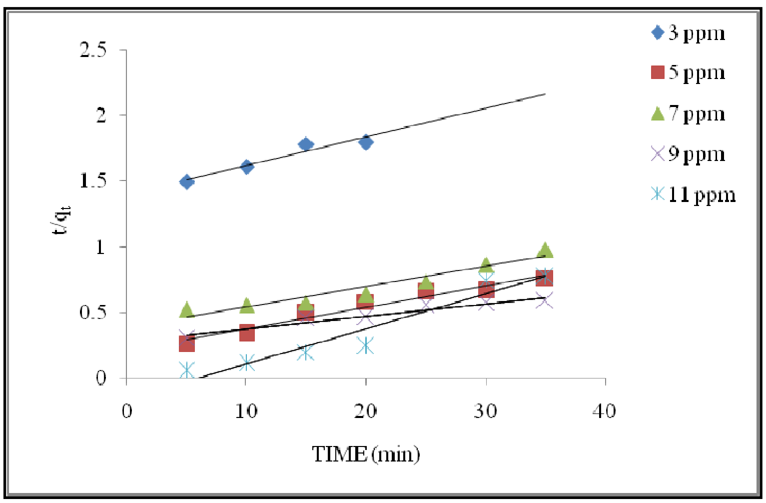

Figure 5.31 Pseudo-second-order Kinetics of Co(II)-TTCNS

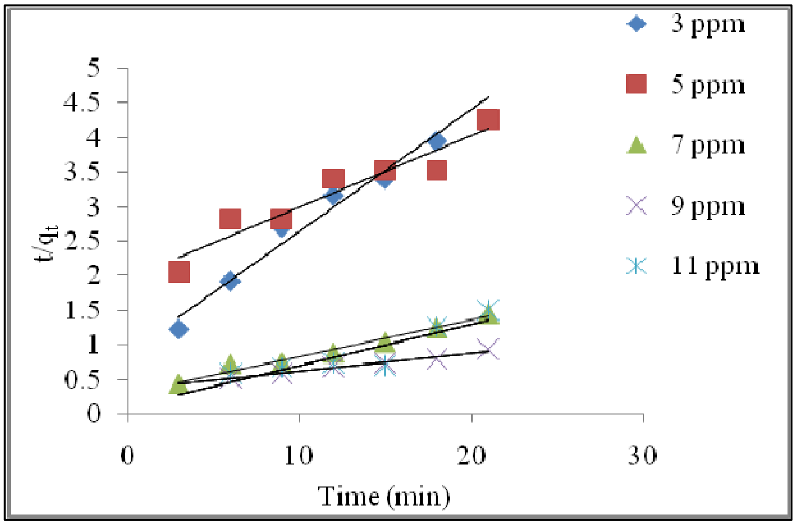

Figure 5.32 Pseudo-second-order kinetics of Co(II)-TAINS

Table 5.21 Pseudo-first-order and pseudo-second-order Kinetic constants at different concentrations

Conc. of metal ions (ppm)	q_e exp. (mg/g)	Pseudo-first-order kinetics				Pseudo-second-order kinetics			
		q_e cal. (mg/g)	$k_1 \times 10^{-2}$ (min^{-1})	R^2	SSE	q_e cal. (mg/g)	$k_2 \times 10^{-3}$ (g/ mg min)	R^2	SSE
Co(II)-TTCNS									
3	18.6	28.57	6.81	0.9510	4.98	45.87	3.4	0.9203	10.3
5	44.8	50.90	10.06	0.9079	2.72	60.60	12.9	0.9551	5.97
7	34.6	50.97	13.70	0.9863	7.32	64.51	6.1	0.9253	11.3
9	53.9	75.82	3.80	0.9024	9.82	37.45	3.1	0.9360	6.2
11	106.4	85.52	10.9	0.9084	9.30	105.26	4.6	0.9296	0.43
Co(II)-TAINS									
3	3.8	2.42	6.88	0.9941	0.61	5.66	35.86	0.9714	0.70
5	21.6	19.86	12.8	0.9082	0.66	37.7	5.54	0.9147	6.08
7	26.8	36.95	12.2	0.9720	3.8	18.8	10.6	0.9720	2.64
9	4.93	8.92	5.08	0.9178	1.78	9.61	2.01	0.9822	2.50
11	8.3	7.58	7.27	0.9576	0.27	16.6	3.70	0.8077	3.13

5.14.3 Elovich model

The kinetic constants α and β were estimated from the intercept and slope values of the Elovich plots of q_t versus ln t (Figures 5.33 and 5.34) for both Co(II)-TTCNS and Co(II)-TAINS systems registered an irregular increase and a perfect decrease respectively.

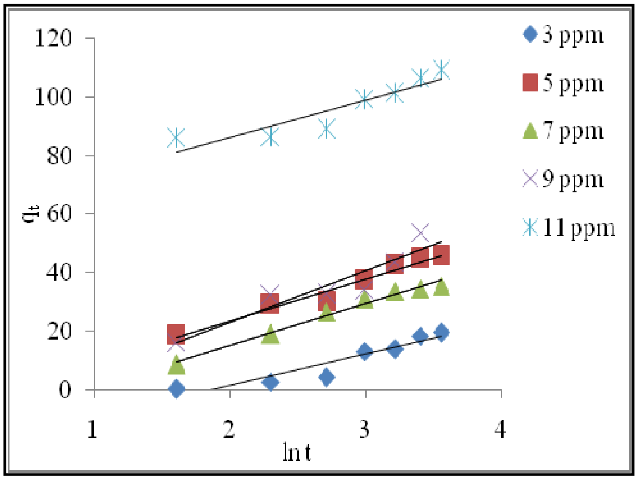

Figure 5.33 Elovich model [Co(II)-TTCNS]

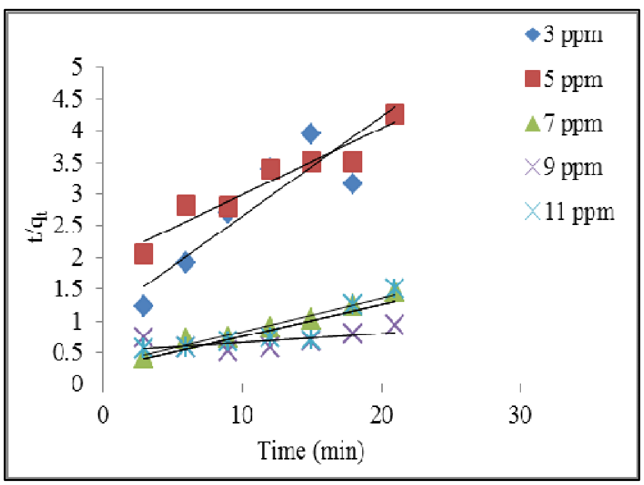

Figure 5.34 Elovich model [Co(II)-TAINS]

Table 5.22 Elovich constants at different initial concentrations

Conc. of metal ions (ppm)	Co(II)-TTCNS			Co(II)-TAINS		
	α	**β**	**R^2**	**α**	**β**	**R^2**
3	1.6	0.093	0.8773	7.11	1.15	0.9385
5	10.	0.069	0.9688	7.28	0.12	0.9674
7	5.6	0.069	0.9800	6.95	0.22	0.9255
9	8.7	0.056	0.8672	8.06	0.09	0.9577
11	14.	0.077	0.8385	10.03	0.13	0.9925

α : (mg/g min), β : (g/mg)

5.14.4 Intraparticle diffusion model

The Weber and Morris intraparticle diffusion model equation (25) is applied to the sorption of systems under investigation. The intraparticle diffusion plots of of q_t versus $t^{1/2}$ at different concentrations, which has two distinct portions[280,263] are presented in figures 5.35 and 5.36. The first linear portion refers to the boundary layer diffusion effect while the second linear portion refers to gradual adsorption stage, where intraparticle diffusion was rate limiting. The K_i (intraparticle rate constant) and C (boundary layer thickness) values obtained from the slopes and intercepts (table 5.23) increased with metal ion concentrations. The linear plots did not pass through the origin. According to Ilhem Ghodbane et al.,[267] this is indicative of some degree of boundary layer control. This further shows that the intraparticle diffusion is not the only rate controlling step for the adsorption of the systems investigated[268].

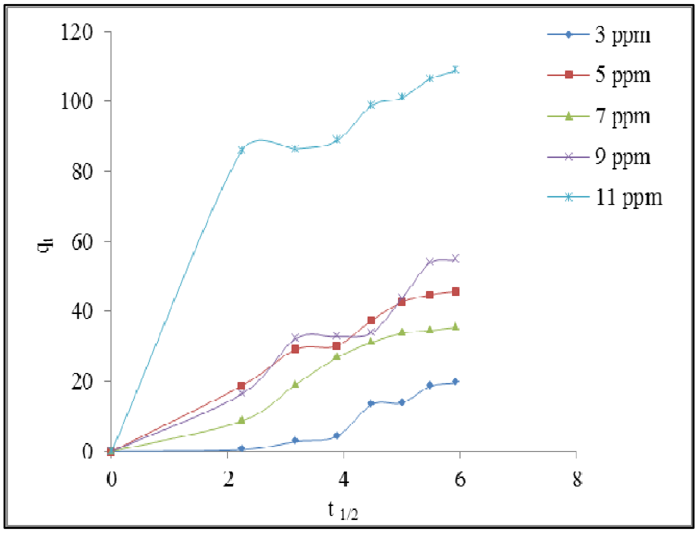

Figure 5.35 Intraparticle diffusion model [Co(II)-TTCNS]

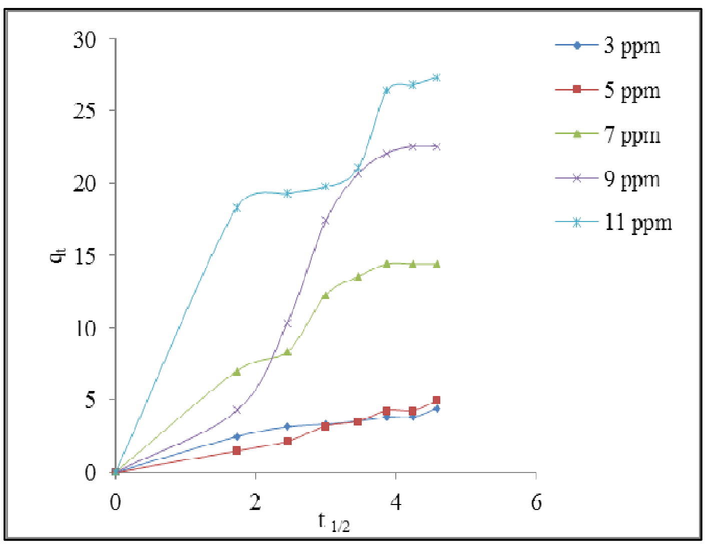

Figure 5.36 Intraparticle diffusion model [Co(II)-TAINS]

Table 5.23 Intraparticle diffusion model constants at different concentrations

Conc. of metal ions (ppm)	Co(II)-TTCNS			Co(II)-TAINS		
	K_i (mg/ g min$^{1/2}$)	C	R^2	K_i (mg/ g min$^{1/2}$)	C	R^2
3	5.75	3.22	0.9330	0.5872	1.5347	0.9476
5	7.03	4.39	0.9687	1.2145	0.6539	0.9802
7	7.31	14.33	0.9281	2.9003	2.3748	0.8897
9	7.51	15.54	0.8369	3.6228	5.2775	0.9034
11	13.16	66.36	0.9169	6.7143	10.617	0.8557

5.15 Adsorption Dynamics

The thermodynamic parameters such as change in free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were calculated using the equations (26) and (27). The ΔH^0, ΔS^0 calculated from the slope and intercept of Vant Hoff plots (figures 5.37 and 5.38) are shown in table 5.24. The positive values of ΔH^0 indicate the presence of an energy barrier in the adsorption process which is endothermic in nature[132]. The negative values of ΔG^0 indicate the feasibility and spontaneous nature of adsorption of metal ions by the adsorbent[279]. The magnitude of ΔG^0 increased with temperature indicating that the sorption was more favourable at higher temperature[259]. The positive values of ΔS^0 suggest that the increased randomness at the solid-solution interface during the adsorption of metal Co(II) in aqueous solutions onto TTCNS and TAINS[256]. The low value of ΔS^0 may imply that no remarkable change in entropy occurred during the sorption of Co(II) on the adsorbents[267]. Similar trend has been observed for adsorbents such as rice bran[271] and rubber wood sawdust[283].

Table 5.24 Thermodynamic constants Co(II)

Temp. K	Co(II)-TTCNS			Co(II)-TAINS		
	$-\Delta G \times 10^{-3}$ kJ/mol	ΔH kJ/mol	ΔS J/mol K	$-\Delta G \times 10^{-3}$ kJ/mol	ΔH kJ/mol	ΔS J/mol K
293	2.54	5.4	18.77	0.793	6.34	21.68
303	2.63			0.409		
313	3.08			0.169		
323	3.50			0.087		
333	3.73			0.053		

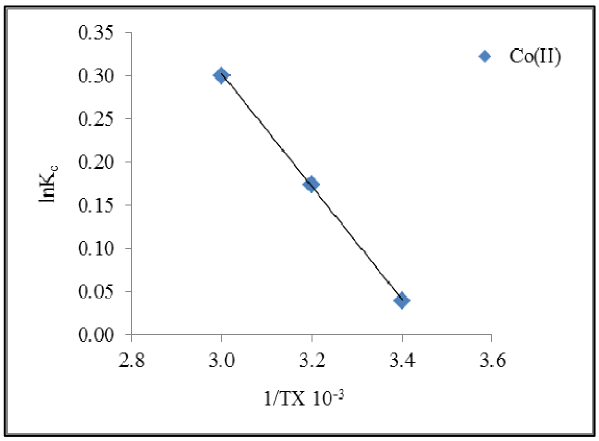

Figure 5.37 Vant Hoff's plot (TTCNS)

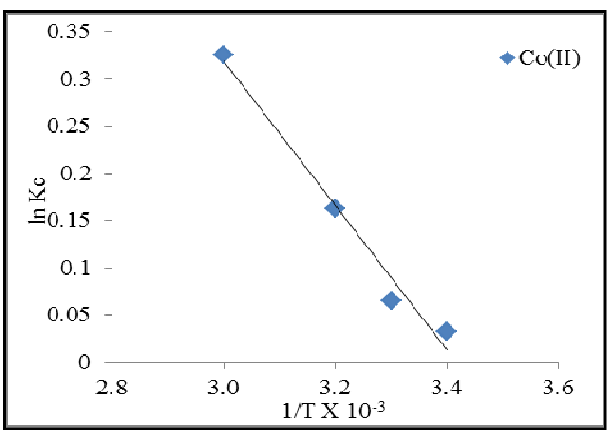

Figure 5.38 Vant Hoff's plot (TAINS)