CHAPTER ٣

RESULTS AND DISCUSSION

Chapter 3

Results and discussion

CKD was utilized to remove heavy metal ions such as: Zn(II), Co(II), Cd(II), and Al(III) from wastewater. Therefore, the parameters affecting heavy metal ions removal from synthetic solution such as; the effect of residence time, the effect of pH, the effect of variation of sorbent amount added the effect of variation initial sorbate concentration (Zn, Co, Cd, and Al ions) and finally studying the effect of temperature on the adsorption of these heavy metal ions.

3.1 Analysis of CKD

CKD was collected from Egyptian cement companies such as; tourah portoland Cement Company, national cement company, Suez Cement Company, assiut Cement Company and beni-suef cement company

The sample of CKD obtained from companies was analyzed by X-ray fluorescence(XRF), the percent composition of the CKD are shown in table and figure (3.1); the main ingredients or the major components of CKD are calcium oxide, sodium oxide, potassium oxide, sulfure-tri-oxide ,silicate and chloride. The alkalinity nature of the dust makes it a good neutralizing agent for acidic wastewater stream.

Table (3.1):X-ray Fluorescence analysis of CKD

Ingredients	% Average Percent
SiO_2	3.14
TiO_2	0.05
Al_2O_3	0.38
Fe_2O_3	0.61
MnO	0.01
MgO	0.22
CaO	24.85
Na_2O	8.61
K_2O	12.95
P_2O_5	0.04
Cl	22.35
SO_3	6.71
L.O.I	19.45

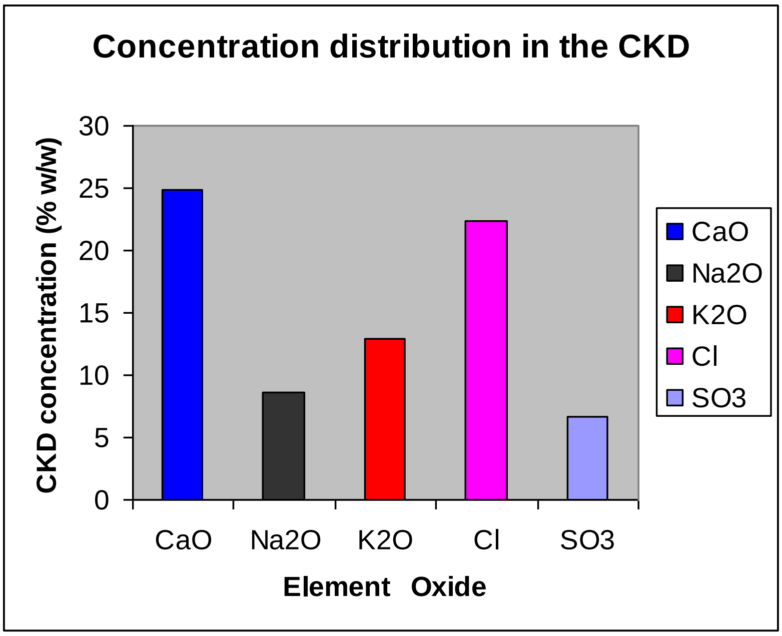

Figure (3.1):X-ray Fluorescence analysis of CKD

3.2 Batch contact time studies

"Kinetics of heavy metal ions removal by CKD"

The batches of adsorption were carried out to investigate removal of heavy metal ions efficiency from a synthetic solution, all experiments were done under the operation conditions 50 ml solution of heavy metal ions Zn(II), Al(III), Co(II) and Cd (II), on temp (24+1) ^{o}C, agitation rate equal to 130 rpm using 0.5 g of CKD having average particle size 3 μ during the adsorption process and within initial concentrations 145.50 mg/L, 75.597 mg/L, 114.66 mg/L and 99.972 mg/L for Zn(II), Al(III), Co(II) and Cd(II) respectively.

3.2.1 Measurement of equilibrium time

The equilibrium time in batch-sorption experiments is the time interval in which the system reaches chemical equilibrium and the concentration of the products and reactants cease to change with respect to time.

$$\frac{\Delta C}{\Delta t} = \mathbf{O} \qquad (1)$$

The EPA[41] have suggested that the equilibrium time should be defined as the minimum time needed to establish a rate of change of the solute concentration in solution equal to or less than 5% per 24-h interval. This definition is an operational definition of equilibrium and is equivalent to a steady state. Cast as an equation, it may be written as

$$\frac{\Delta c}{\Delta t} \leq 0.05 Per \text{ 24h Interval} \qquad (2)$$

Jones et al. [42] have suggested a less rigorous approach based on the minimum time needed to establish a rate of change of the solute concentration equal to, or less than, 10% during a 6 h period.

the effect of contact time on the percent removal , residual concentration and adsorbent amount of heavy metal ions Zn(II), Al(III), Co(II) and Cd(II) on CKD are indicated in tables(3.2), (3.3), (3.4), (3.5) and figures (3.5, 3.6 and 3.7), (3.8, 3.9 and 3.10), (3.11, 3.12 and 3.13), (3.14, 3.15 and 3.16) respectively .

Results (Fig. 3.2 and 3.3) indicate that the removal efficiency increased with increase in contact time before equilibrium is reached. Other parameters such as dose of adsorbent, pH of solution and agitation speed were kept at optimum, while temperature was kept at 30 ^{o}C .

It is observed that for Al(III) ions, the percentage removal is nearly 100% even throughout the all contact times. Hence the Al(III) required the shortest contact time.

In case of Zn(II) and Cd(II) ions, sharp rise in percentage removal occurred with increasing contact time. It can be seen that Zn and Cd removal efficiency by using CKD increased from 80% to 95% when contact time was increased from 20 to 40 min. On other hand, percentage removal of Co(II) increased gradually with contact time, reaching nearly 100% removal only at around 4 h.

It is evident from the results that the contact time required to attain equilibrium is dependent on the initial concentration of heavy metal ions. For the same concentration, the percentage removal of heavy metal ion increased with increase of contact time till equilibrium is attained.

The optimal contact time to attain equilibrium with CKD was experimentally found to be about 40 min for Zn(II), 5 min. for Al(III), 1 h for Cd(II) and 4 h for Co(II). This result is important, as equilibrium time is one of the important parameters for an economical wastewater treatment system.

Also the effect of contact time on the adsorbent amount of heavy metal ions Zn (II), Al(III), Co(II) and Cd(II) on CKD are shown in tables(3.2), (3.3), (3.4), (3.5) respectively and figure **(**Fig. 3.4) . It is suggested that the adsorption of metal ions proceeds mainly via complex formation with hydroxyl groups of the adsorbent and ionic interactions respectively.

It has been observed that [43] the mechanism of metal ion removal from the aqueous metal ions involved four steps: (i) migration of metal ions from the bulk solution to the surface of the adsorbent; (ii) diffusion through boundary layer to CKD surface; (iii) adsorption at a binding site and (iv) intra particle diffusion into the interior of the CKD. The boundary layer resistance will be affected by the rate of sorption and increasing the agitation time will reduce this resistance and increase the mobility of the ions. However, because the process is time dependent, after about 40 min, 5 min, 1 hr and 4 hr for Zn(II), Al(III), Cd(II) and Co(II), respectively of agitation, adsorption remains slightly or relatively constant. This observation is in agreement with the proposed mechanism obtained from the sorption characteristic study.

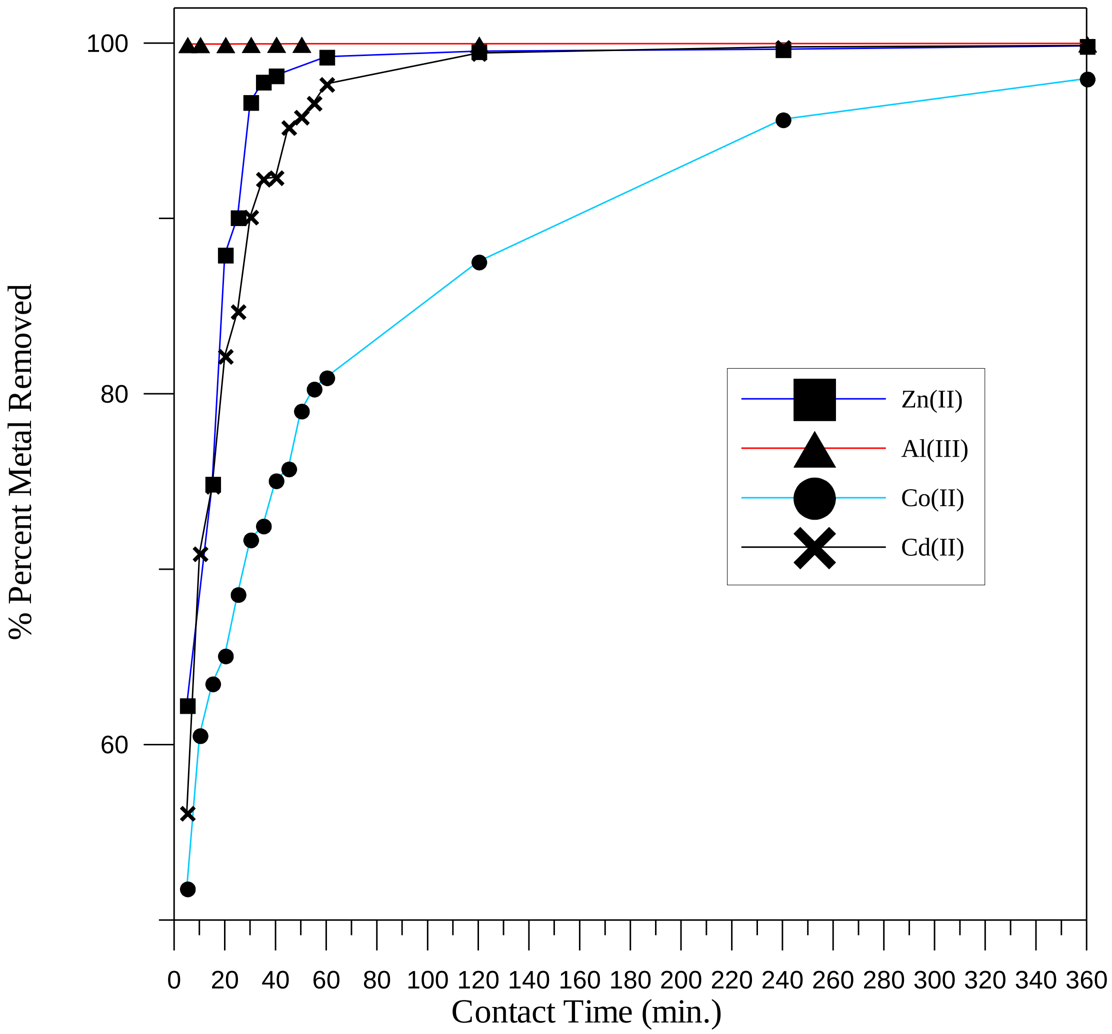

Figure 3.2 Effect of contact time on the percent heavy metal ions removal by using CKD.

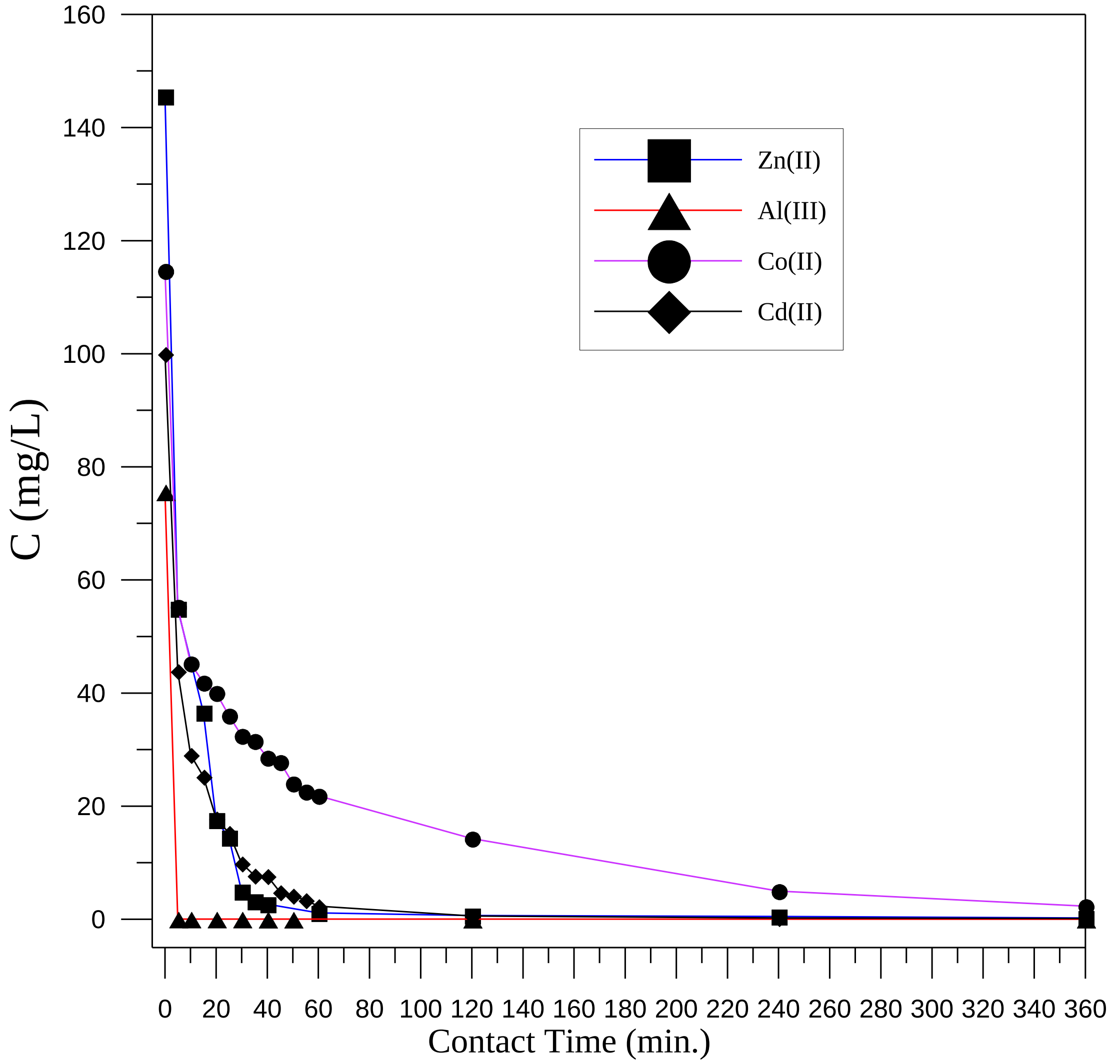

Figure 3.3 Effect of contact time on the residual concentration of heavy metal ions by using CKD.

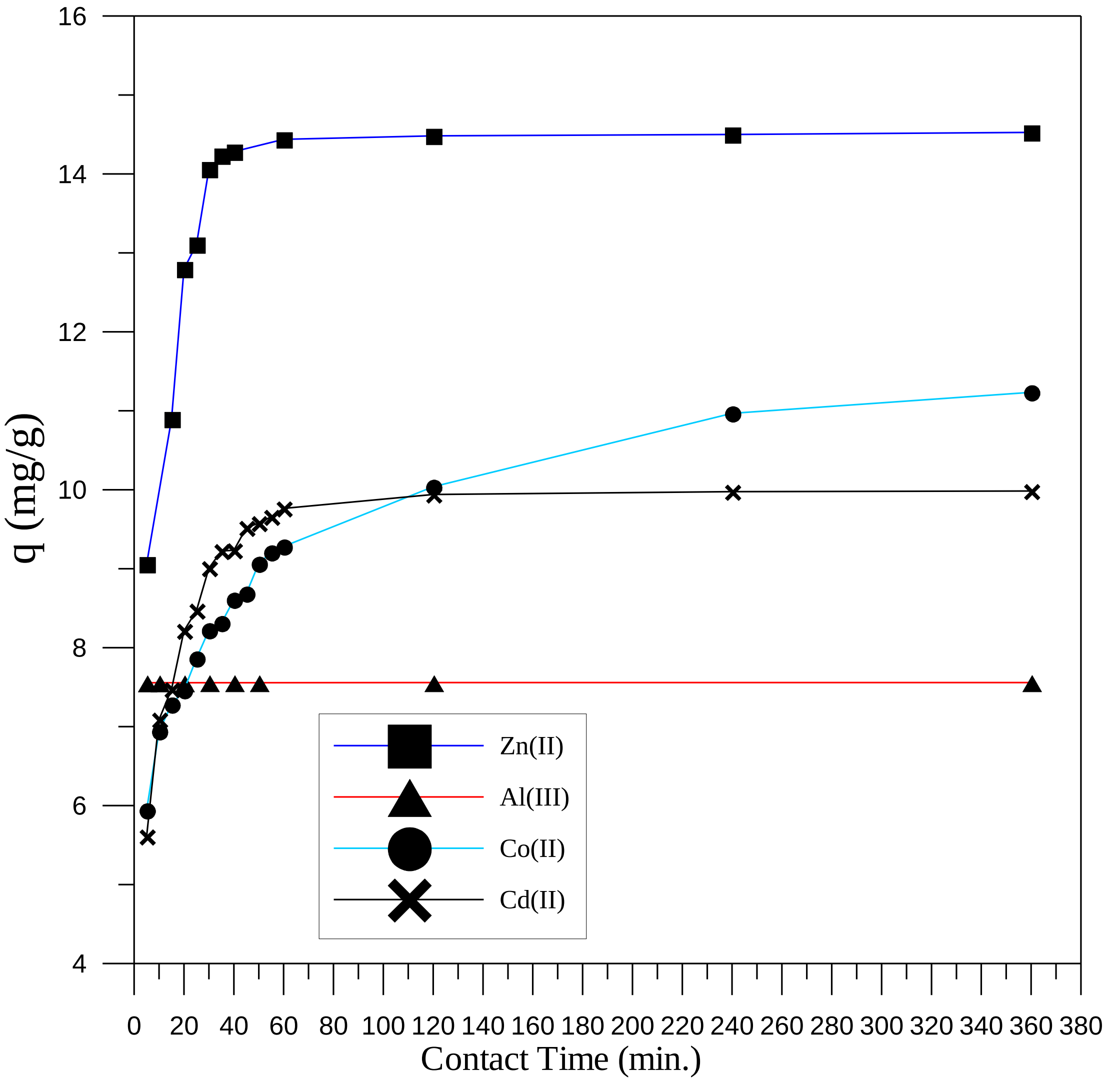

Figure 3.4 Effect of contact time on the adsorbent amount of heavy metal ions by using CKD

Table 3.2 Effect of contact time on **Zn** metal ion removal within initial concentration **145.50 mg/L** by using CKD, at pH (8.77-8.90), temp 30 ^{o}C, 10 g CKD / L and 130 rpm.

pH	Contact time **(min.)**	Residual conc. **C (mg/L)**	Adsorbent amount **q (mg/g)**	% Percent Removal **$(C_o-C)/C_o*100$**	Distribution coefficient $(C_o-C)/ C*$ v/m
8.77 - 8.90	0	145.50	0	0	0
	5	54.917	9.0583	62.2564	164.9453
	15	36.550	10.895	74.8797	298.0848
	20	17.538	12.7962	87.9464	729.6271
	25	14.442	13.1058	90.0742	907.4782
	30	4.8878	14.06122	96.6407	2876.799
	35	3.1891	14.23109	97.8082	4462.416
	40	2.6766	14.28234	98.1604	5336.001
	60	1.1277	14.43723	99.225	12802.37
	120	0.67657	14.48234	99.535	21405.54
	240	0.50381	14.49962	99.6537	28779.93
	360	0.23179	14.52682	99.8407	62672.34

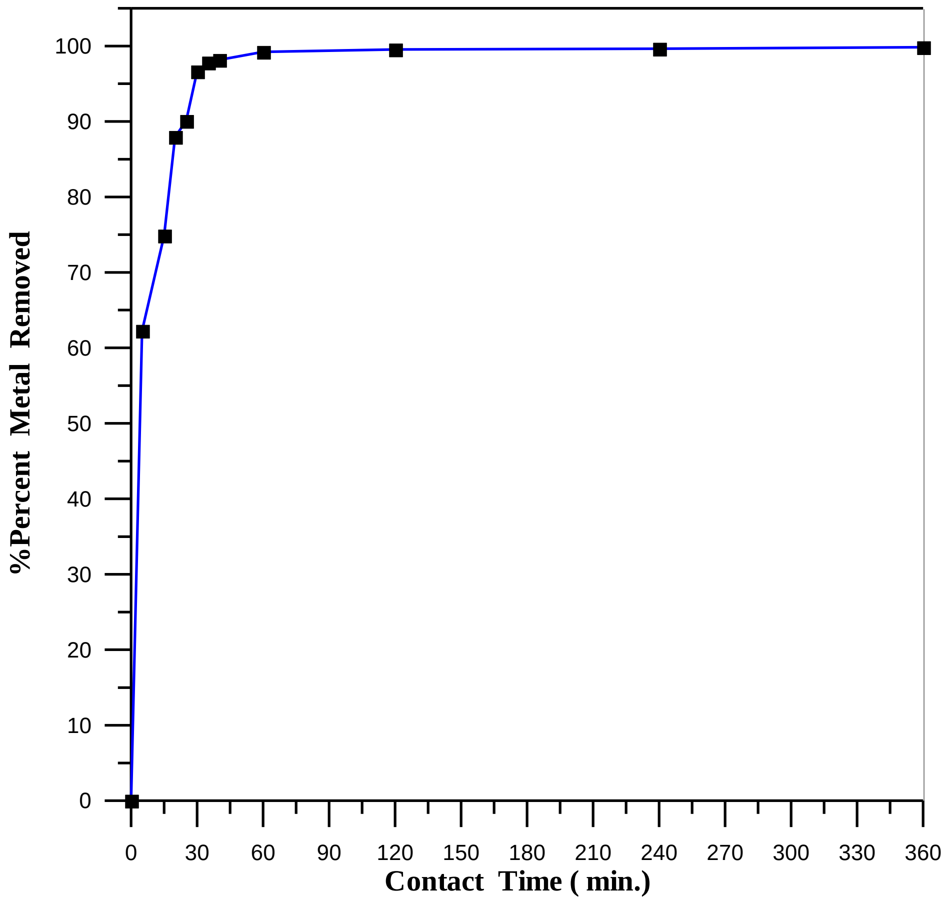

Figure 3.5 Effect of contact time on Zn metal ion removal within initial concentration **145.50 mg/L** by using CKD, at pH (8.77-8.90), 10 g CKD / L, and 130 rpm.

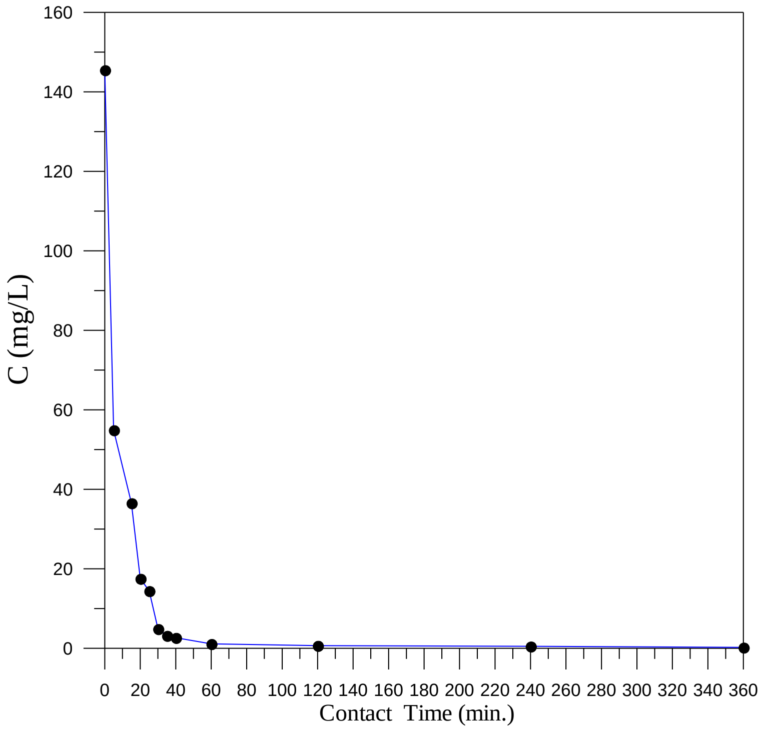

Figure 3.6 Effect of contact time on the residual concentration of Zn metal ion within initial concentration **145.50 mg/L** by using CKD, at pH (8.77-8.90), 10 g CKD / L, and 130 rpm.

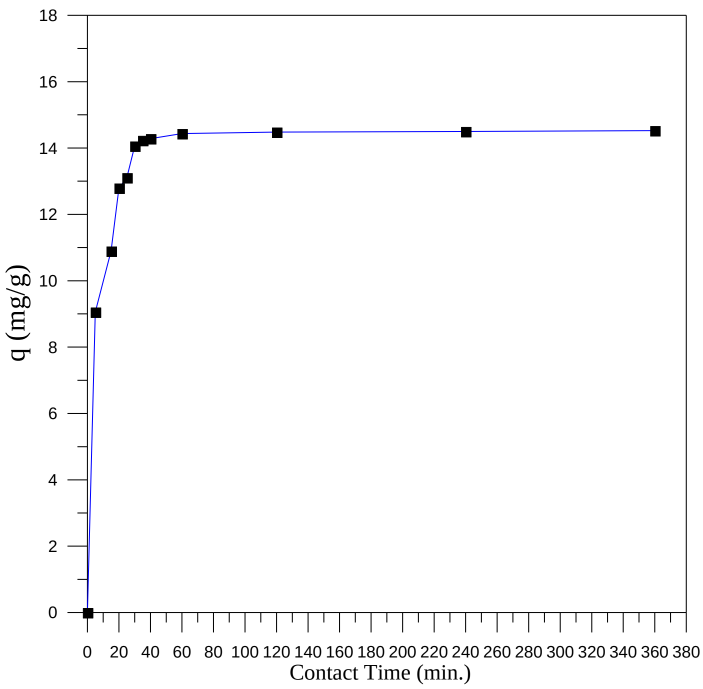

Figure 3.7 Effect of contact time on the adsorbent amount of Zn metal ion within initial concentration **145.50 mg/L** by using CKD, at pH (8.77-8.90), 10 g CKD / L, and 130 rpm.

Table 3.3 Effect of contact time on **Al** metal ion removal within initial concentration **75.597 mg/L** by using CKD, at pH (7.62 - 7.80), 10 g CKD / L, and 130 rpm.

pH	Contact time **(min.)**	Residual conc. **C (mg/L)**	Adsorbent amount **q (mg/g)**	% Percent Removal **$(C_o-C)/C_o*100$**	Distribution coefficient **$(C_o-C)/C*v/m$**
7.62 - 7.80	0	75.597	0	0	0
	5	0.04301	7.555399	99.9431	175666.1
	10	0.04248	7.555452	99.9438	177859
	20	0.04196	7.555504	99.9445	180064.4
	30	0.03537	7.556163	99.9532	213632
	40	0.03247	7.556453	99.9571	232721.1
	50	0.03062	7.556638	99.9595	246787.7
	120	0.02509	7.557191	99.9668	301203.3
	360	0.01718	7.557982	99.9773	439929.1

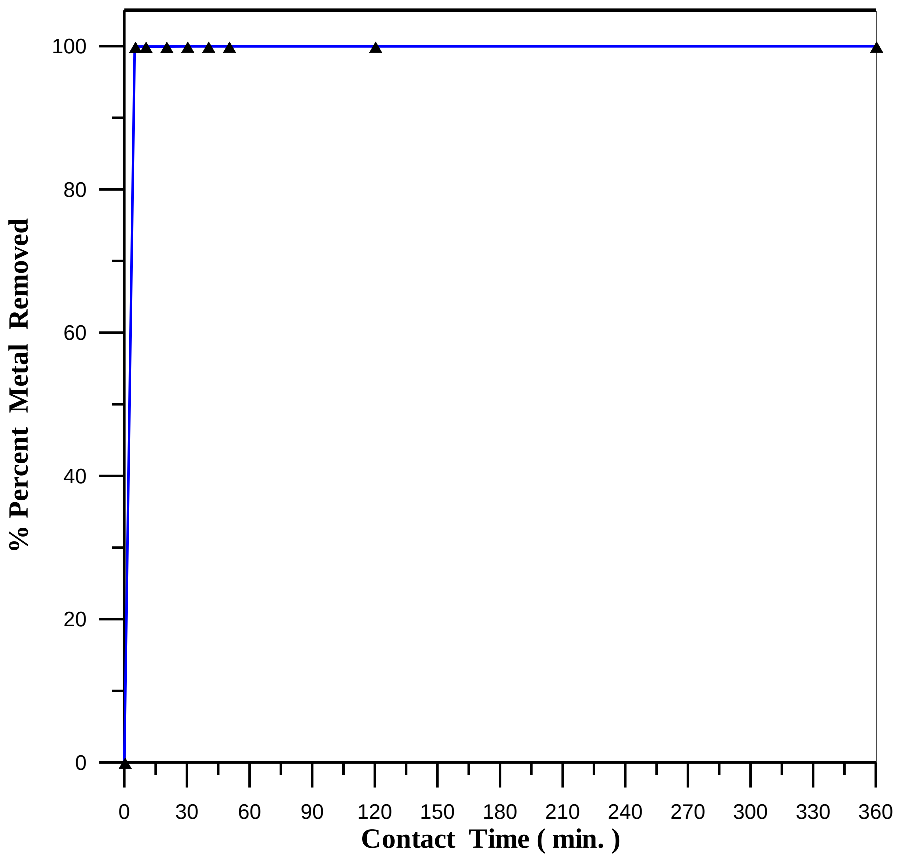

Figure 3.8 Effect of contact time on Al metal ion removal within initial concentration **75.597 mg/L** by using CKD, at pH (7.80- 7.63), 10 g CKD / L, and 130 rpm.

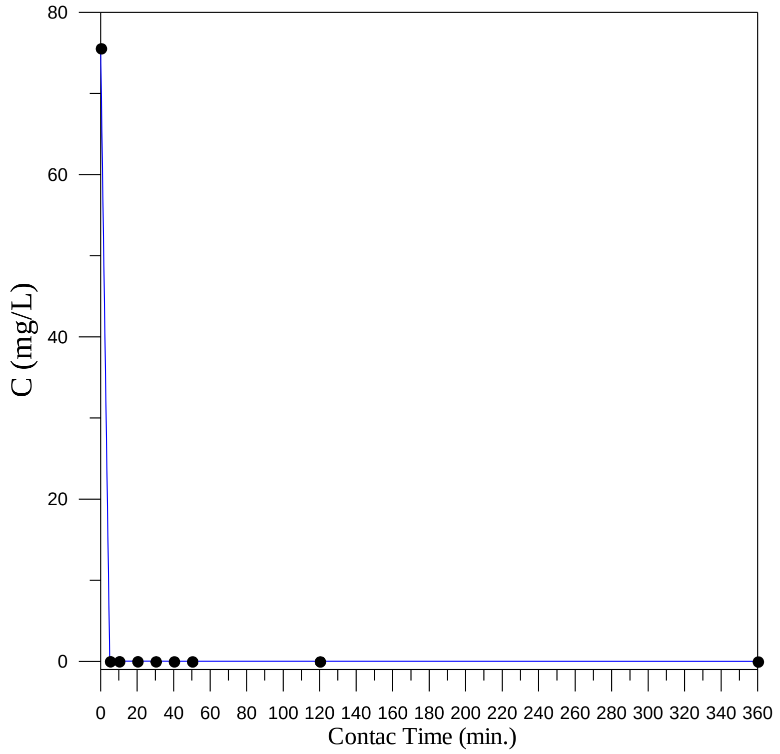

Figure 3.9 Effect of contact time on the residual concentration of Al metal ion within initial concentration **75.597 mg/L** by using CKD, at pH (7.80- 7.63), 10 g CKD / L, and 130 rpm.

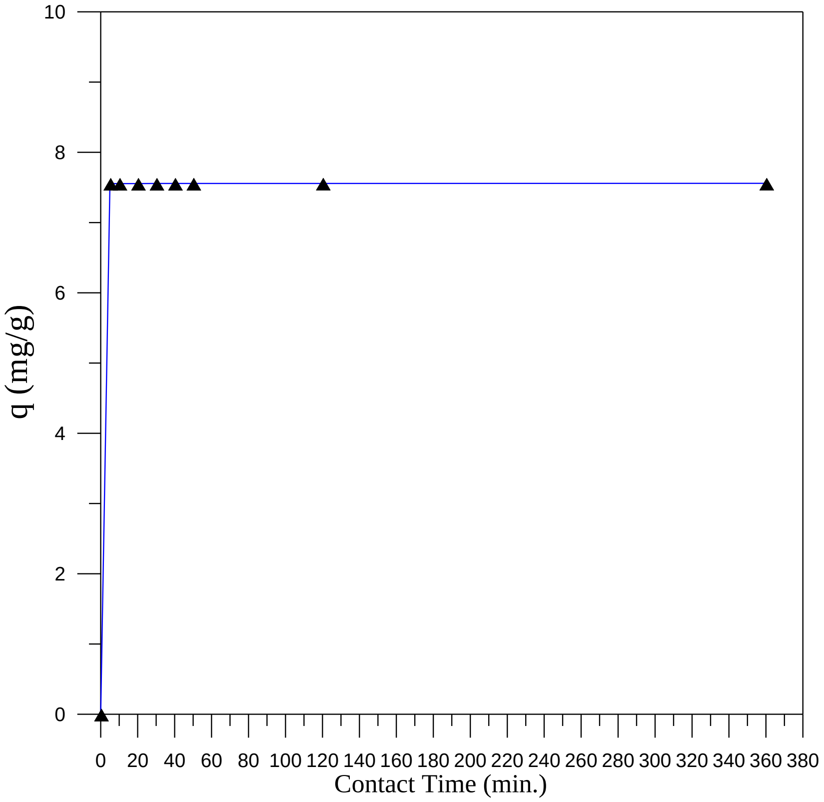

Figure 3.10 Effect of contact time on the adsorbent amount of Al metal ion within initial concentration **75.597 mg/L** by using CKD, at pH (7.80- 7.63), 10 g CKD / L, and 130 rpm.

Table 3.4 Effect of contact time on Co metal ion removal within initial concentration **114.66 mg/L** by using CKD, at pH (8.64- 10.24), 10 g CKD / L and 130 rpm.

pH	Contact time **(min.)**	Residual conc. **C (mg/L)**	Adsorbent amount **q (mg/g)**	% Percent Removal **$(C_o-C)/C_o$*100**	Distribution coefficient **$(C_o-C)/C$* v/m**
	0	114.66	0	0	0
8.64	5	55.259	5.9401	51.8062	107.4956
8.54	10	45.245	6.9415	60.5399	153.4203
8.52	15	41.855	7.2805	63.4964	173.9458
8.54	20	40.033	7.4627	65.0855	186.4137
8.72	25	36.018	7.8642	68.5871	218.3408
8.69	30	32.445	8.2215	71.7033	253.3981
8.62	35	31.539	8.3121	72.4935	263.5499
10.15	40	28.580	8.608	75.0741	301.1896
10.40	45	27.806	8.6854	75.7492	312.357
10.53	50	24.025	9.0635	79.0468	377.2529
10.55	55	22.587	9.2073	80.3009	407.6371
10.48	60	21.847	9.2813	80.9463	424.8318
9.97	120	14.280	10.038	87.5458	702.9412
10.45	240	4.9816	10.96784	95.6553	2201.67
10.24	360	2.3161	11.23439	97.98	4850.563

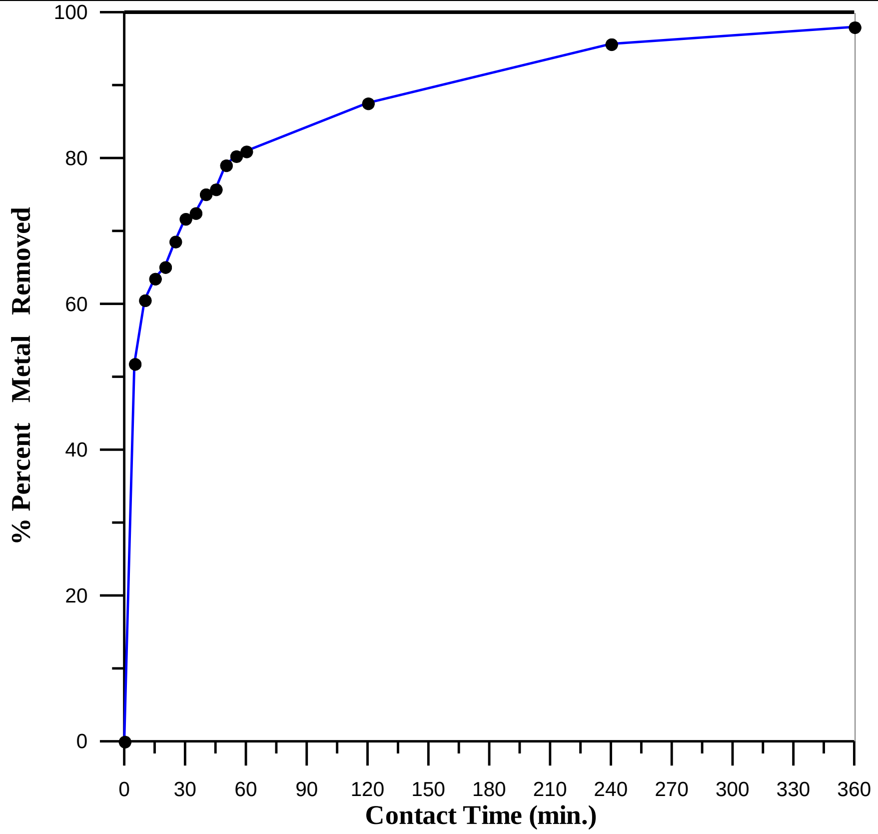

Figure 3.11 Effect of contact time on Co metal ion removal within initial concentration **114.66 mg/L** by using CKD, at pH (8.64- 10.24), 10 g CKD / L, and 130 rpm.

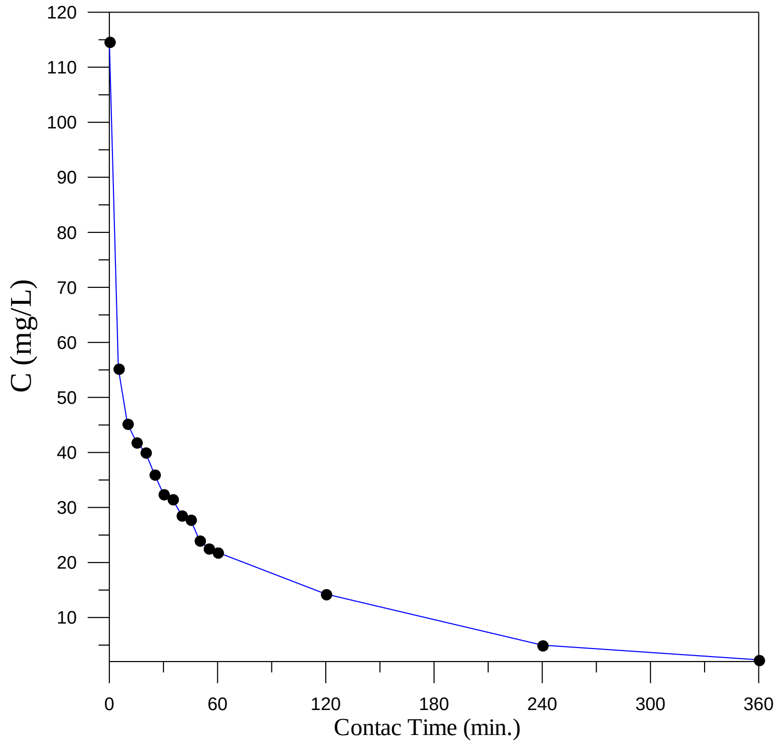

Figure 3.12 Effect of contact time on the residual concentration of Co metal ion within initial concentration **114.66 mg/L** by using CKD, at pH (8.64- 10.24), 10 g CKD / L, and 130 rpm.

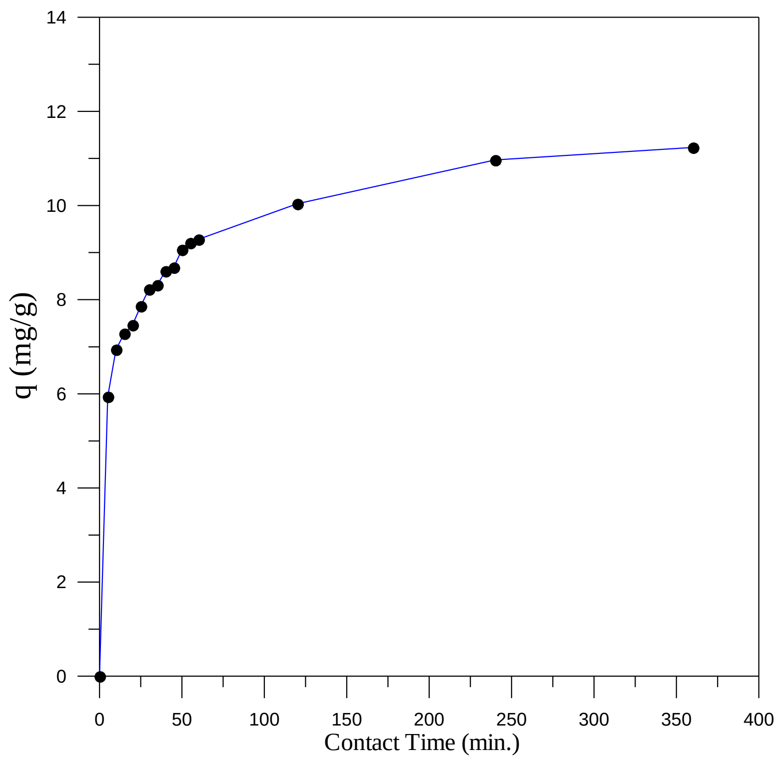

Figure 3.13 Effect of contact time on the adsorbent amount of Co metal ion within initial concentration **114.66 mg/L** by using CKD, at pH (8.64- 10.24), 10 g CKD / L, and 130 rpm.

Table 3.5 Effect of contact time on **Cd** metal ion removal within initial concentration **99.972 mg/L** by using CKD, at pH (8.73-10.64), 10 g CKD / L, and 130 rpm.

pH	Contact time **(min.)**	Residual conc. **C (mg/L)**	Adsorbent amount **q (mg/g)**	% Percent Removal **$(C_o-C)/C_o*100$**	Distribution coefficient **$(C_o-C)/ C* v/m$**
	0	99.972	0	0	0
8.73	5	43.873	5.6099	56.11471	127.8668
9.10	10	29.077	7.0895	70.91486	243.8181
9.02	15	25.229	7.4743	74.76393	296.2583
9.29	20	17.827	8.2145	82.16801	460.7898
9.04	25	15.278	8.4694	84.71772	554.3527
9.23	30	9.8894	9.00826	90.10783	910.9006
	35	7.7330	9.2239	92.26483	1192.797
9.29	40	7.6416	9.23304	92.35626	1208.26
9.46	45	4.7858	9.51862	95.21286	1988.93
9.48	50	4.1930	9.5779	95.80583	2284.259
9.48	55	3.3985	9.65735	96.60055	2841.651
9.70	60	2.3258	9.76462	97.67355	4198.392
10.04	120	0.56897	9.940303	99.43087	17470.7
10.42	240	0.21640	9.97556	99.78354	46097.78
10.64	360	0.13740	9.98346	99.86256	72659.83

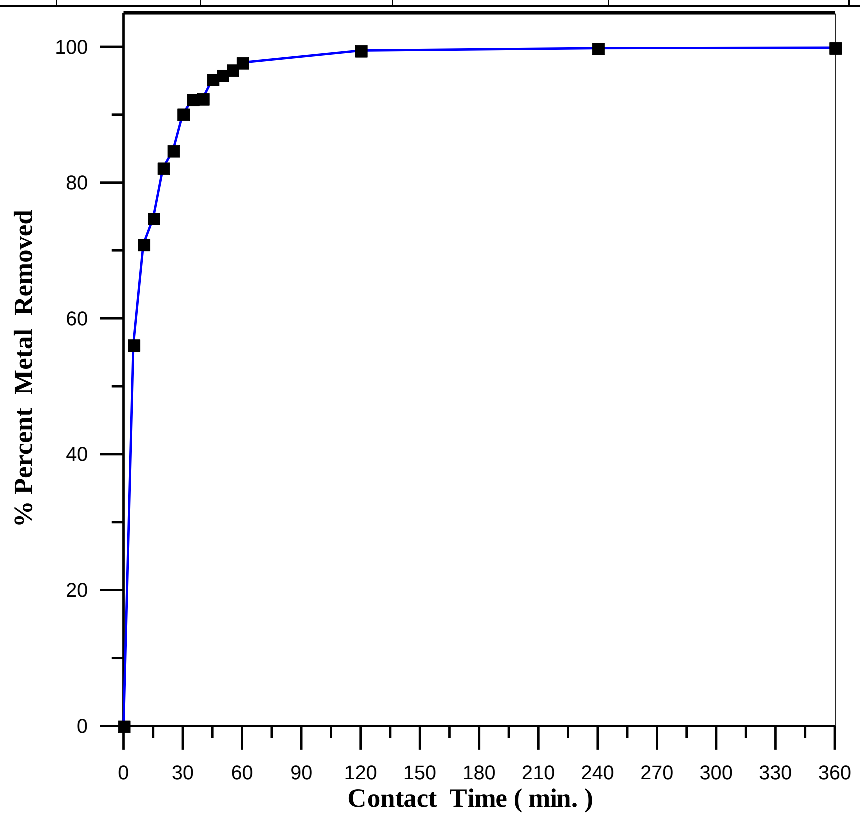

Figure 3.14 Effect of contact time on Cd metal ion removal within initial concentration **99.972 mg/L** by using CKD, at pH (8.73-10.64), 10 g CKD / L, and 130 rpm.

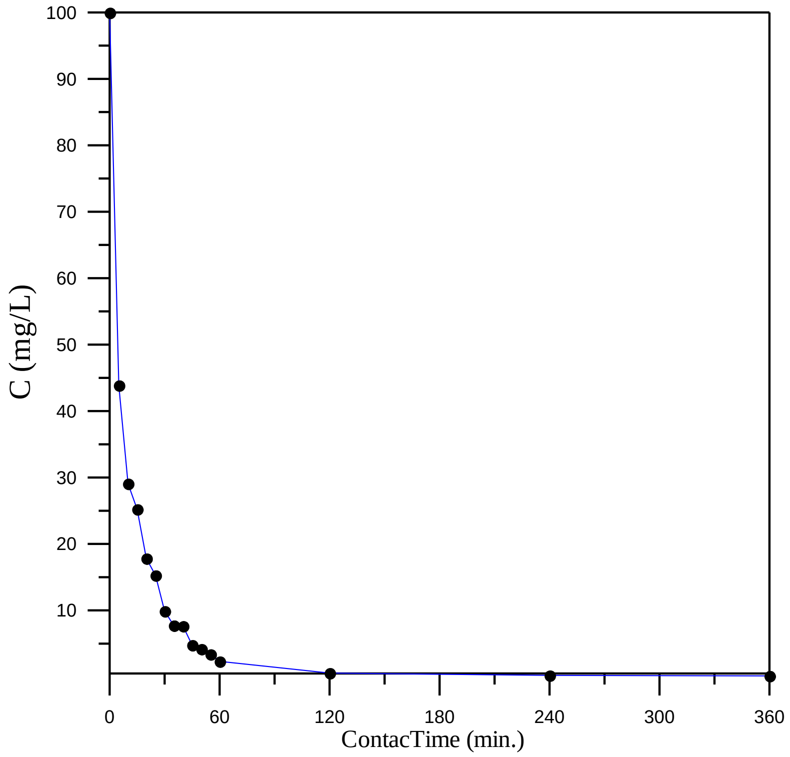

Figure 3.15 Effect of contact time on the residual concentration of Cd metal ion within initial concentration **99.972 mg/L** by using CKD, at pH (8.73-10.64), 10 g CKD / L, and 130 rpm.

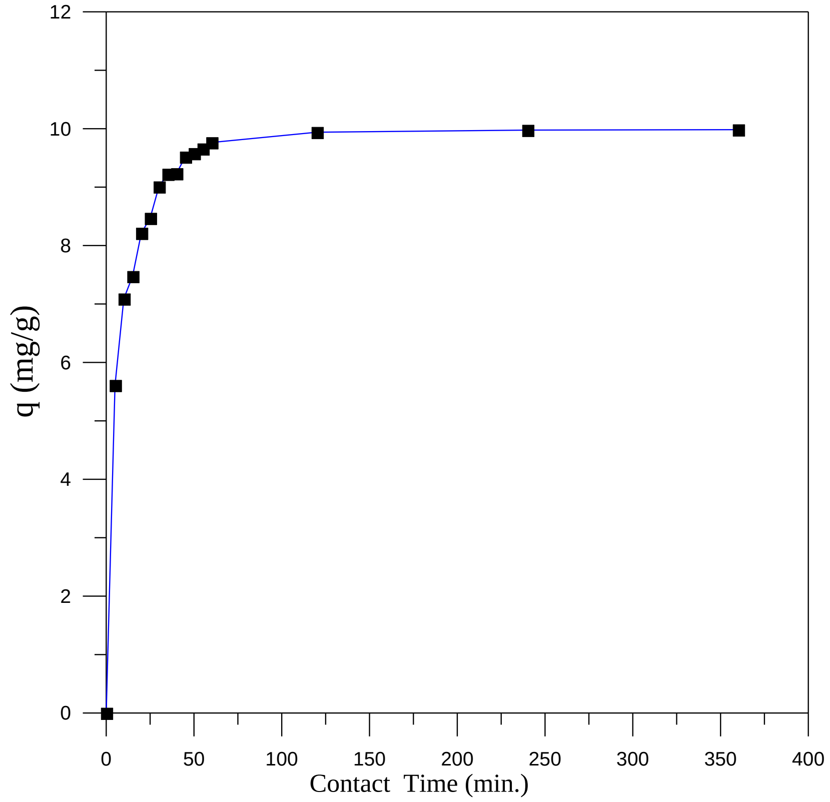

Figure 3.16 Effect of contact time on the adsorbent amount of Cd metal ion within initial concentration **99.972 mg/L** by using CKD, at pH (8.73-10.64), 10 g CKD / L, and 130 rpm.

3.3 Effect of pH

pH is one of the most important parameters controlling uptake of heavy metal ions from wastewater and aqueous solutions. The Effect of pH value on the percent removal of heavy metal ions Zn(II), Al(III), Co(II) and Cd(II) on CKD are indicated in tables (3.6), (3.7), (3.8), (3.9) and figures (3.19), (3.20), (3.21), (3.22) respectively and summarized in figure (3.18) which shows the percent removal of the four heavy metal ions as a function of pH at heavy metal concentrations of 384.55, 123.60, 150.40, 258.51 mg/l for Zn(II), Al(III), Co(II), Cd(II), respectively and a CKD concentration of 10 g/L.

In general, the amount of heavy metal ions removed increased as pH increased, and sharply reached over 90% removal at a specific pH value. As shown in diagram (3.17) given **by Heechan et al [44].** , the precipitation of the heavy metal ions was less than 20% at pH's below 8, indicating that the removal of the metal ions was mainly accomplished by adsorption. As pH increased from 5.5 to 8, it can be expected that the CKD surface becomes more negatively charged. Thus, more favorable electrostatic attraction forces enhanced cationic metal ion adsorption as pH increased. However, the dependence of heavy metal ions adsorption on pH was different for each metal ion.

The removal of zinc ions was about 80% at pH 6.5 and it increased to 99% at pH 8. For aluminum ions, 85% was removed at pH 5 and it increased to 99% at pH 6. For cadmium ions, 90% was removed at pH 5.5 and it increased to 99% at pH 6.2 .For Cobalt ions, removal increased proportionally with increasing pH from 50% at pH 6 to 90% at pH 8. The percentage adsorption increases with pH to attain a maximum at pH 6-8 and thereafter it decreased with further increase in pH. The maximum removal of Zn(II) and Co(II) at pH 8 were found to be nearly 99 and 90%, respectively, whereas, for Al(III) 99% removal at pH 6 and for Cd(II) 99% removal at pH 6.2.

In all cases, over 99% of all the four metal ions were removed except cobalt reached 90% at pH 8. It is often suggested that the tendency of metal cations to adsorb on oxide surfaces is highly correlated with their tendency to undergo hydrolysis reactions in solution [45]. Metal cations in aqueous solutions hydrolyze according to the generalized expression for divalent metals.

$$M^{2+}\text{ (aq.) } + nH_2O = M\,(OH)^{\,2-n} + nH^+$$

Explanation of mechanism of adsorption

The maximum adsorption at pH 8 may be attributed to the partial hydrolysis of M^+, resulting in the formation of MOH^+ and $M(OH)_2$. $M(OH)_2$ would be adsorbed to a greater extend on the non-polar adsorbent surface compared to MOH^+.With increase of pH from 4 to 8, the metal exists as $M(OH)_2$ in the medium and surface protonation of adsorbent is minimum, leading to the enhancement of metal adsorption. At higher pH, that is, above optimum pH of 8, increase in OH^- ions caused a decrease in adsorption of metal ions at adsorbent–adsorbate interface [46].

Lower solubilities of hydrolysed metal ions species may be another reason for the maximum adsorption at pH 8. Since, in lower pH range, metal is present predominantly as metal ions in the adsorptive solution, there is a competition between H^+ and M^+ ions for adsorption at the ion-exchangeable sites, leading to a low removal of metal. The extensive repulsion of metal ions due to protonation of the adsorbent surface at lower pH may be another reason for decrease in adsorption of metal ions in lower pH range.

The mechanism of metal ion adsorption may also be explained as:

The increase in metal ions removal as the pH increases can be explained on the basis of a decrease in competition between proton and metal cations for the same functional groups and by the decrease in positive surface charge, which results in a lower electrostatic repulsion between the surface and the metal ions. Decrease in adsorption at higher pH (above pH 8) is due to the formation of soluble hydroxy complexes [47]. The difference in adsorption behaviour of different heavy metal ions may be because of difference in their ion exchange capacity on the surface depending on their charge density, extent of hydrolysis and solubility of hydrolysed metal ions in solution under present experimental conditions.

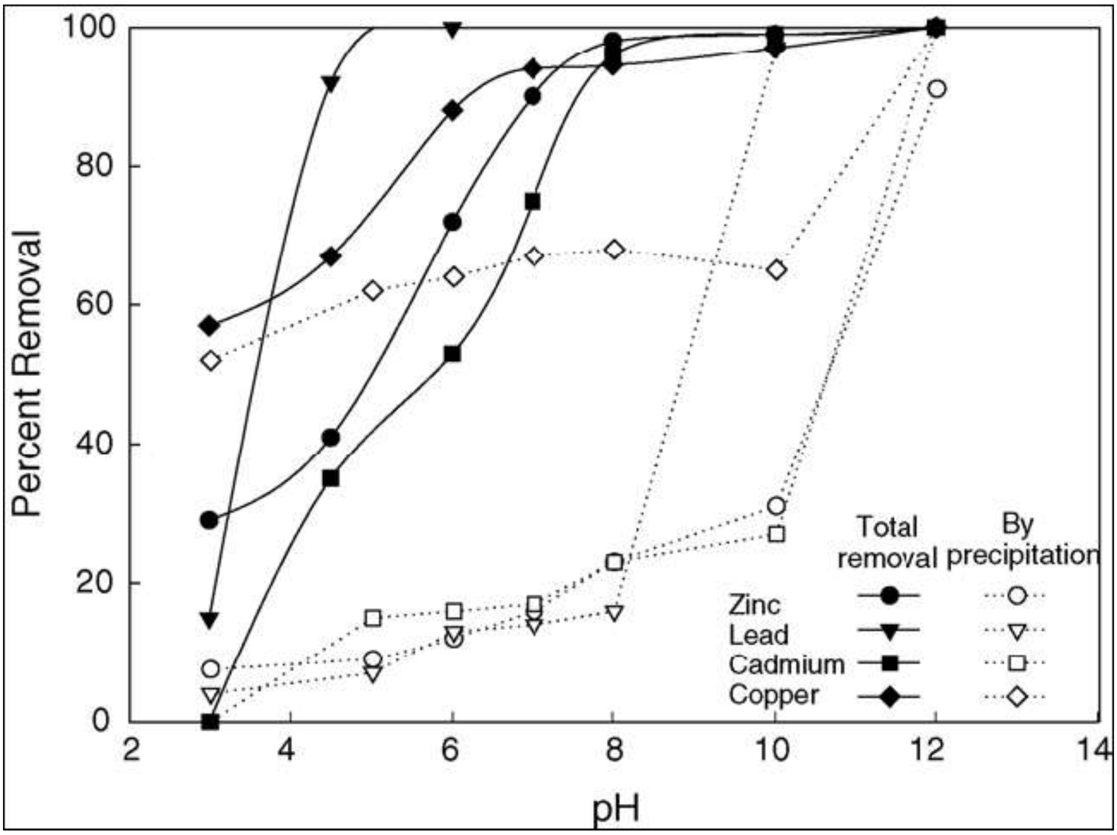

Figure 3.17 **the diagram given by Heechan**

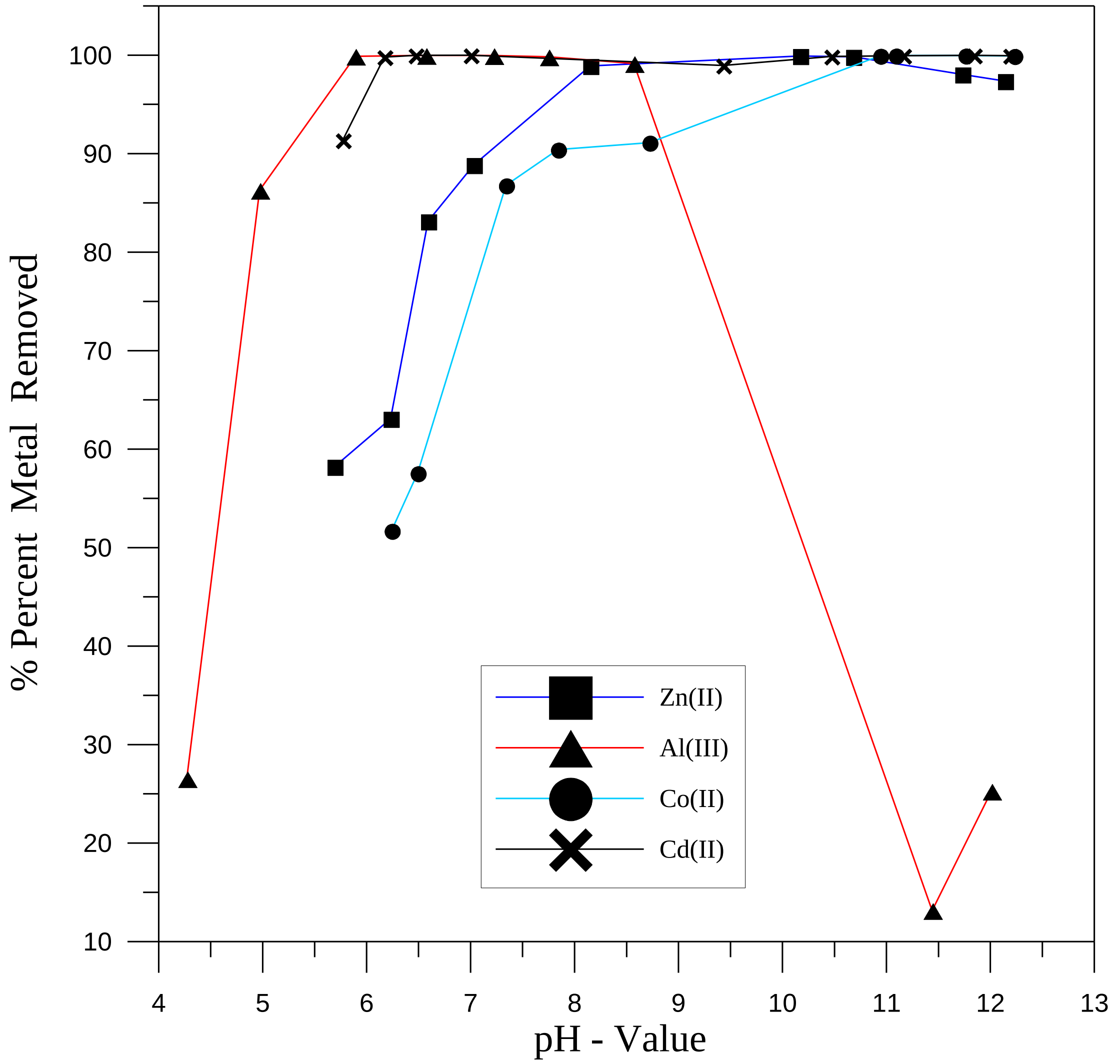

Figure 3.18 Effect of different pH - values on heavy metal ions removal by using 10 g CKD / L.

Table 3.6 Effect of different pH - values on **Zn** metal ion removal within initial concentration **384.55 mg/L** by using CKD, at 40 min., 130 rpm and 10 g CKD / L.

pH values		Residual conc. **C (mg / L)**	Adsorbent amount **q (mg / g)**	% Percent Removal **$(C_o-C)/C_o$*100**	Distribution coefficient **$(C_o-C)/C$* v/m**
Before Adding CKD	**After**				
1.68	5.69	160.71	22.384	58.2083	139.2819
1.72	6.23	141.93	24.262	63.09193	170.9434
1.79	6.59	64.847	31.9703	83.13691	493.0112
2.07	7.03	42.888	34.1662	88.84722	796.6378
4.53	8.15	4.2110	38.0339	98.90495	9032.035
7.60	10.17	0.29002	38.426	99.92458	132494.3
10.30	10.68	0.60986	38.39401	99.84141	62955.46
11.36	11.73	7.4780	37.7072	98.05539	5042.418
11.82	12.14	10.135	37.4415	97.36445	3694.277

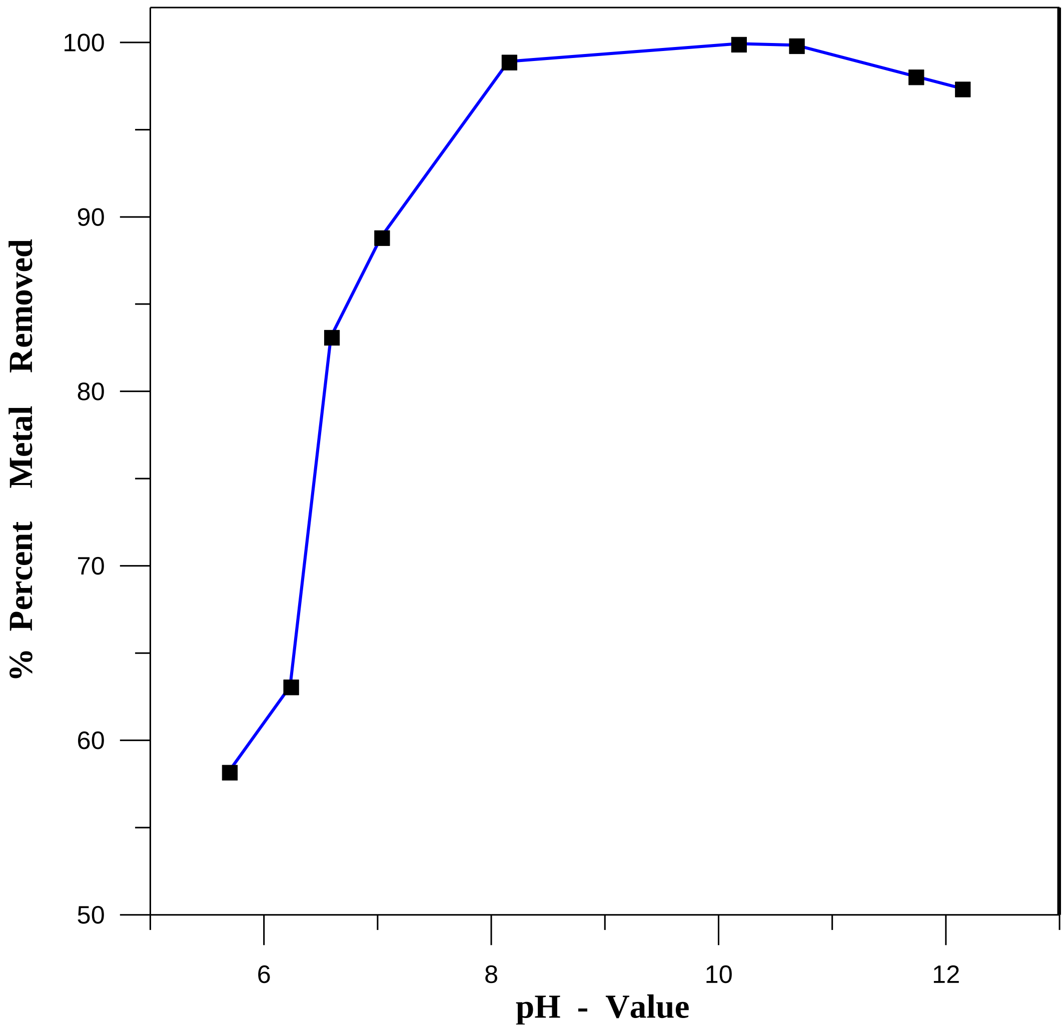

Figure 3.19 Effect of different pH - values on Zn metal ion removal within initial concentration **384.55 mg/L** by using CKD, at 40 min., 130 rpm and 10 g CKD / L.

Table 3.7 Effect of different pH - values on **Al** metal ion removal within initial concentration **123.60 mg/L** by using CKD, at 5 min., 130 rpm and 10 g CKD / L.

pH values		Residual conc. **C (mg / L)**	Adsorbent amount **q (mg / g)**	% Percent Removal **$(C_o-C)/C_o$*100**	Distribution coefficient **$(C_o-C)/C$* v/m**
Before Adding CKD	After				
1.40	4.27	90.792	3.2808	26.54369	36.13534
1.65	4.97	16.957	10.6643	86.28074	628.9025
1.86	5.89	0.13788	12.34621	99.88845	89543.17
2.02	6.57	0.03224	12.35678	99.97392	383274.7
3.84	7.22	0.04647	12.35535	99.9624	265878.1
4.28	7.75	0.20905	12.3391	99.83087	59024.61
4.73	8.57	1.0448	12.25552	99.15469	11730.02
11.63	11.44	107.34	1.626	13.15534	15.14813
12.07	12.01	92.367	3.1233	25.26942	33.81402

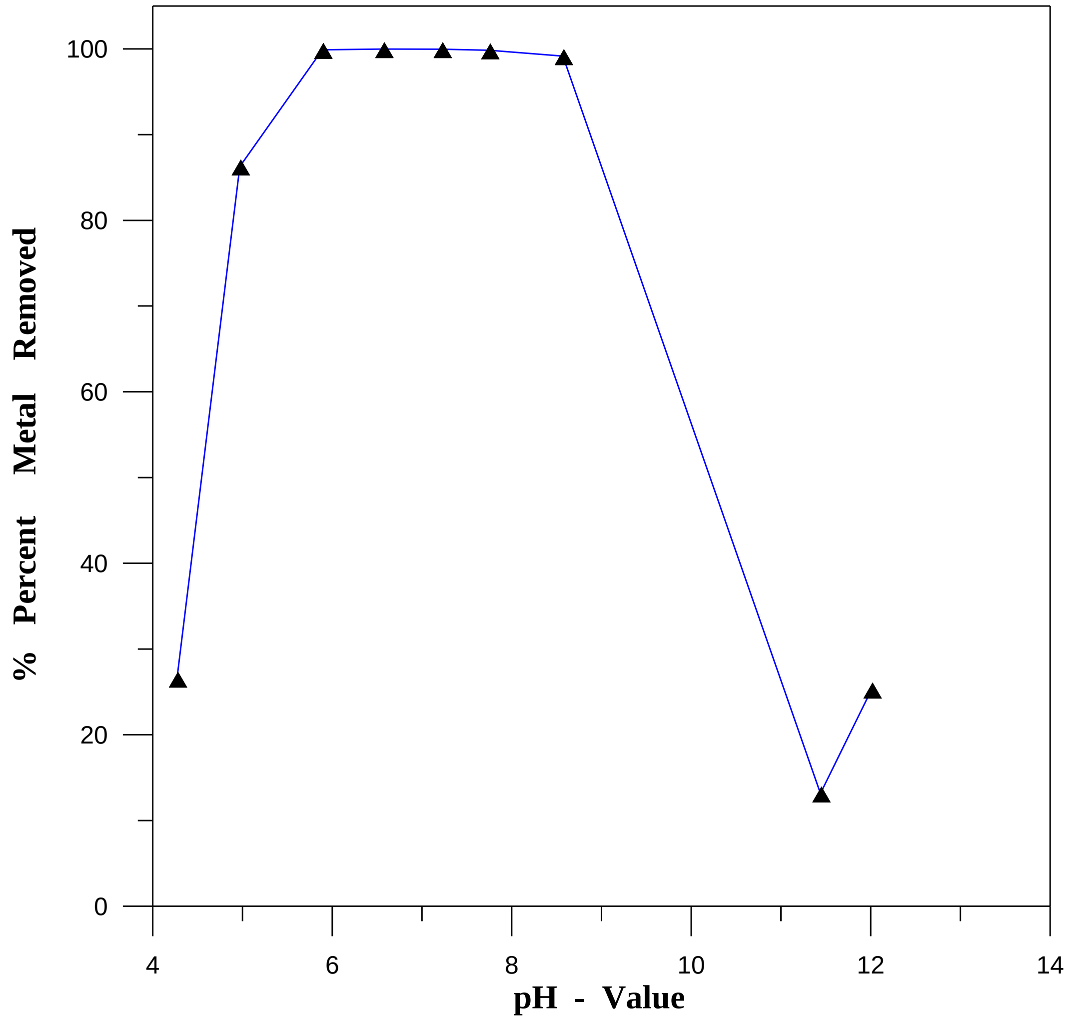

Figure 3.20 Effect of different pH - values on Al metal ion removal within initial concentration **123.60 mg/L** by using CKD, at 5 min., 130 rpm and 10 g CKD / L.

Table 3.8 Effect of different pH - values on **Co** metal ion removal within initial concentration **150.40 mg/L** by using CKD, at 4 hours, 130 rpm and 10 g CKD / L.					
pH values		Residual conc. **C (mg / L)**	Adsorbent amount **q (mg / g)**	% Percent Removal **$(C_o-C)/C_o*100$**	Distribution coefficient **$(C_o-C)/ C* v/m$**
Before Adding CKD	**After**				
1.23	6.24	72.623	7.7777	51.71343	107.0969
1.36	6.49	63.826	8.6574	57.5625	135.6406
1.80	7.34	19.875	13.0525	86.78524	656.7296
2.10	7.84	14.410	13.599	90.41888	943.7196
4.89	8.72	13.357	13.7043	91.11902	1026.001
9.08	10.94	0.08348	15.03165	99.94449	180062.9
10.95	11.09	0.05211	15.03479	99.96535	288520.2
11.92	11.76	0.05385	15.03462	99.9642	279194.3
12.28	12.23	0.11978	15.02802	99.92036	125463.5

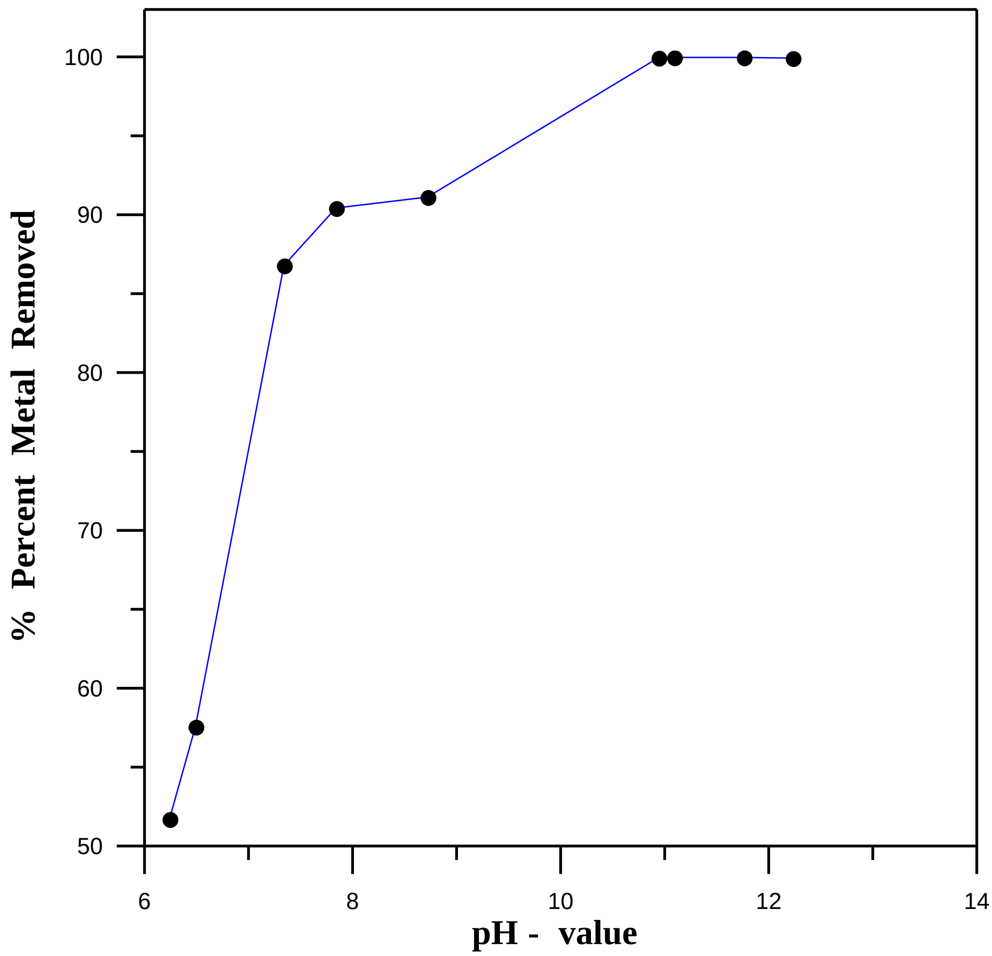

Figure 3.21 Effect of different pH - values on Co metal ion removal within initial concentration **150.40 mg/L** by using CKD, at 4 hours, 130 rpm and 10 g CKD / L.

Table 3.9 Effect of different pH - values on **Cd** metal ion removal within initial concentration **258.51mg/L** by using CKD, at 1 hour, 130 rpm and 10 g CKD / L.

pH values		Residual conc.	Adsorbent amount	% Percent Removal	Distribution coefficient
Before Adding CKD	**After**	**C (mg / L)**	**q (mg / g)**	**$(C_o\text{-}C)/C_o*100$**	**$(C_o\text{-}C)/ C* v/m$**
1.17	5.77	22.312	23.6198	91.369	1058.614
1.27	6.17	0.49830	25.80117	99.80724	51778.39
1.39	6.47	0.03374	25.84763	99.98695	766082.6
1.57	7	0.02481	25.84852	99.9904	1041859
5.09	9.43	2.7199	25.57901	98.94786	9404.394
9.78	10.47	0.34365	25.81664	99.86707	75124.79
11.28	11.16	0.12474	25.83853	99.95175	207139.1
11.76	11.84	0.05762	25.84524	99.97771	448546.3
12.11	12.19	0.11657	25.83934	99.95491	221663.7

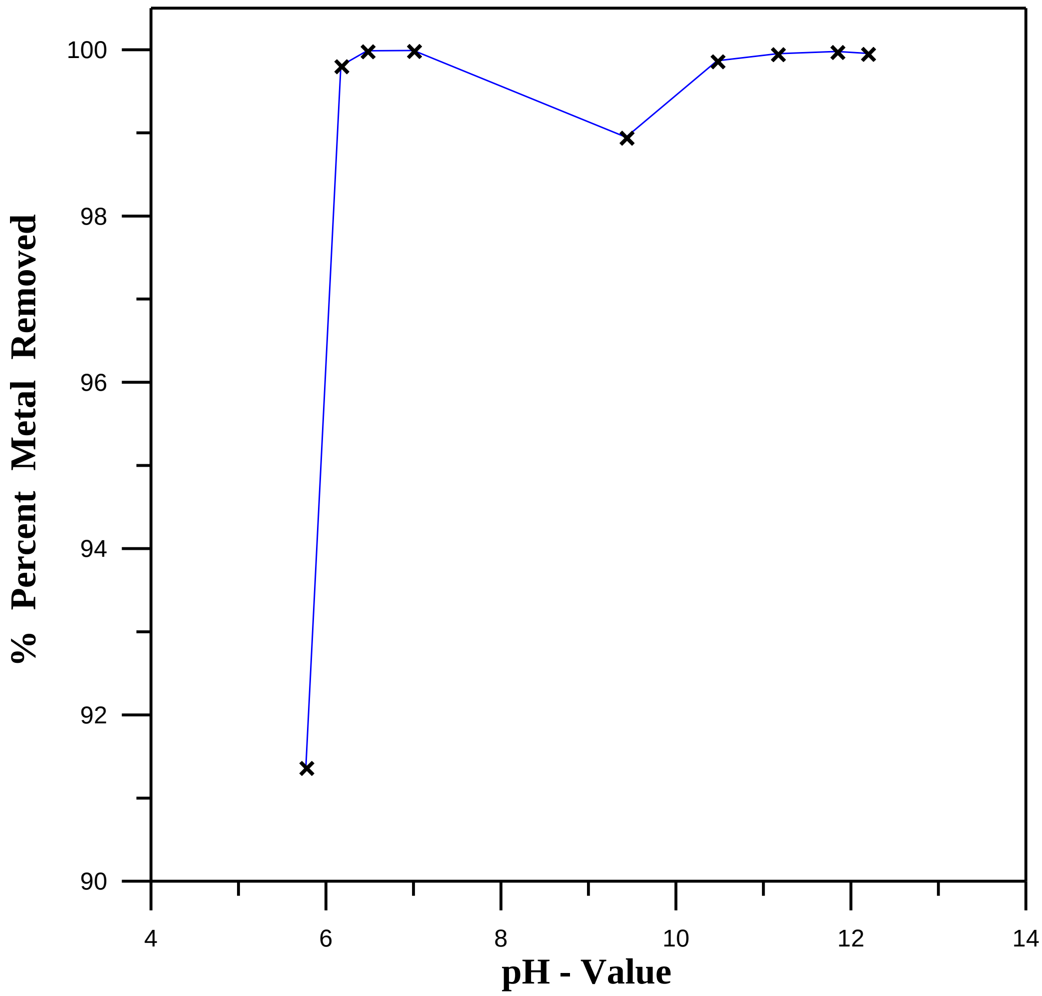

Figure 3.22 Effect of different pH - values on Cd metal ion removal within initial concentration **258.51 mg/L** by using CKD, at 1 hour, 130 rpm and 10 g CKD / L.

3.4 Equilibrium isotherm of heavy metal ions

All experiments were done under the following conditions; 50 ml of heavy metal ions Zn(II), Al(III), Co(II) and Cd(II) solutions, agitation rate 130 rpm, and the solution temperature was 30 ^oC using 0.5 g of CKD having average particle size 3 µ in adsorption process at equilibrium times .

Study of equilibrium isotherm, the effect of initial conc. and adsorption isotherm for removal of heavy metal ions Zn(II), Al(III), Co(II) and Cd(II) on CKD are indicated in tables (3.10), (3.11), (3.12), (3.13) and figures (3.24, 3.25 and 3.26), (3.27, 3.28 and 3.29), (3.30, 3.31 and 3.32), (3.33, 3.34 and 3.35) respectively . and figure (3.23) which shows the equilibrium isotherm of heavy metal ions adsorption by using CKD at 30 ^oC Using metal ion concentrations (384.55-1825.8), (123.60- 958.95), (150.40- 956.17) and (258.51-1500) for Zn(II), Al(III), Co(II) and Cd(II), respectively. The removal curves are indicating the formation of monolayer coverage on the outer surface of adsorbent [48].

It is known that the adsorption of cations on oxide surfaces is mainly affected via coordination with surface hydroxyl groups [49]. In this study, it is clear that the high alkalinity of CKD suspension as well as the surface hydroxyl groups of that material is the dominant features that enhance adsorbability. Thus, the adsorption of the acidic metal ions to strongly alkaline suspensions of CKD would suddenly change the pH of the suspension. The adsorption of the metal ions on CKD may take place just upon mixing via complex formation with the surface hydroxyl groups, which may be further enhanced as a result of the suspension alkalinity. The binding of different metal ions to surface groups is expected to be related to their hydrolysis properties.

The mechanism of heavy metal ions removal from acidic wastewater may be explained as following [50]:

(1) Heavy metal ions hydrolysis:

$$X_2O + H_2O \rightarrow X(OH)$$

$$MSO_4 + X(OH) \rightarrow M(OH)_n \downarrow + XSO_4$$

where:

X: K, Na, and Ca M: Zn, Al, Co, Cd. and n: 2, 3

(2) Adsorption of heavy metal ions using the CKD fine particles:

$$M(OH)_n + CKD \rightarrow CKD - \{-M(OH)_n\}$$

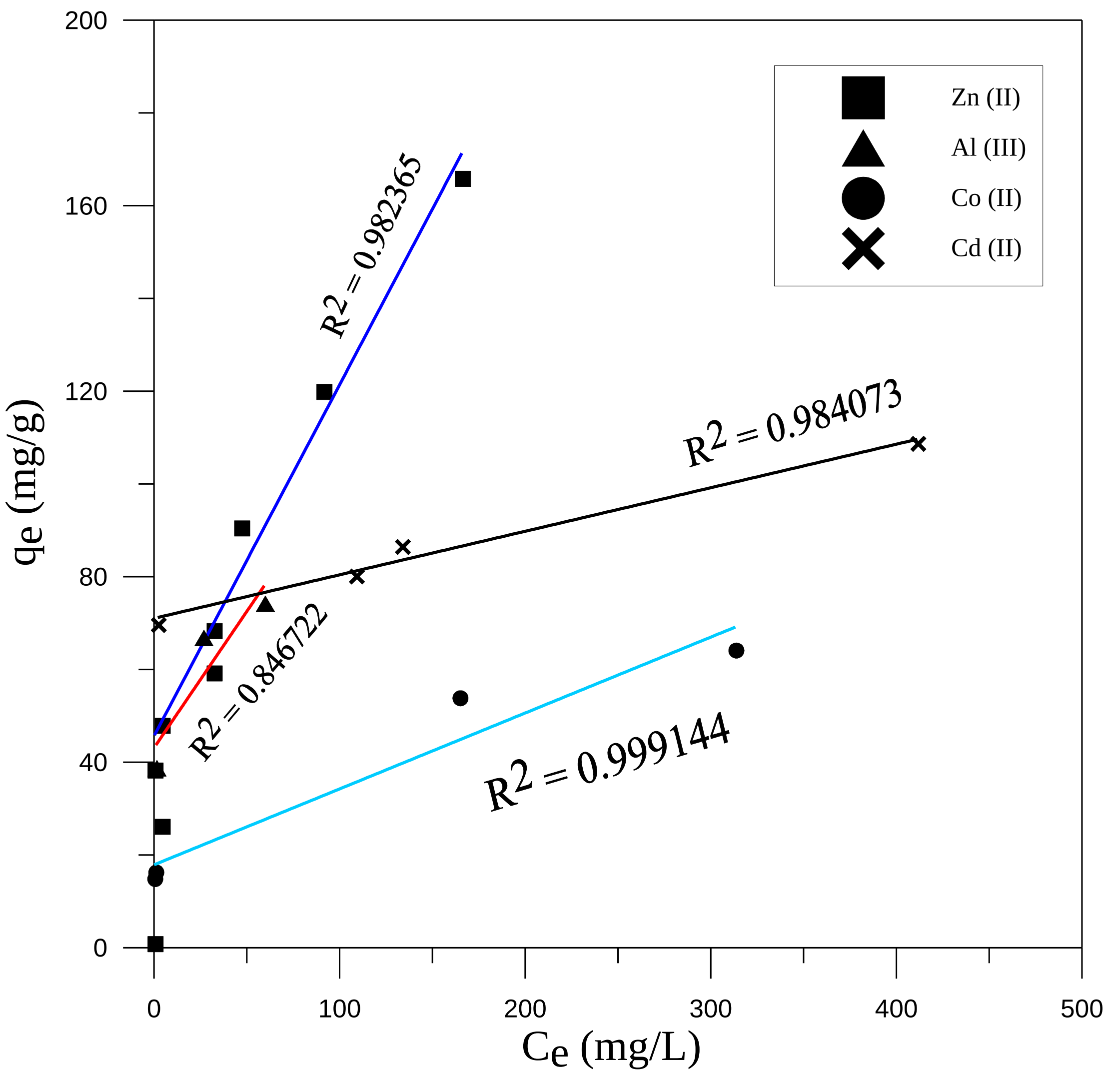

Figure 3.23 Equilibrium isotherm of heavy metal ions adsorption by using CKD at 30 ^{o}C

Table 3.10 Effect of initial concentration on the percent removal of **Zn** metal ions by using CKD, at pH (8-10.17), 40 min., 130 rpm, temp 30 ^{o}C and 10 g CKD / L.				
Initial Conc. **C_o (mg / L)**	Residual conc. **C (mg / L)**	Adsorbent amount **q (mg / g)**	% Percent Removal **$(C_o-C)/C_o*100$**	Distribution coefficient **$(C_o-C)/ C* v/m$**
384.55	0.29002	38.426	99.92458	132.4943
484.88	4.0610	48.0819	99.16247	11.83992
716.95	32.112	68.4838	95.52103	2.132654
953.24	46.912	90.6328	95.07868	1.931975
1292	91.227	120.0773	92.93909	1.316247
1825.8	165.86	165.994	90.91576	1.000808

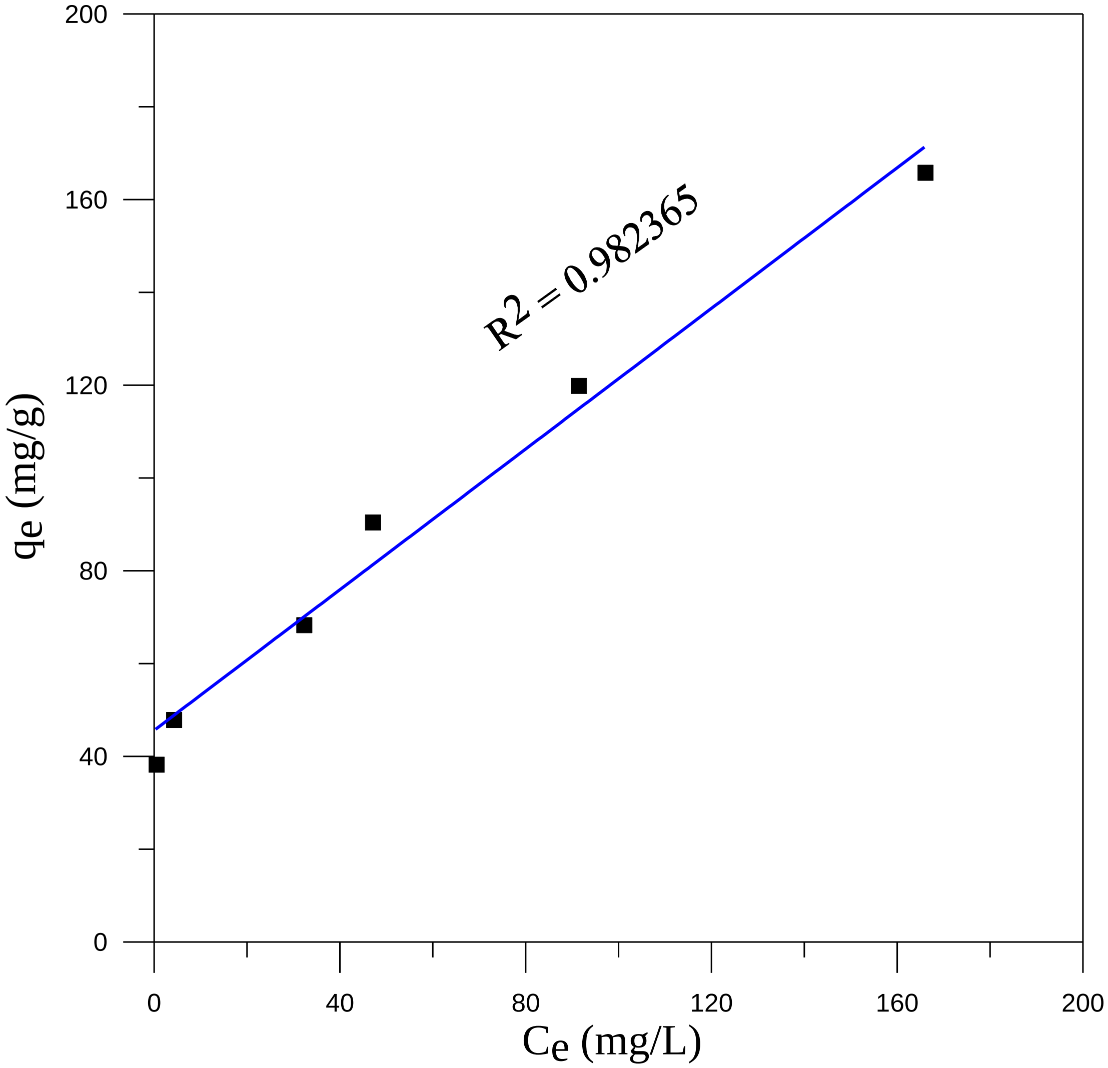

Figure 3.24 Equilibrium isotherm of Zn(II) adsorption by using CKD at 30 ^{o}C.

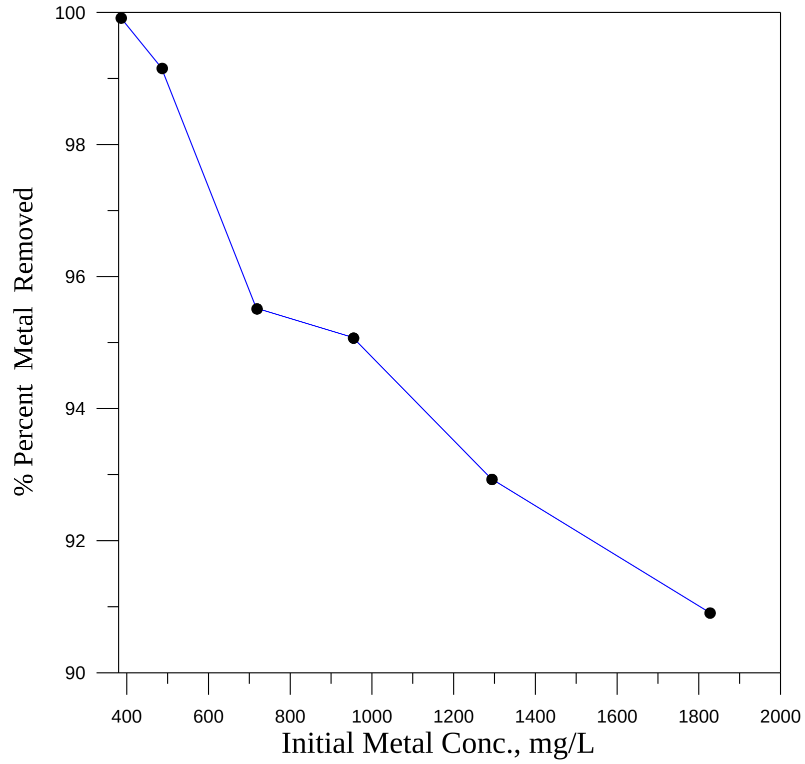

Figure 3.25 Effect of initial concentration on the percent removal of Zn metal ion by using CKD, at pH (8-10.17), 40 min., 130 rpm, temp 30 ^{o}C and 10 g CKD / L.

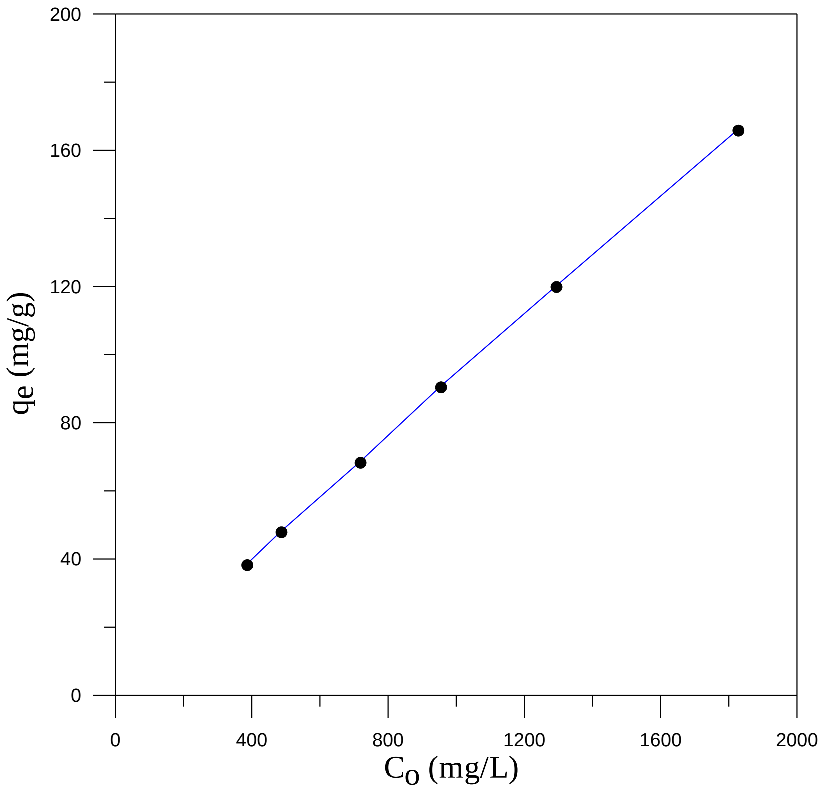

Figure 3.26 Adsorption isotherm of Zn(II) by using CKD at 30 ^{o}C

Table 3.11 Effect of initial concentration on the percent removal of **Al** metal ion by using CKD, at pH (5.89-8.57), 5 min., 130 rpm , temp 30 ^{o}C and 10 g CKD / L.				
Initial Conc. **C_o (mg / L)**	Residual conc. **C (mg / L)**	Adsorbent amount **q (mg / g)**	% Percent Removal **$(C_o\text{-}C)/C_o*100$**	Distribution coefficient **$(C_o\text{-}C)/ C* v/m$**
123.60	0.04647	12.35535	99.9624	265.8781
390.09	1.014117	38.90759	99.74003	38.36598
696.43	26.316	67.0114	96.2213	2.546413
803.10	59.377	74.3723	92.60652	1.252544
958.95	205.06	75.389	78.61619	0.367644

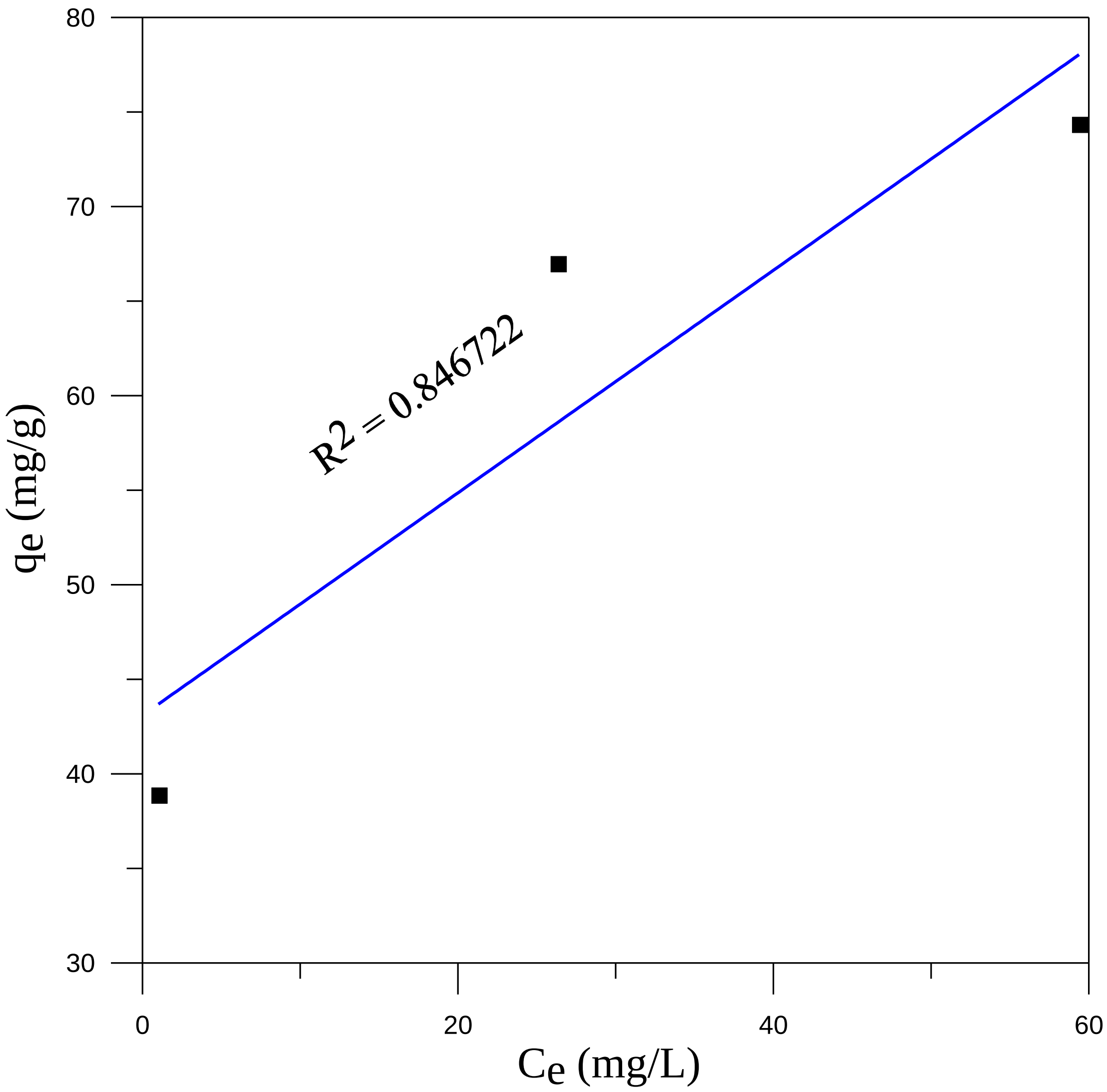

Figure 3.27 Equilibrium isotherm of Al(III) adsorption by using CKD at 30 ^{o}C

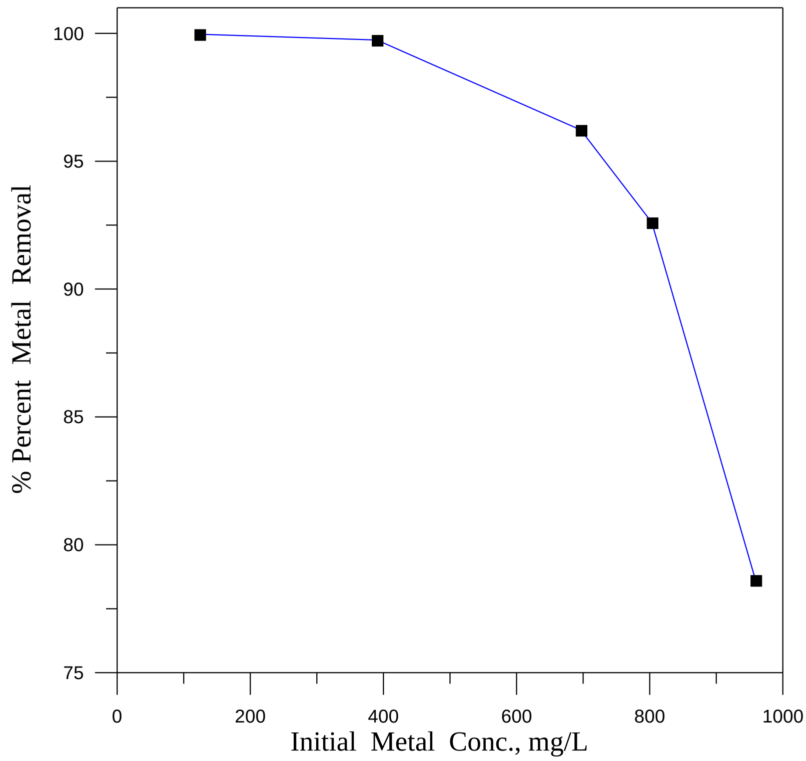

Figure 3.28 Effect of initial concentration on the percent removal of Al metal ion by using CKD, at pH (5.89-8.57), 5 min., 130 rpm , temp 30 ^{o}C and 10 g CKD / L.

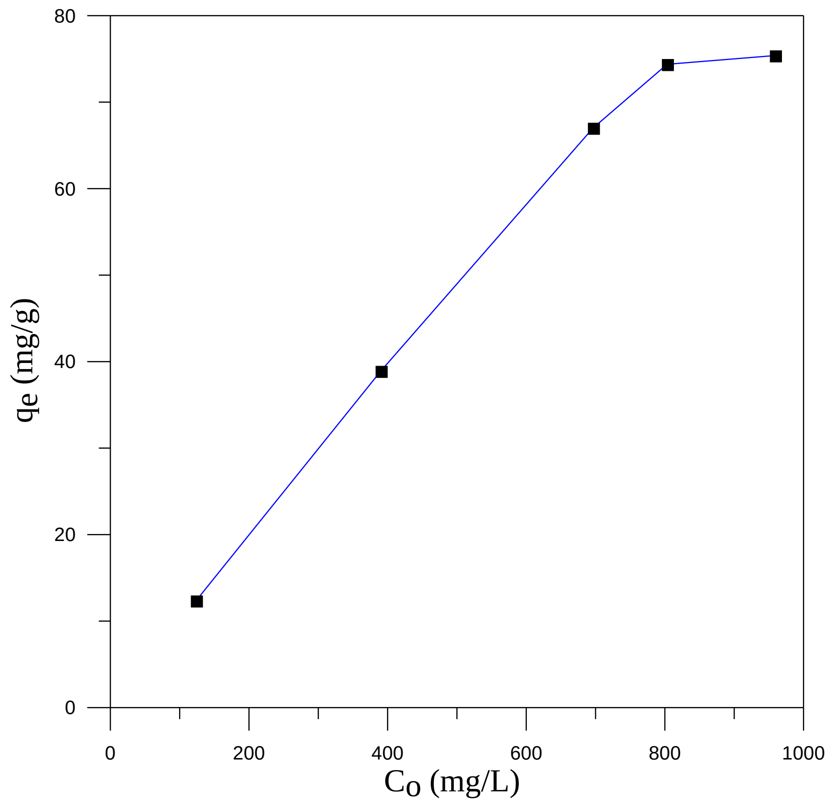

Figure 3.29 Adsorption isotherm of Al(III) by using CKD at 30 ^{o}C

Table 3.12 Effect of initial concentration on the percent removal of **Co** metal ion by using CKD, at pH (8-10.94), 4 hour, 130 rpm , temp 30 ^oC and 10 g CKD / L.				
Initial Conc. **C_o (mg / L)**	Residual conc. **C (mg / L)**	Adsorbent amount **q (mg / g)**	% Percent Removal **$(C_o$-C)/C_o*100**	Distribution coefficient **(C_o-C)/ C* v/m**
150.40	0.08348	15.03165	99.94449	180.0629
165.22	0.648323	16.45717	99.6076	25.38421
704.65	164.53	54.012	76.65082	0.328281
956.17	313.21	64.296	67.24327	0.205281

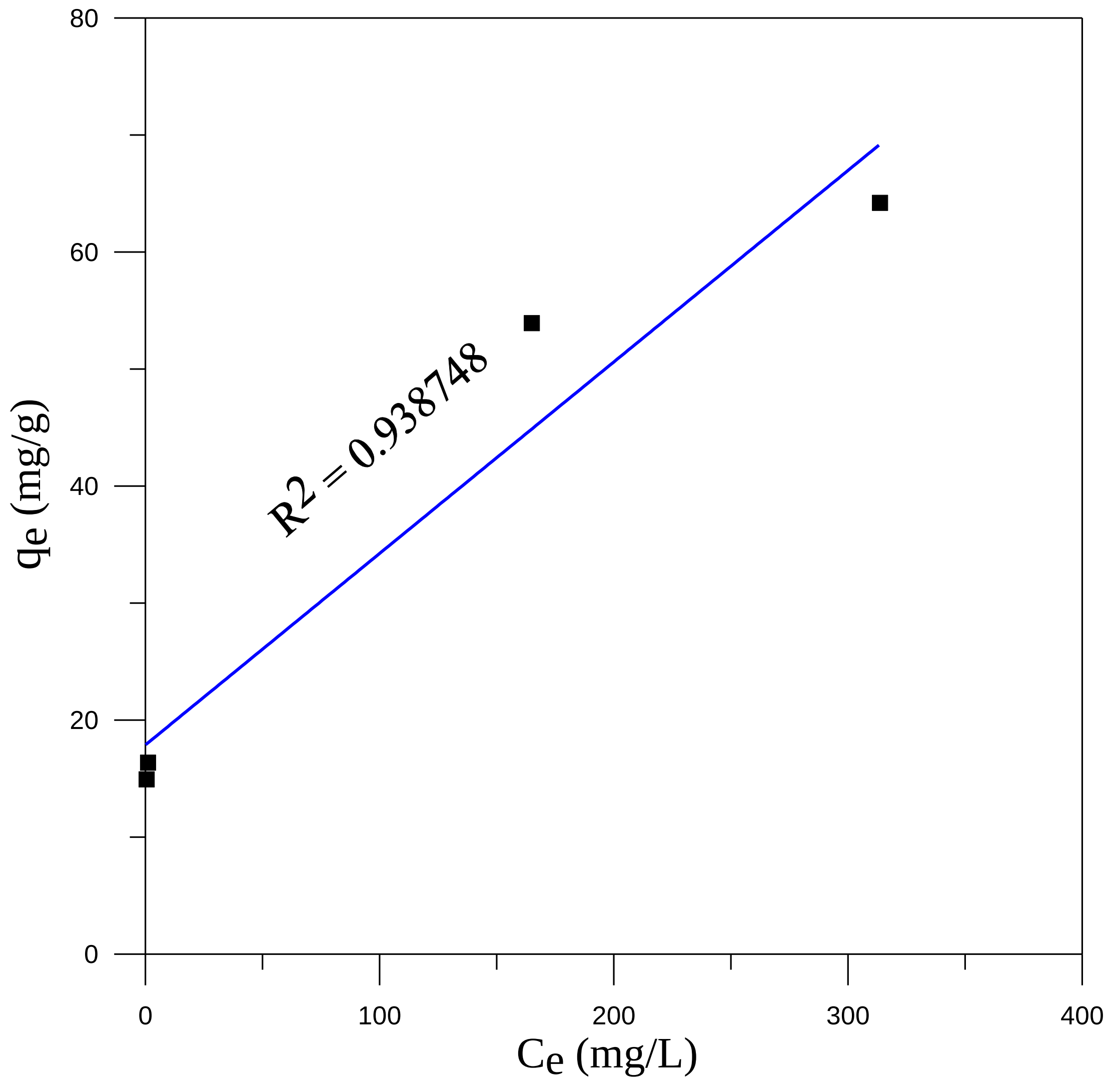

Figure 3.30 Equilibrium isotherm of Co(II) adsorption by using CKD at 30 ^oC

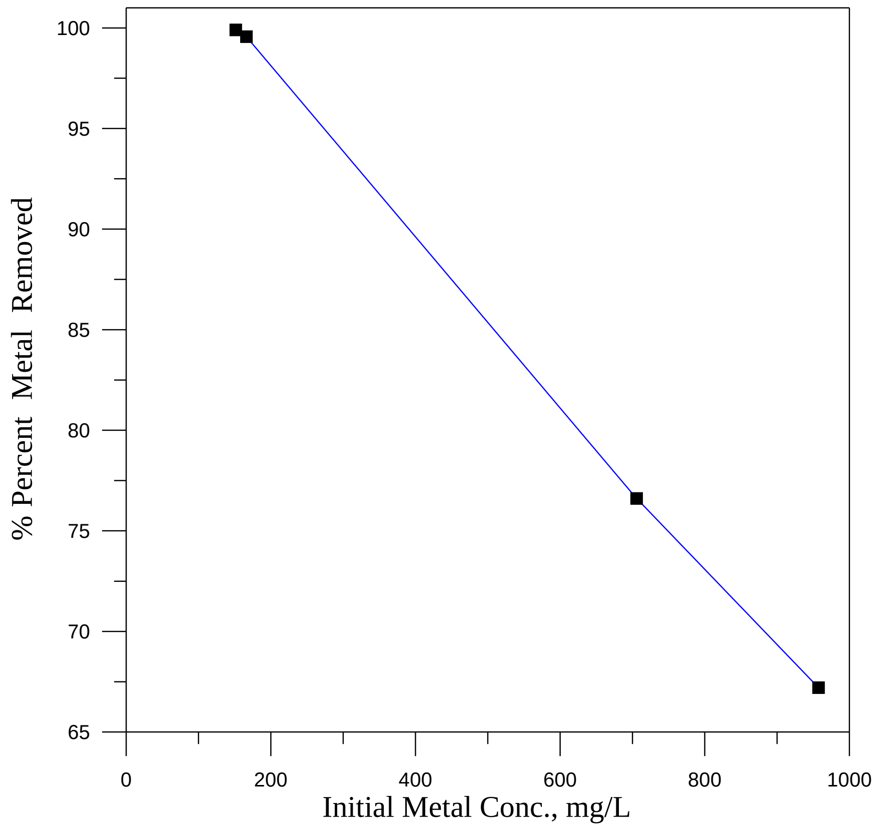

Figure 3.31 Effect of initial concentration on the percent removal of Co metal ion by using CKD, at pH (8-10.94), 4 hour, 130 rpm , temp 30 ^{o}C and 10 g CKD / L.

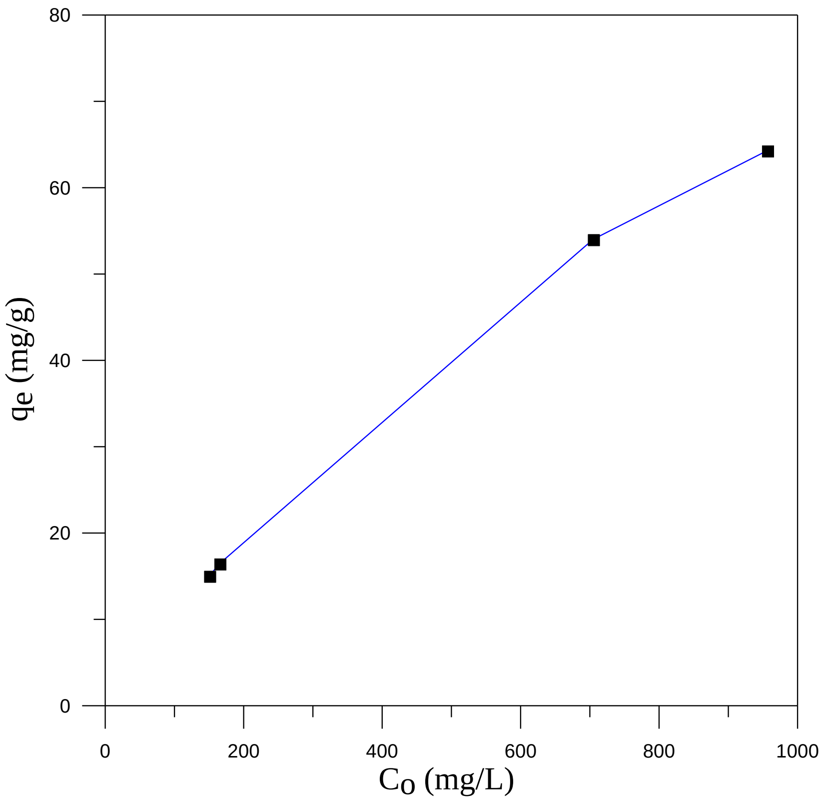

Figure 3.32 Adsorption isotherm of Co(II) by using CKD at 30 ^{o}C

Table 3.13 Effect of initial concentration on the percent removal of **Cd** metal ion by using CKD, at pH (6.17-12.19), 1hour, 130 rpm , temp 30 ^{o}C and 10 g CKD / L.				
Initial Conc. **C_o (mg / L)**	Residual conc. **C (mg / L)**	Adsorbent amount **q (mg / g)**	% Percent Removal **$(C_o\text{-}C)/C_o$*100**	Distribution coefficient **$(C_o\text{-}C)$/ C* v/m**
258.51	0.34365	25.81664	99.86707	75.12479
393	0.71743	39.22826	99.81745	54.67886
700	2.0080	69.7992	99.71314	34.76056
911.41	108.71	80.27	88.07233	0.738387
1000	133.52	86.648	86.648	0.648951
1500	411.25	108.875	72.58333	0.264742

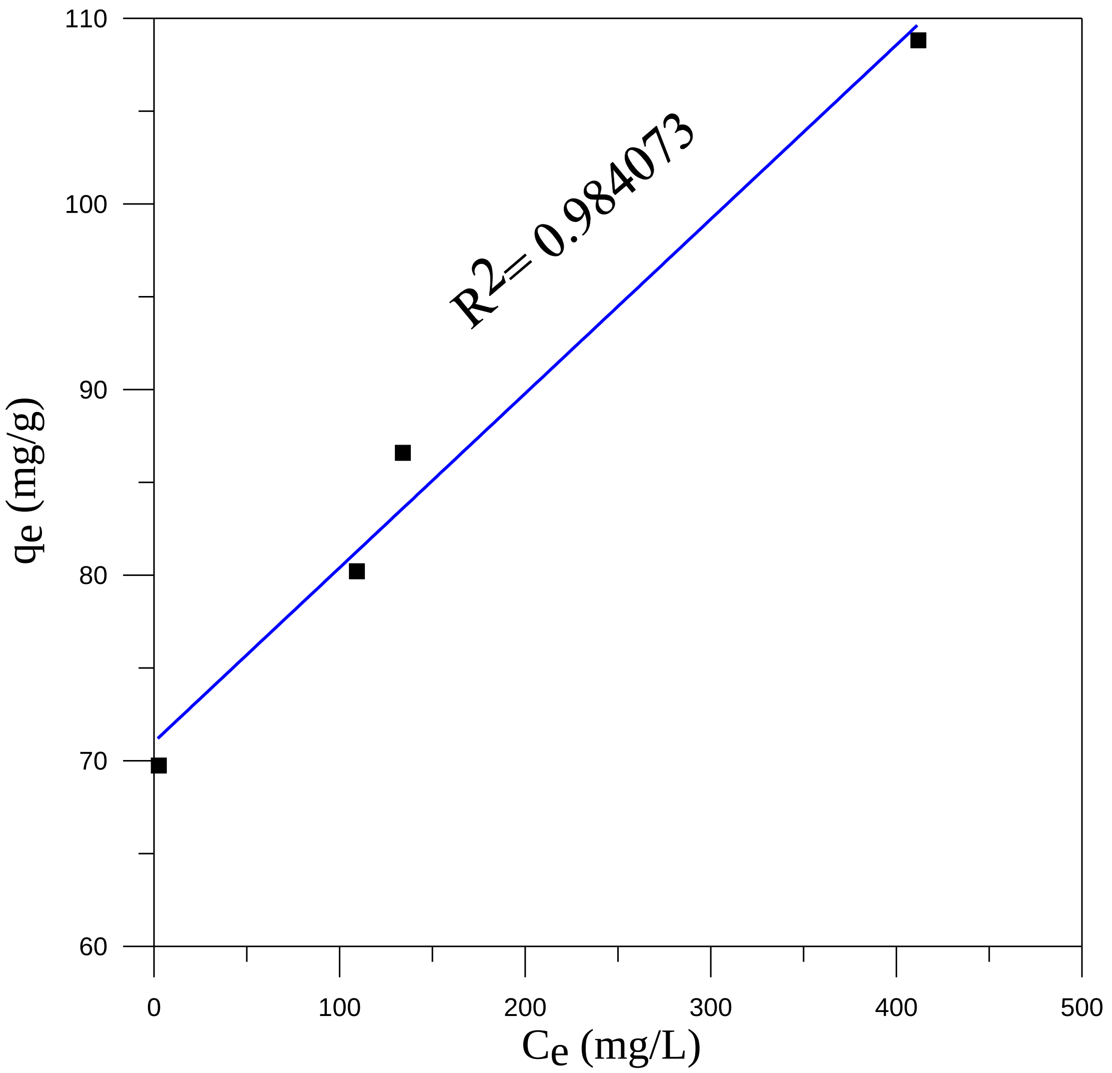

Figure 3.33 Equilibrium isotherm of Cd(II) adsorption by using CKD at 30 ^{o}C

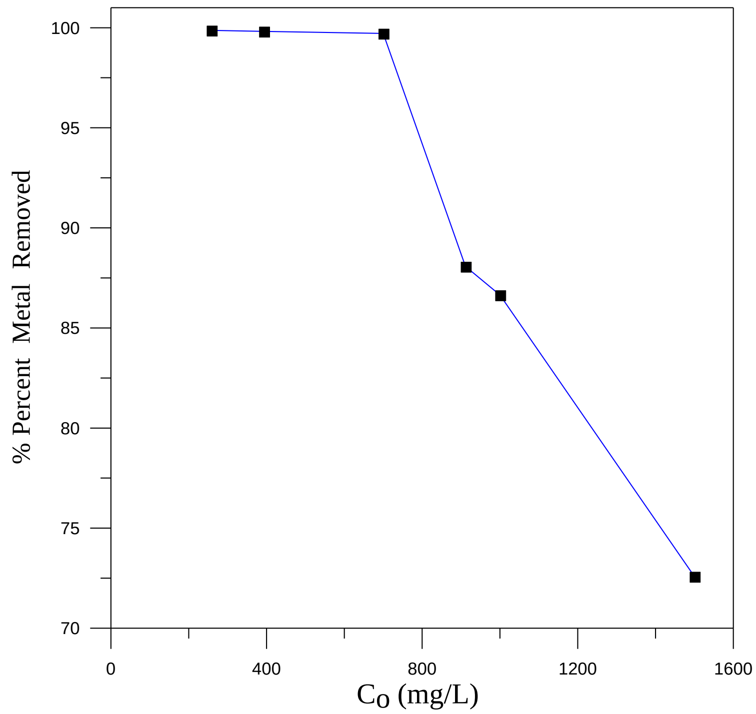

Figure 3.34 Effect of initial concentration on the percent removal of Cd metal ion by using CKD, at pH (6.17-12.19), 1hour, 130 rpm , temp 30 ^{o}C and 10 g CKD / L.

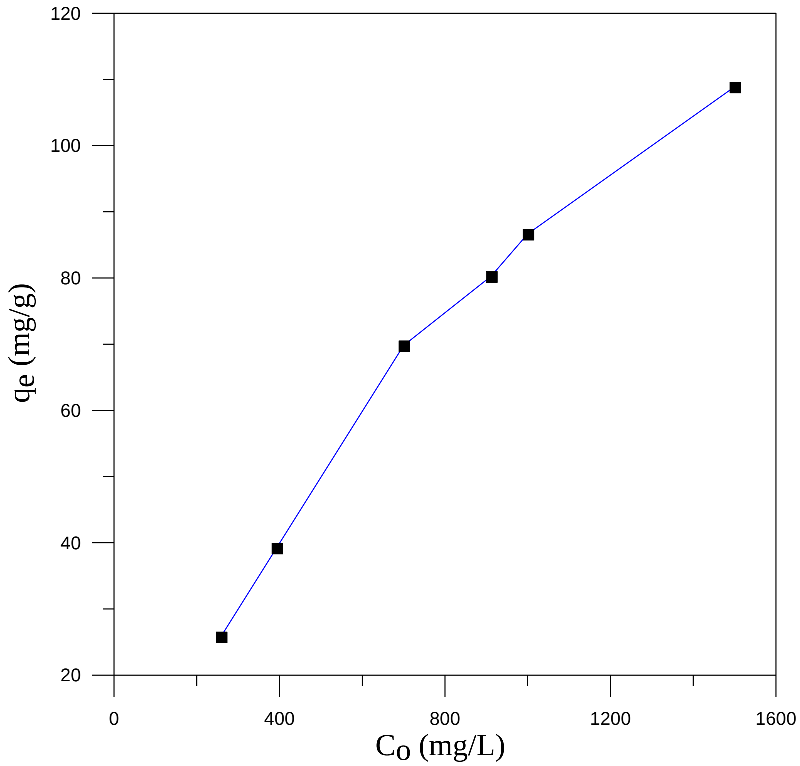

Figure 3.35 Adsorption isotherm of Cd(II) by using CKD at 30 ^{o}C

3.5 Effect of adsorbent dose

The results for percent adsorptive removal of heavy metal ions with respect to adsorbent dose are shown in fig. (3.36) over the range 10–30 g/L, at pH 5.89 and 6.17 for Al(III) and Cd(II), respectively and 8 for Zn(II) and Co(II), the percentage removal of heavy metal ions is seen to increase with adsorbent dose. From (Fig. 3.36), the percentage removal of Al(II) ions show 100% removal throughout the range of concentrations studied (within initial concentration **803.10 mg/L**). It is observed that there is a sharp increase in percentage removal with adsorbent dose for Zn(II) and Cd (II) ions but in case of Co(II) ions, there is gradual increase in percentage removal with increasing dose.

It is apparent that the percent removal of heavy metal ions increased rapidly with increase in the dose of the adsorbents due to the greater availability of the exchangeable sites or surface area. Moreover, the percentage of metal ion adsorption on adsorbent is determined by the adsorption capacity of the adsorbent for various metal ions.

Influence of sorbent dose on adsorbent amount. The dependence of Zn(II), Al(III), Co(II) and Cd(II) sorption amount on sorbent dose was studied by varying the amount of adsorbents from 10 to 30 g/L, at pH 5.89 and 6.17 for Al(III) and Cd(II), respectively and 8 for Zn(II) and Co(II), while keeping other parameters (agitation speed, and temperature) constant. Figure (3.37) presents the Zn(II), Al(III), Co(II) and Cd(II) adsorbent amount. Form the figure (3.37), it can be observed that

At lower initial metal ion concentrations, adsorbent amount of heavy metal ions decreased with increase sorbent dose, due to huge adsorption sites compared to available heavy metal ions in solution.

However, at higher concentrations the adsorbent amount of heavy metal ions increase with increase sorbent dose until reached the maximum metal ion sorption by sorbent dose CKD (the maximum metal sorption was obtained at low sorbent dose when residual metal ion concentration is more than adsorbent metal ion concentration thereafter decreased again in adsorbent amount with increasing sorbent dose. Hence, the adsorbent amount of heavy metal ions depends on the initial metal ions concentration.

the effect of adsorbent dose on the percent removal and adsorbent amount of heavy metal ions Zn(II), Al(III), Co(II) and Cd(II) on CKD are indicated in tables(3.14), (3.15), (3.16), (3.17) and figures (3.38 and 3.39), (3.40 and 3.41), (3.42 and 3.43), (3.44 and 3.45) respectively .

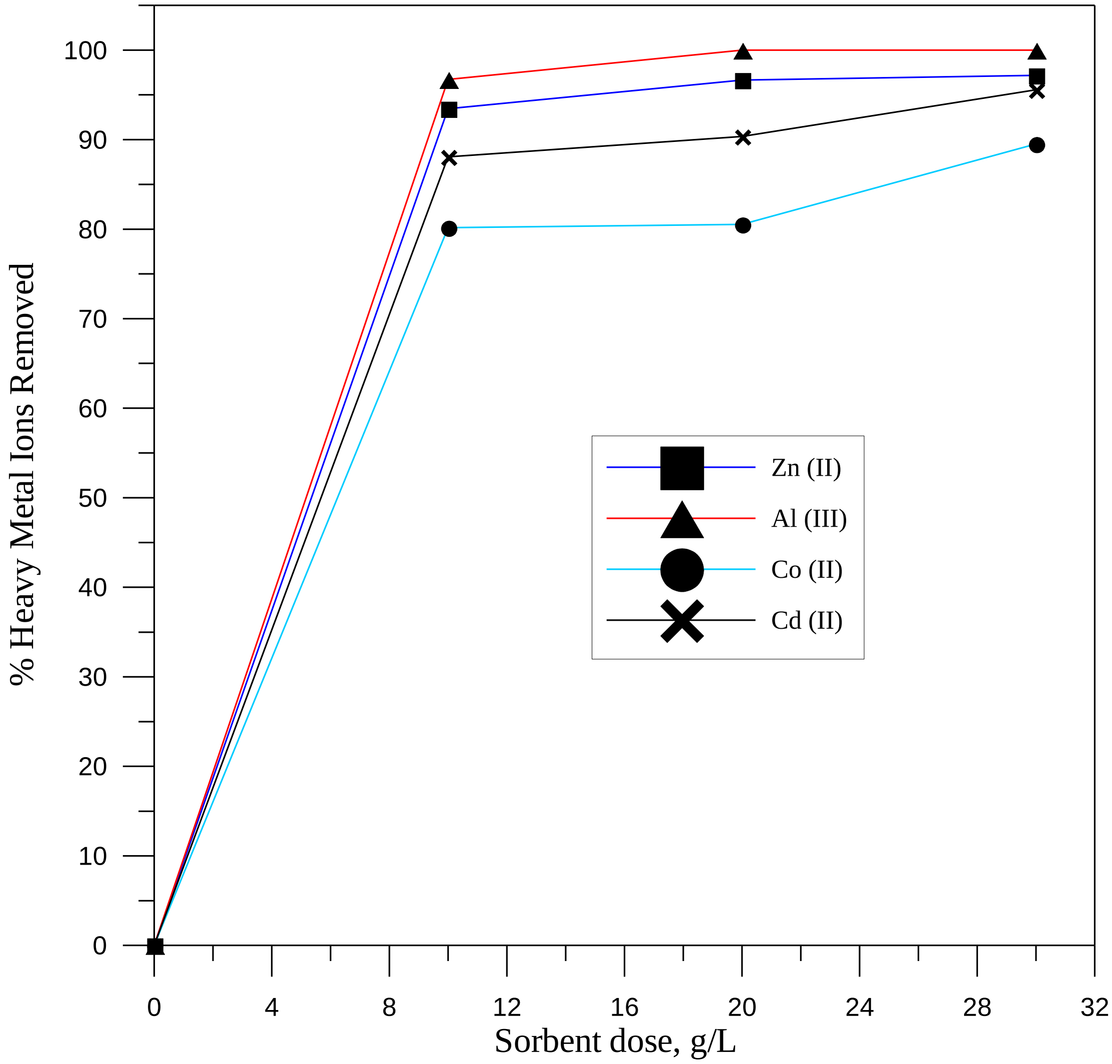

Figure 3.36 Effect of variation sorbent dose on heavy metal ions removal by using CKD, at 130 rpm and temp 30 ^{o}C.

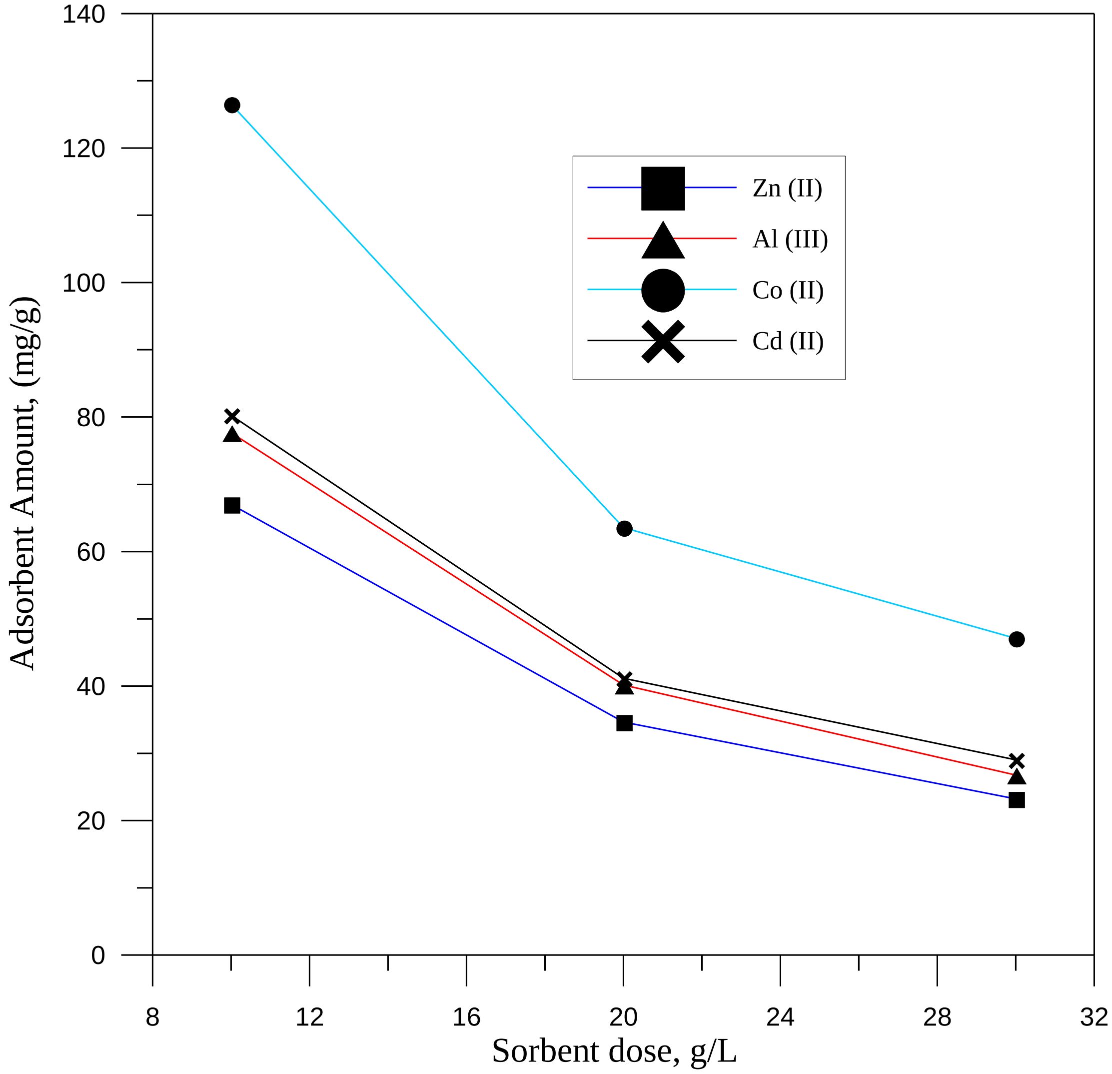

Figure 3.37 Effect of variation sorbent dose on the adsorbent amount of heavy metal ions by using CKD, at 130 rpm and temp 30 ^{o}C.

Table 3.14 Effect of variation sorbent dose on **Zn** metal ions removal within initial concentration **716.95 mg/L** by using CKD, at pH (8-10.17), 40 min., 130 rpm and temp 30 ^{o}C.

Sorbent amount g /L	Residual Conc. **C (mg / L)**	Adsorbent amount **q (mg / g)**	% Percent Removal **$(C_o\text{-}C)/C_o$*100**	Distribution coefficient **$(C_o\text{-}C)/$ C* v/m**
10	46.912	67.0038	93.45673	1428.287
20	23.990	34.648	96.65388	2888.537
30	20.247	23.22343	97.17595	3441.018

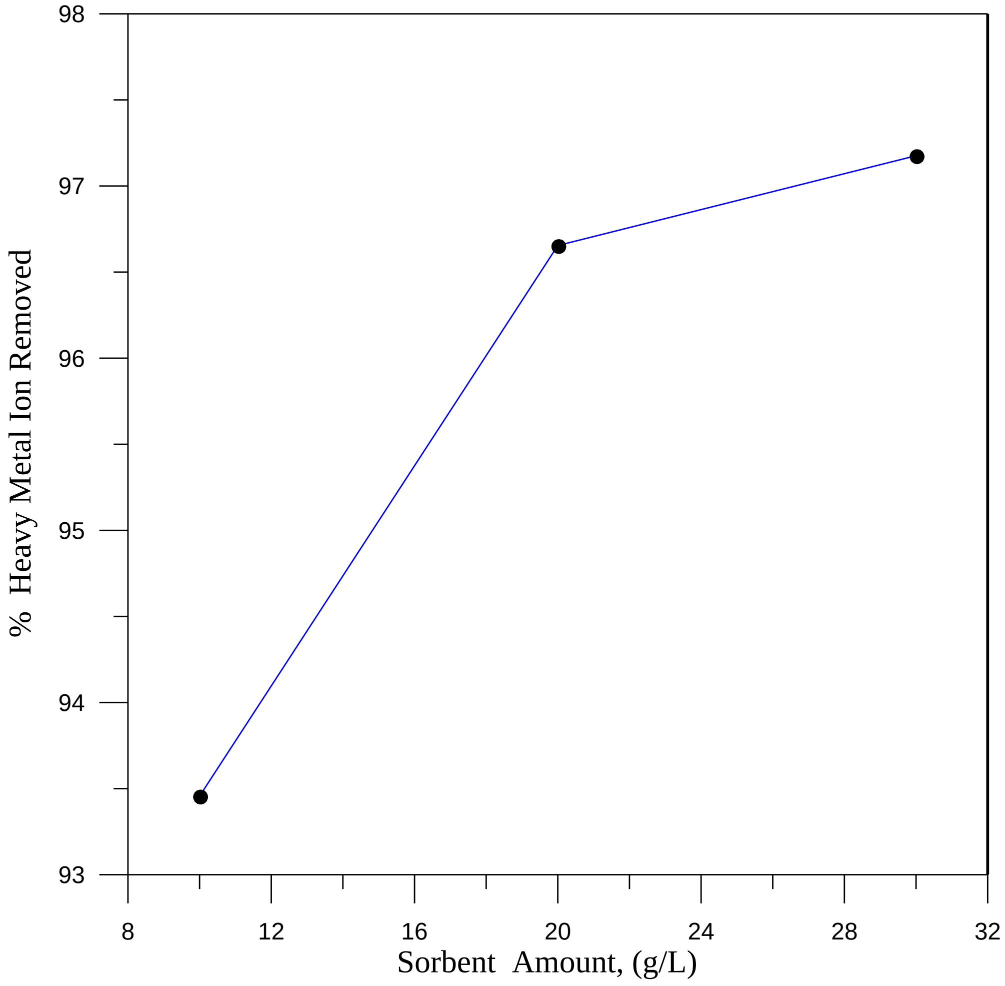

Figure 3.38 Effect of variation sorbent dose on Zn metal ions removal within initial concentration **716.95 mg/L** by using CKD, at pH (8-10.17), 40 min., 130 rpm and temp 30 ^{o}C.

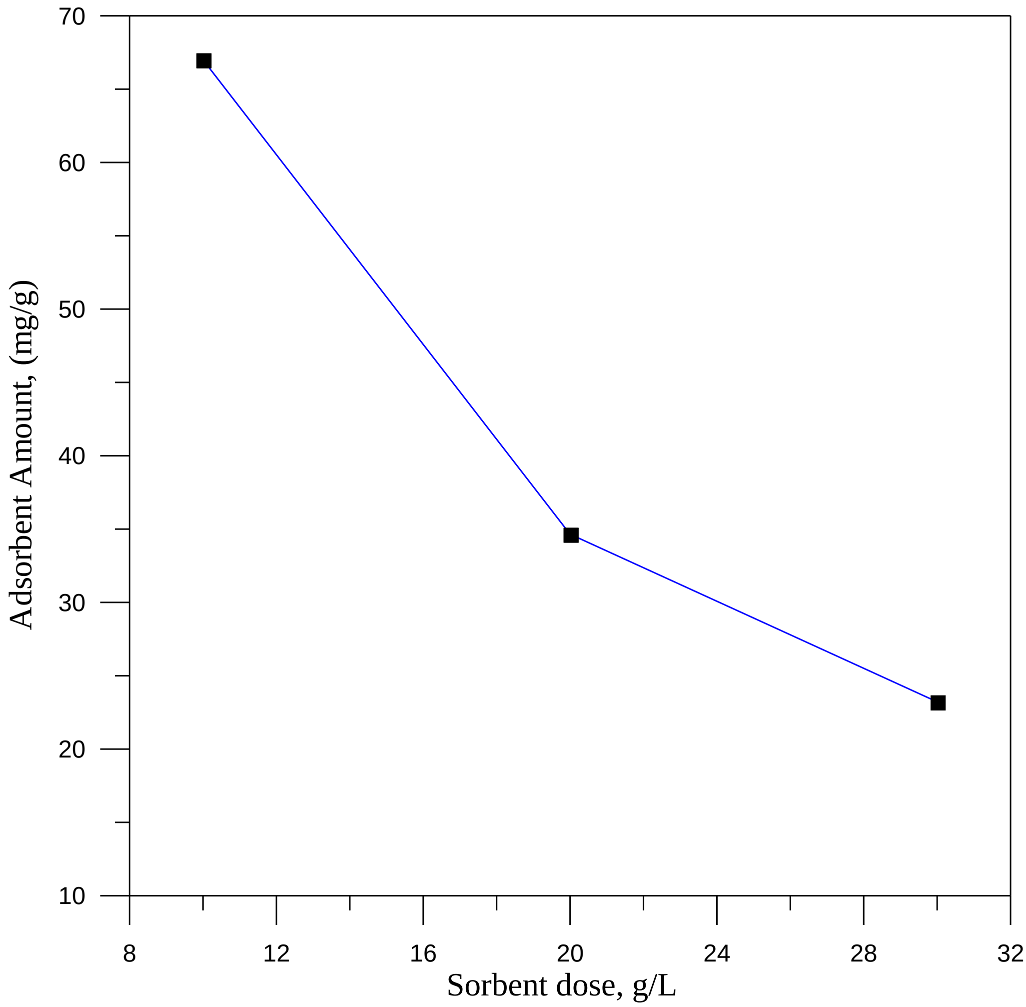

Figure 3.39 Effect of variation sorbent dose on the adsorbent amount of Zn metal ionswithin initial concentration **716.95 mg/L** by using CKD, at pH (8-10.17), 40 min., 130 rpm and temp 30 ^{o}C.

Table 3.15 Effect of variation sorbent dose on **Al** metal ions removal within initial concentration **803.10 mg/L** by using CKD, at pH (5.89-8.57), 5 min., 130 rpm and temp 30 ^{o}C.

Sorbent amount g / L	Residual Conc. **C (mg / L)**	Adsorbent amount **q (mg / g)**	% Percent Removal **$(C_o-C)/C_o*100$**	Distribution coefficient **$(C_o-C)/ C* v/m$**
10	26.316	77.6784	96.7232	2951.756
20	0.10669	40.14967	99.98672	752641.6
30	0.08531	26.76716	99.98938	941290.2

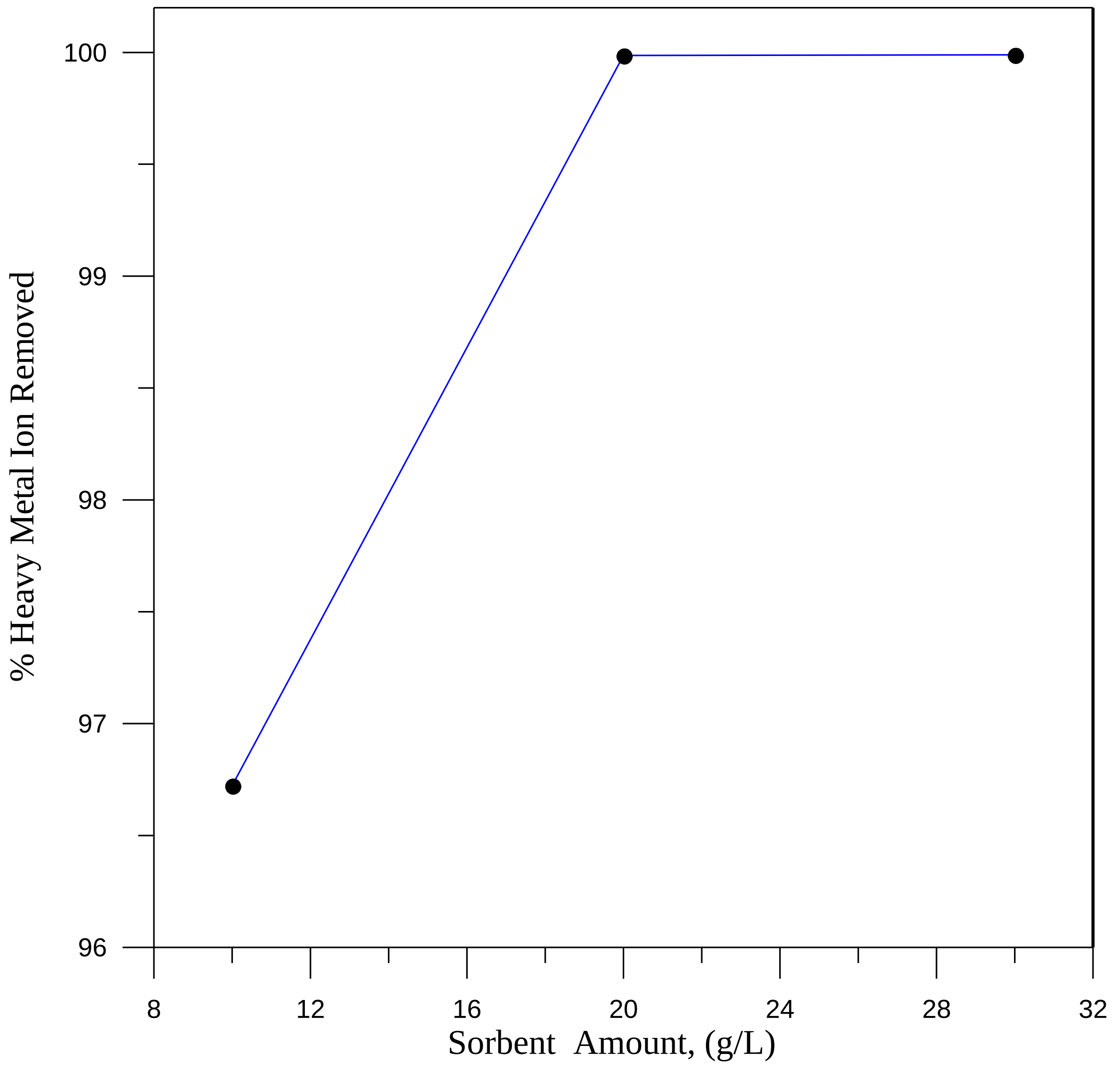

Figure 3.40 Effect of variation sorbent dose on Al metal ions removal within initial concentration **803.10 mg/L** by using CKD, at pH (5.89-8.57), 5 min., 130 rpm and temp 30 ^{o}C.

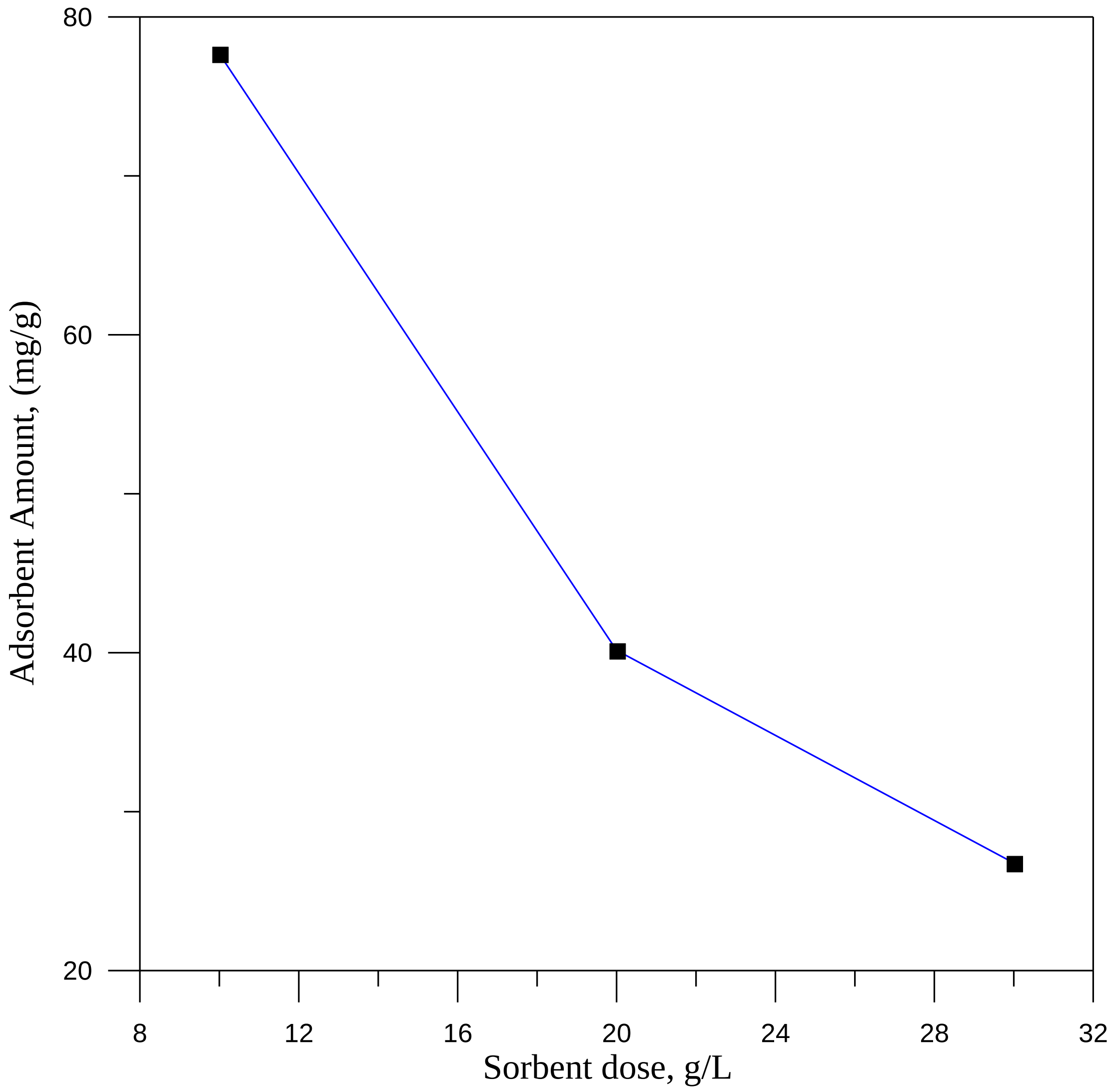

Figure 3.41 Effect of variation sorbent dose on the adsorbent amount of Al metal within initial concentration **803.10 mg/L** by using CKD, at pH (5.89-8.57), 5 min., 130 rpm and temp 30 ^{o}C.

Table 3.16 Effect of variation sorbent dose on **Co** metal ions removal within initial concentration **1578.6 mg/L** by using CKD, at pH (8-10.94), 4 hour, 130 rpm and temp 30 ^oC.

Sorbent amount g/L	Residual Conc. **C (mg / L)**	Adsorbent amount **q (mg / g)**	% Percent Removal **$(C_o-C)/C_o*100$**	Distribution coefficient **$(C_o-C)/ C* v/m$**
10	313.21	126.539	80.159	404.0069
20	307.35	63.5625	80.53022	413.6164
30	165.68	47.09733	89.50462	852.8006

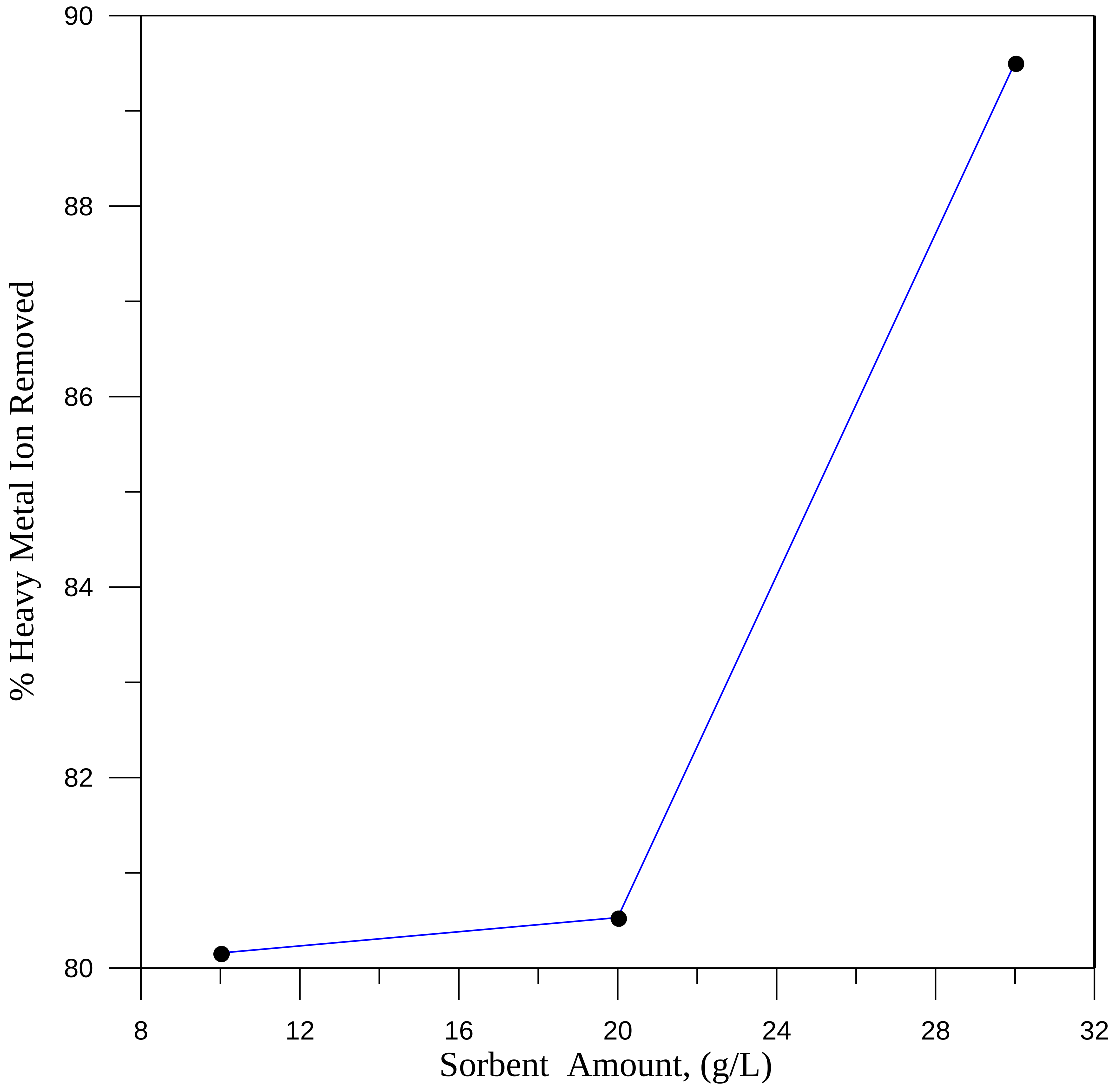

Figure 3.42 Effect of variation sorbent dose on Co metal ionsremoval within initial concentration **1578.6 mg/L** by using CKD, at pH (8-10.94), 4 hour, 130 rpm and temp 30 ^oC.

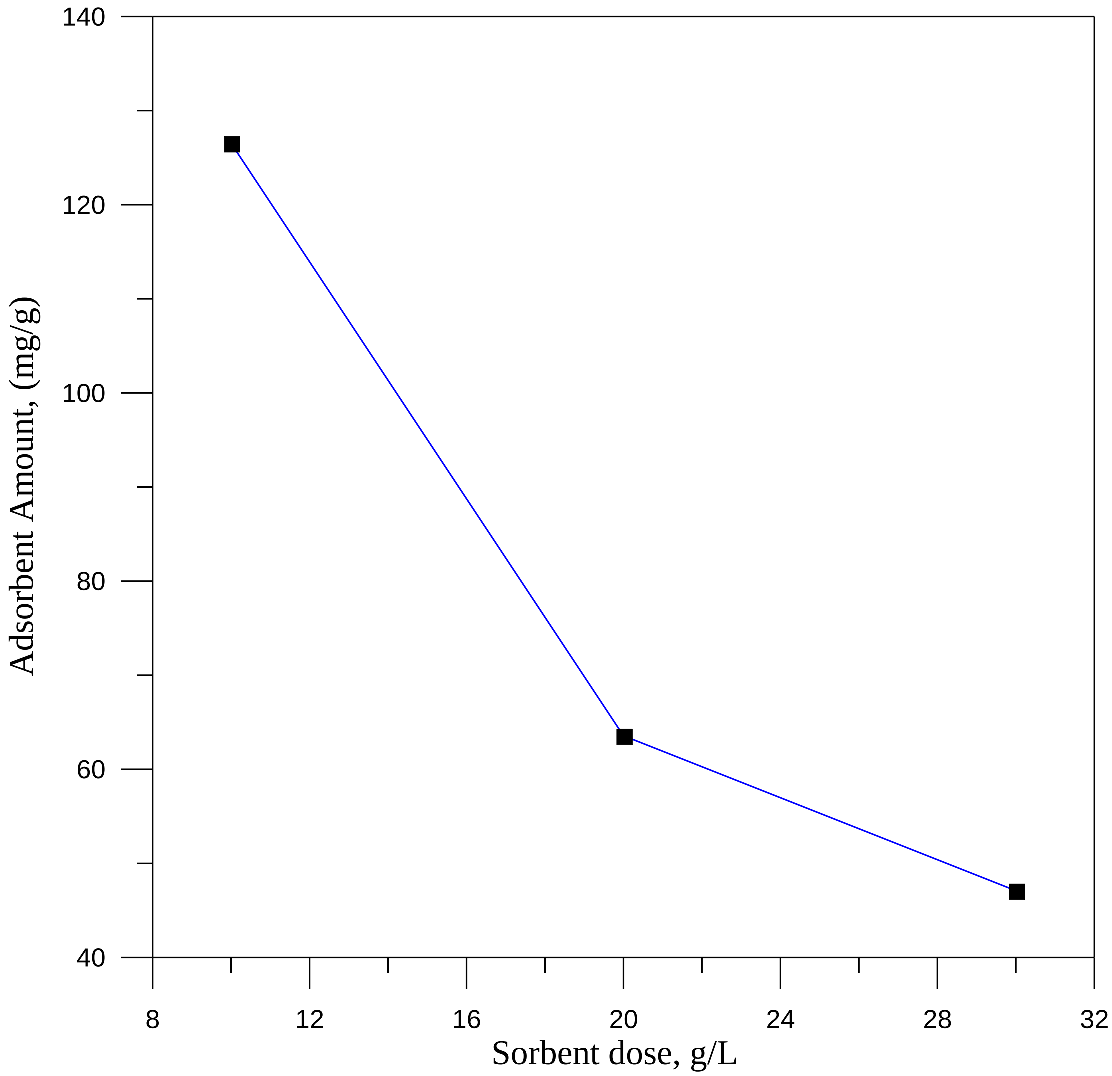

Figure 3.43 Effect of variation sorbent dose on the adsorbent amount of Co metal ions within initial concentration **1578.6 mg/L** by using CKD, at pH (8-10.94), 4 hour, 130 rpm and temp 30 ^{o}C.

Table 3.17 Effect of variation sorbent dose on **Cd** metal ions removal within initial concentration **911.41 mg/L** by using CKD, at pH (6.17-12.19), 1hour, 130 rpm and temp 30 ^{o}C.				
Sorbent amount g/L	Residual Conc. **C (mg / L)**	Adsorbent amount **q (mg / g)**	% Percent Removal **$(C_o\text{-}C)/C_o$*100**	Distribution coefficient **$(C_o\text{-}C)/$ C* v/m**
10	108.71	80.27	88.07233	738.3865
20	88	41.1705	90.34463	935.6932
30	40.424	29.03287	95.56467	2154.626

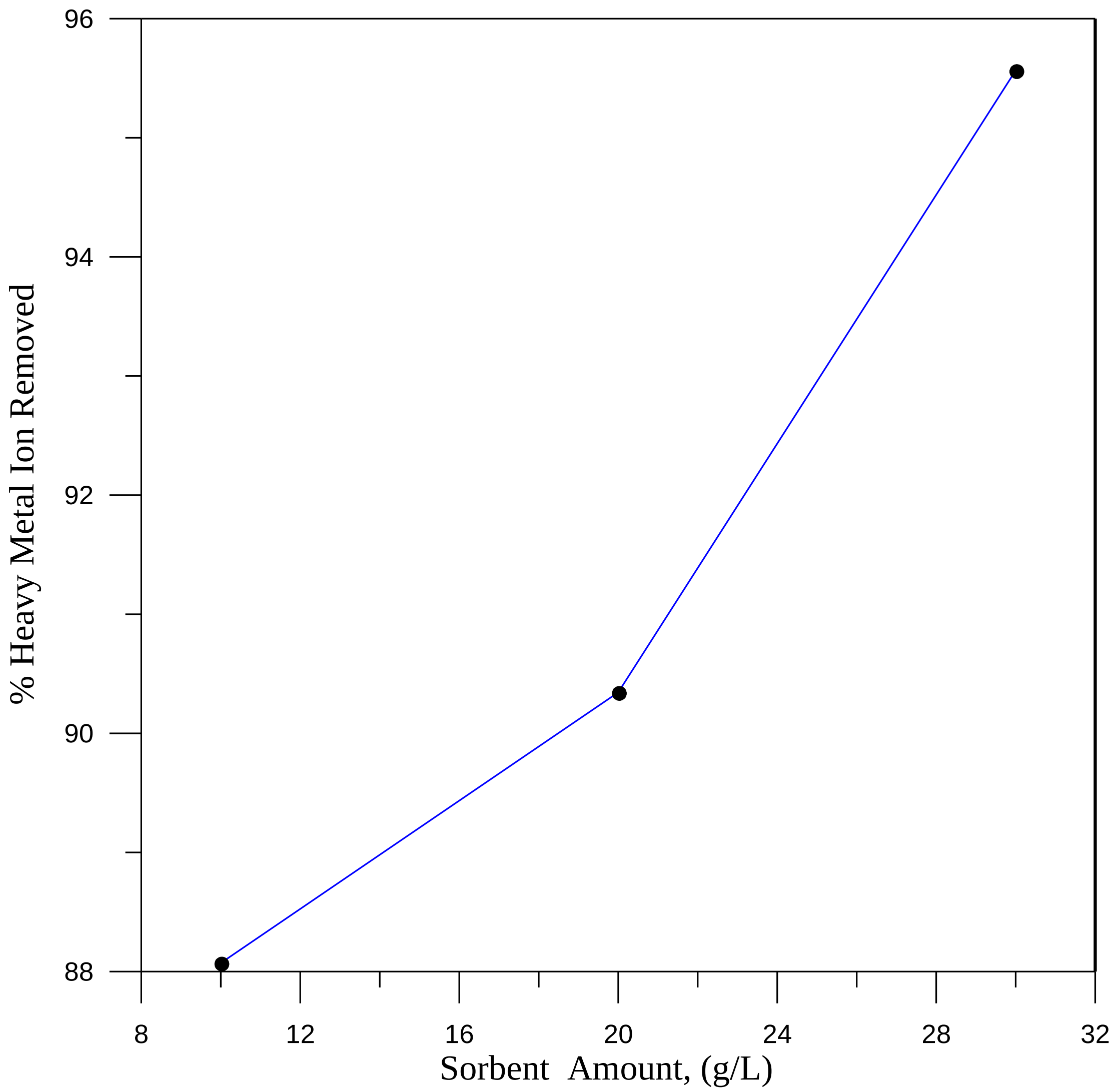

Figure 3.44 Effect of variation sorbent dose on Cd metal ions removal within initial concentration **911.41 mg/L** by using CKD, at pH (6.17-12.19), 1hour, 130 rpm and temp 30 ^{o}C.

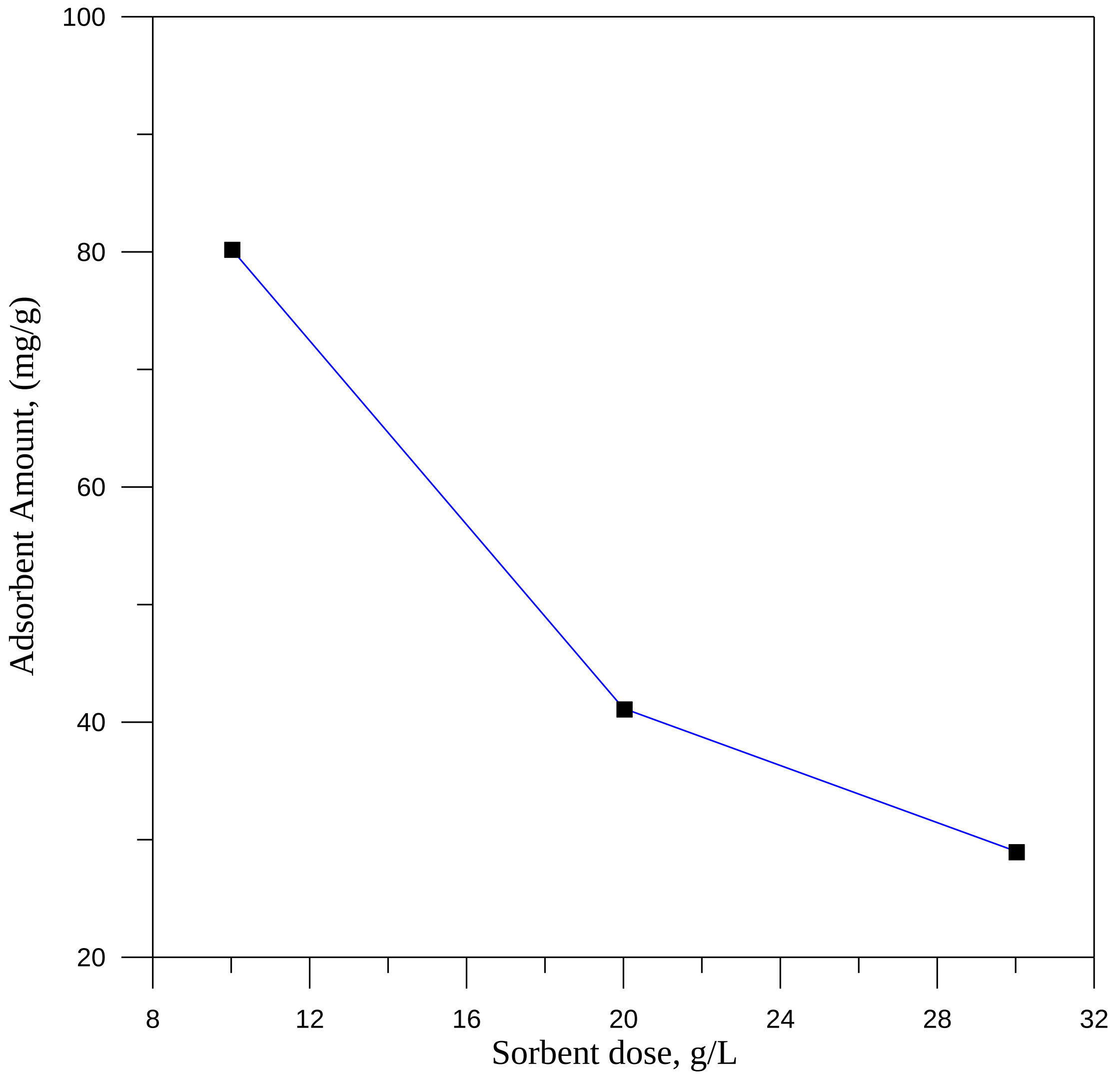

Figure 3.45 Effect of variation sorbent dose on the adsorbent amount of Cd metal ions within initial concentration **911.41 mg/L** by using CKD, at pH (6.17-12.19), 1hour, 130 rpm and temp 30 ^{o}C.

3.6 The Effect of initial concentration of heavy metal ions

The batch of adsorption was carried out by using different heavy metal ions concentration from (384.55-1825.8), (123.60- 958.95), (150.40- 956.17) and (258.51-1500) for Zn(II), Al(III), Co(II) and Cd(II), respectively.

All experiments were done under the following conditions 50 ml of heavy metal ions solution at pH 5.89 and 6.17 for Al(III) and Cd(II), respectively and 8 for Zn(II) and Co(II), agitation rate 130 rpm, and the solution temperature was 30 ^{o}C using 0.5 g of CKD having average particle size 3µ in adsorption process at equilibrium times.

The effect of initial conc. on the percent removal and adsorbent amount of heavy metal ions Zn(II), Al(III), Co(II) and Cd(II) on CKD are indicated in tables(3.18), (3.19), (3.20), (3.21) and figures (3.48and 3.49), (3.50 and 3.51), (3.52 and 3.53), (3.54 and 3.55) respectively at 30 ^{o}C using different metal ions concentrations.

The effect of initial concentration on the percentage removal of heavy metal ions by CKD is shown in fig. (3.46.) It can be seen from the figure that the percentage removal decreases with the increase in initial heavy metal concentration. For Zn (II) is seen the percentage removal is almost complete (nearly 90-100%) throughout the initial metal ions concentration range (384.55-1825.8) mg/L for 10 g/L adsorbent dose, at pH 5.89 and equilibrium contact time. For Cd(II) and Al(III) at same adsorbent dose and equilibriums contact time, there are gradually drop in percentage removal at higher initial concentration, whereas for Co(II) the percentage removal is highly effective >80% below 600 mg/l initial concentration after which percentage removal decreases sharply to below 70%. At higher initial concentrations, Cd(II) shows greater percentage removal than Al(III). At lower initial metal ion concentrations, sufficient adsorption sites are available for adsorption of the heavy metal ions. Therefore, the fractional adsorption is independent of initial metal ion concentration. However, at higher concentrations the numbers of heavy metal ions are relatively higher compared to availability of adsorption sites. Hence, the percent removal of heavy metal ions depends on the initial metal ions concentration and decreases with increase in initial metal ions concentration. The difference in percentage removal of different heavy metal ions at the same initial metal ions concentration, adsorbent dose and contact time may be attributed to the difference in their chemical affinity and ion exchange capacity with respect to the chemical functional groups on the surface of the adsorbent.

The percentages of removal of Zn(II), Al(III), Co(II) and Cd(II) solutions, in which concentrations were 100–2000 mg/L, were evaluated by using CKD showed high removal efficiency for all metals. These results are shown in fig. (3.46.) In these adsorbants, high removal efficiency (95%) was obtained over the Zn(II), Cd(II) and Al(III) concentration range 100–800 mg/L. However, the removal percentage gradually decreased with increasing the concentration (>800 mg/L).

Therefore, this method is suitable for the removal of relatively high and low concentration heavy metal ions such as rinsing wastewater from plating factory although pre-treatment such as dilution seems to be needed for very high concentration.

The Effect of initial concentration on the adsorbent amount of heavy metal ions by using CKD is shown in fig. (3.47.) from the figure high sorption capacities were observed for the four metals. The binding capacity experiments revealed the direct proportional between initial conc. and adsorption amount (this explains that maximum capacities were not reached yet over all used initial conc.) the following amounts of metal ions bound per gram of CKD: 165.994mg/g, 75.389 mg/g, 64.296 mg/g and 108.875mg/g for Zn(II), Al(III), Co(II) and Cd(II), respectively.

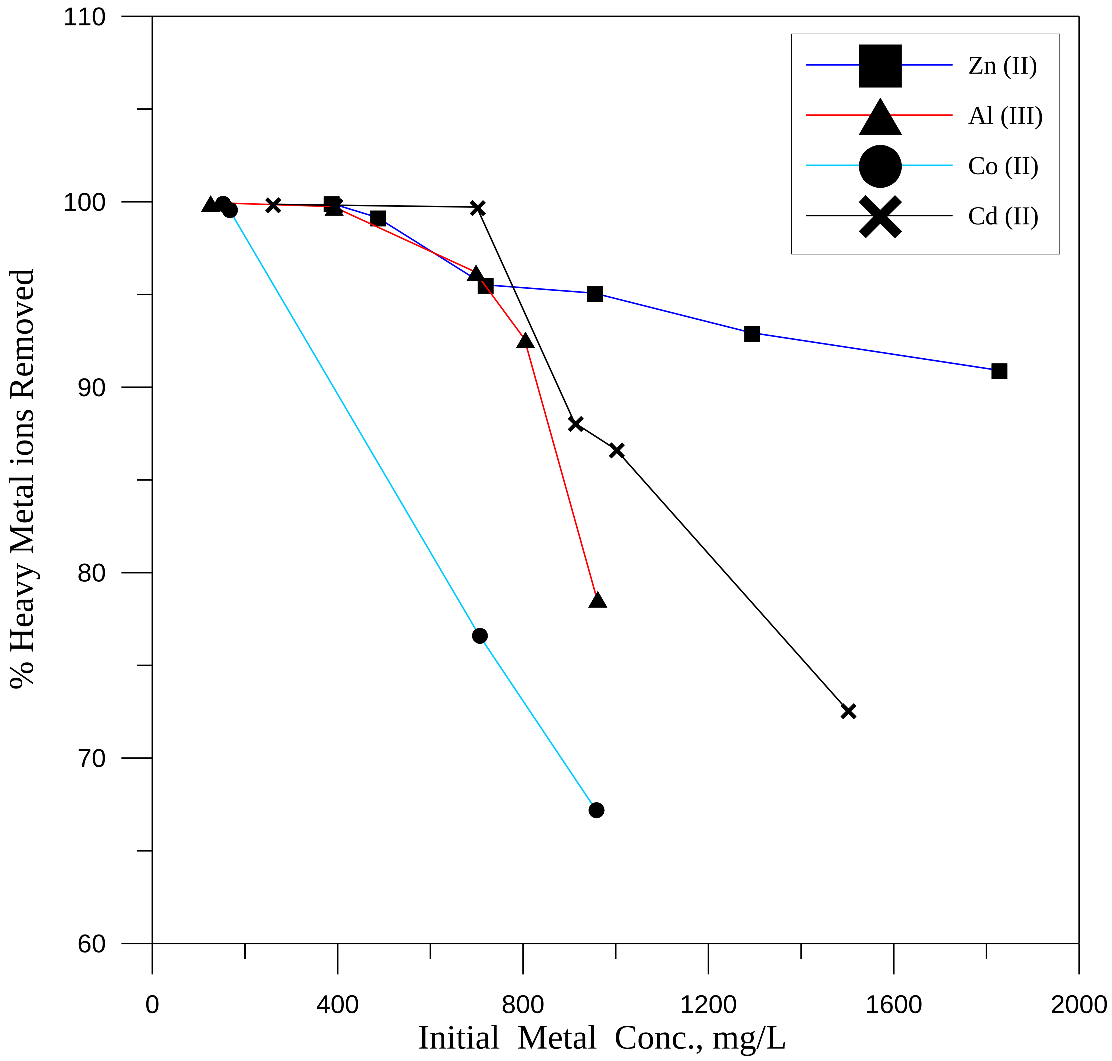

Figure 3.46 Effect of initial concentration on the percent removal of heavy metal ions by using CKD.

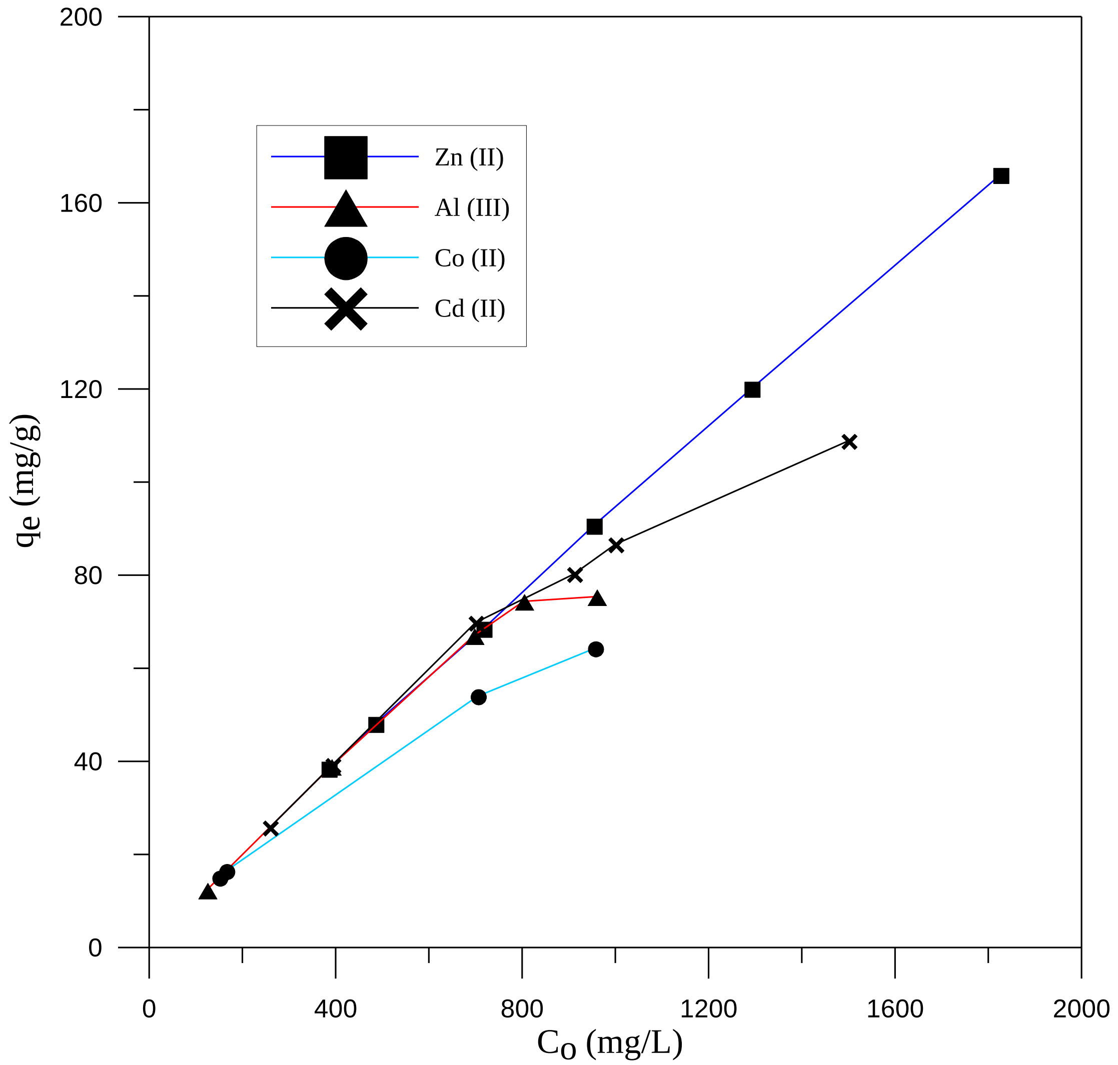

Figure 3.47 Effect of initial concentration on the adsorbent amount of heavy metal ions by using CKD.

Table 3.18 Effect of initial concentration on the percent removal of **Zn** metal ions by using CKD, at pH (8-10.17), 40 min., 130 rpm, temp 30 ^{o}C and 10 g CKD / L.

Initial Conc. **C_o (mg / L)**	Residual conc. **C (mg / L)**	Adsorbent amount **q (mg / g)**	% Percent Removal **$(C_o-C)/C_o*100$**	Distribution coefficient **$(C_o-C)/C*v/m$**
384.55	0.29002	38.426	99.92458	66.24715
484.88	4.0610	48.0819	99.16247	5.919958
716.95	32.112	68.4838	95.52103	1.066327
953.24	46.912	90.6328	95.07868	0.965987
1292	91.227	120.0773	92.93909	0.658124
1825.8	165.86	165.994	90.91576	0.500404

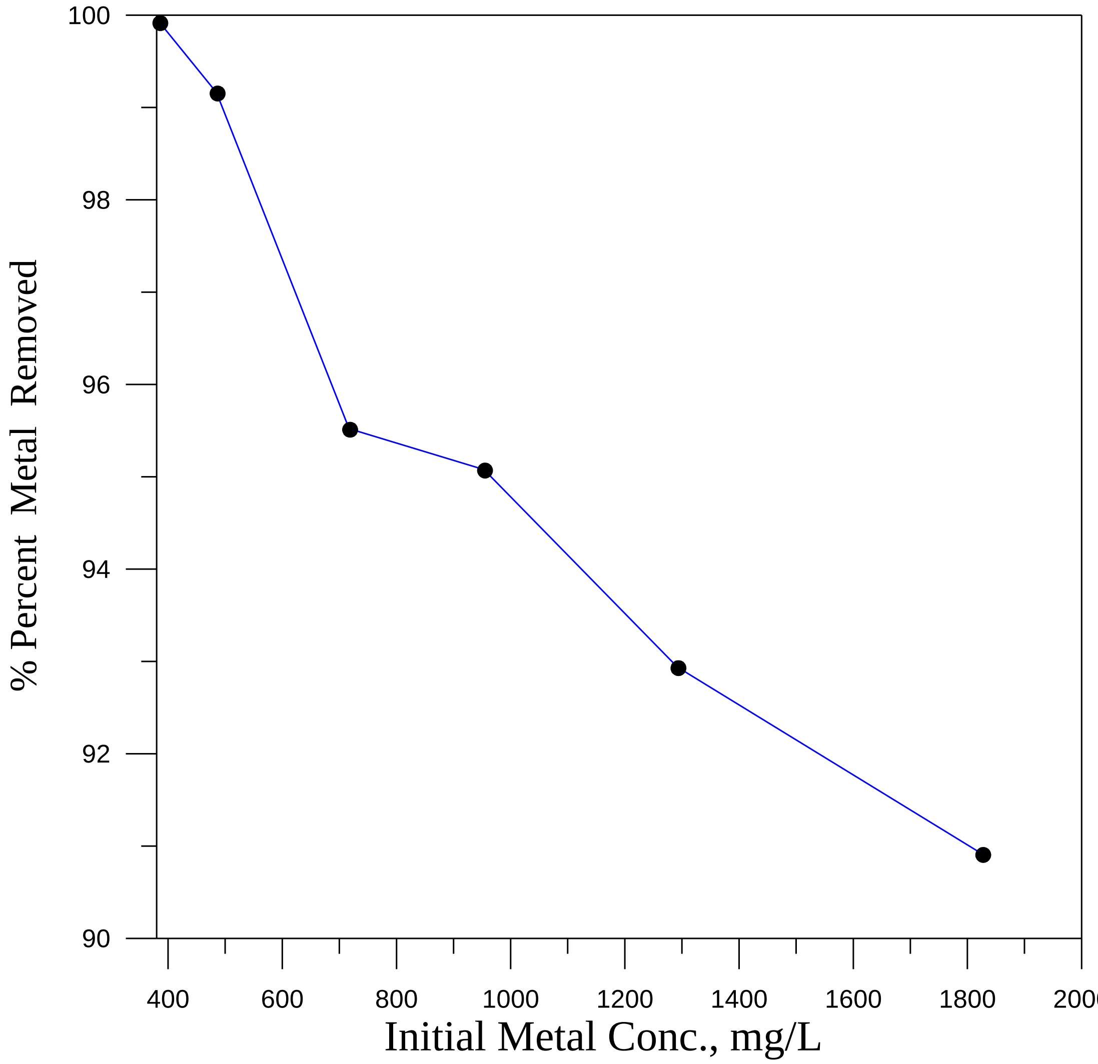

Figure 3.48 Effect of initial concentration on the percent removal of Zn metal ions by using CKD, at pH (8-10.17), 40 min., 130 rpm, temp 30 ^{o}C and 10 g CKD / L.

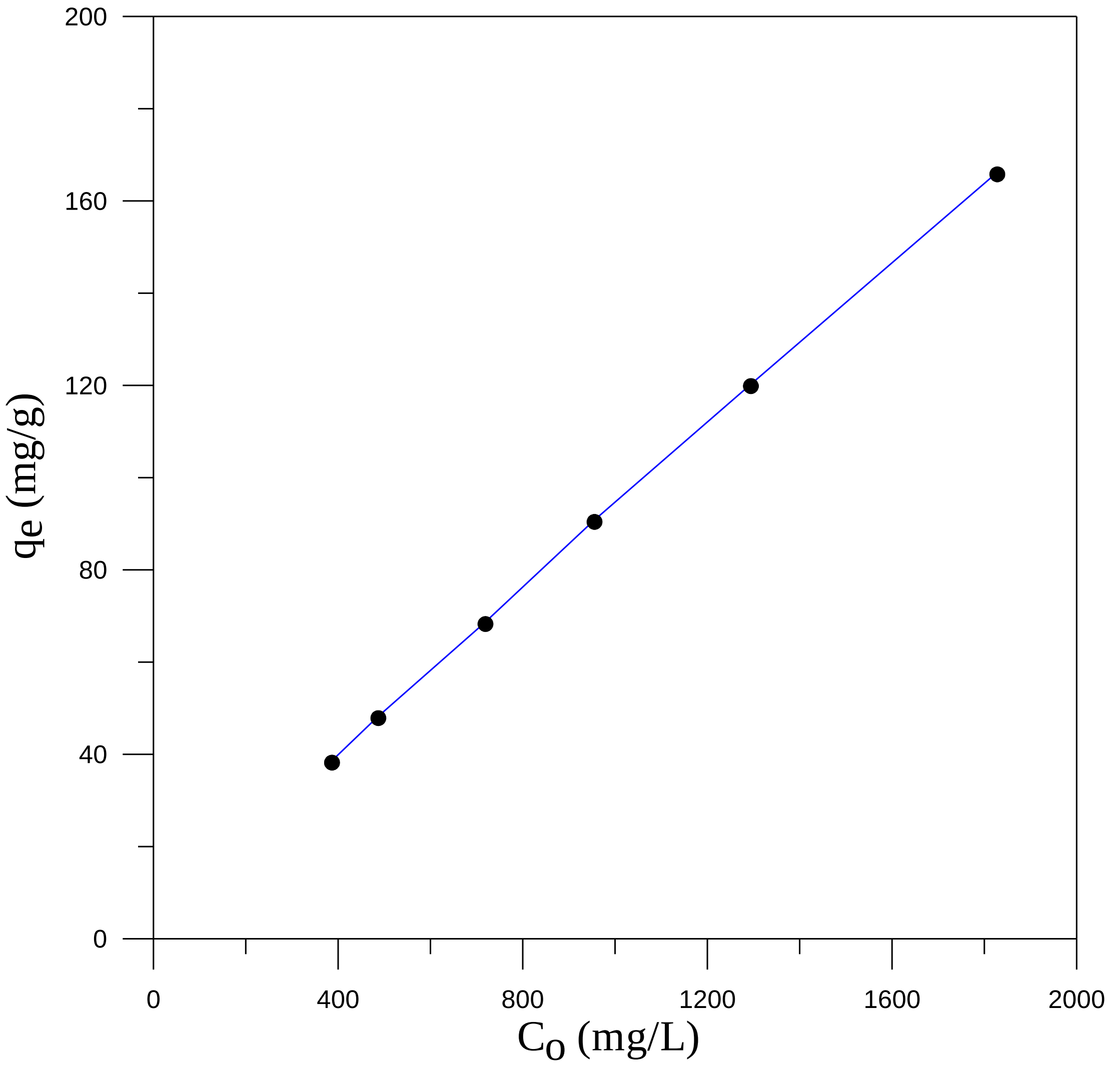

Figure 3.49 Effect of initial concentration on the adsorbent amount of **Zn** metal ions by using CKD, at pH (8-10.17), 40 min., 130 rpm, temp 30 ^{o}C and 10 g CKD / L.

Table 3.19 Effect of initial concentration on the percent removal of **Al** metal ions by using CKD, at pH (5.89-8.57), 5 min., 130 rpm , temp 30 °C and 10 g CKD / L.				
Initial Conc. **C_o (mg / L)**	Residual conc. **C (mg / L)**	Adsorbent amount **q (mg / g)**	% Percent Removal **$(C_o\text{-}C)/C_o$*100**	Distribution coefficient **$(C_o\text{-}C)/$ C* v/m**
123.60	0.04647	12.35535	99.9624	132.939
390.09	1.014117	38.90759	99.74003	19.18299
696.43	26.316	67.0114	96.2213	1.273206
803.10	59.377	74.3723	92.60652	0.626272
958.95	205.06	75.389	78.61619	0.183822

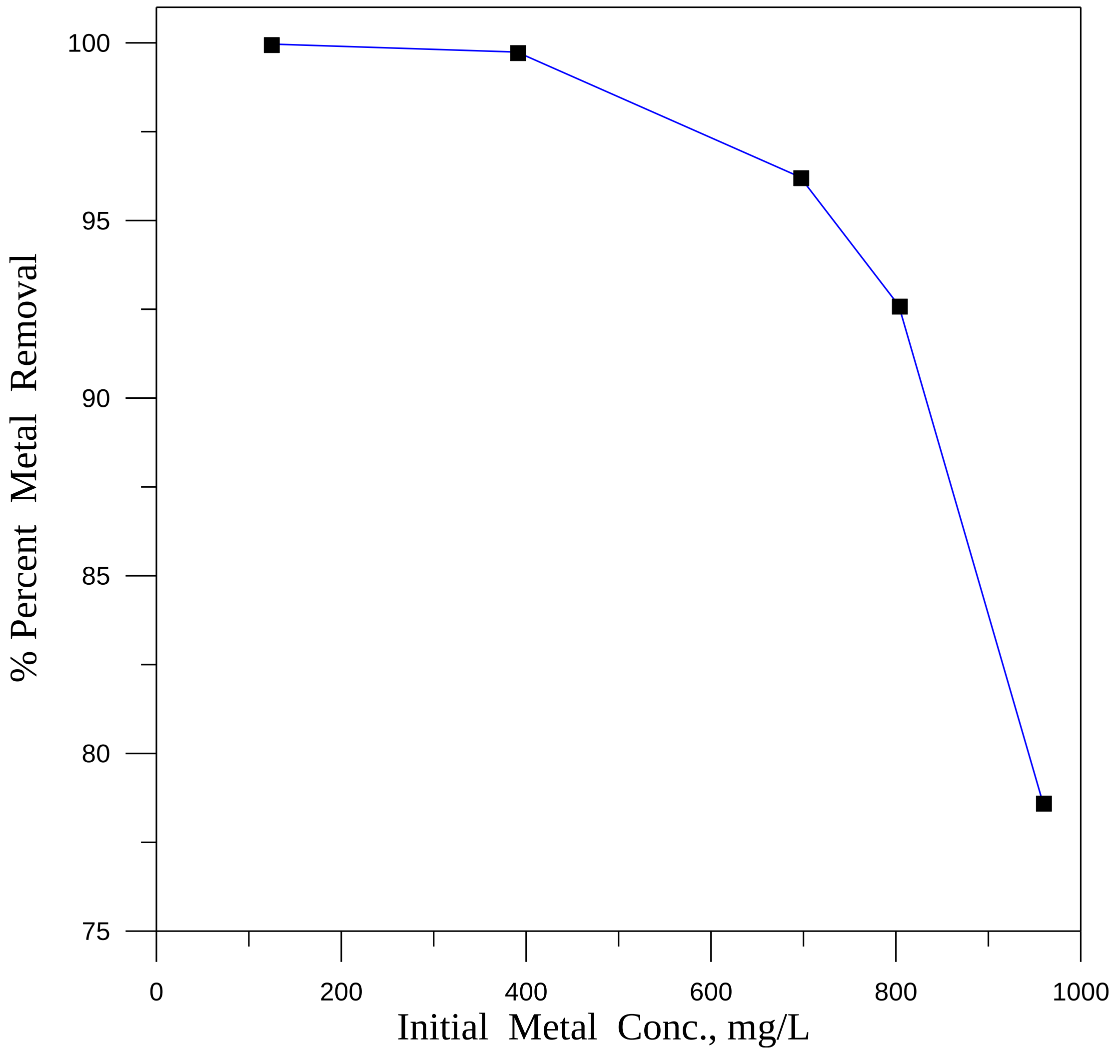

Figure 3.50 Effect of initial concentration on the percent removal of Al metal ion by using CKD, at pH (5.89-8.57), 5 min., 130 rpm, temp 30 °C and 10 g CKD / L.

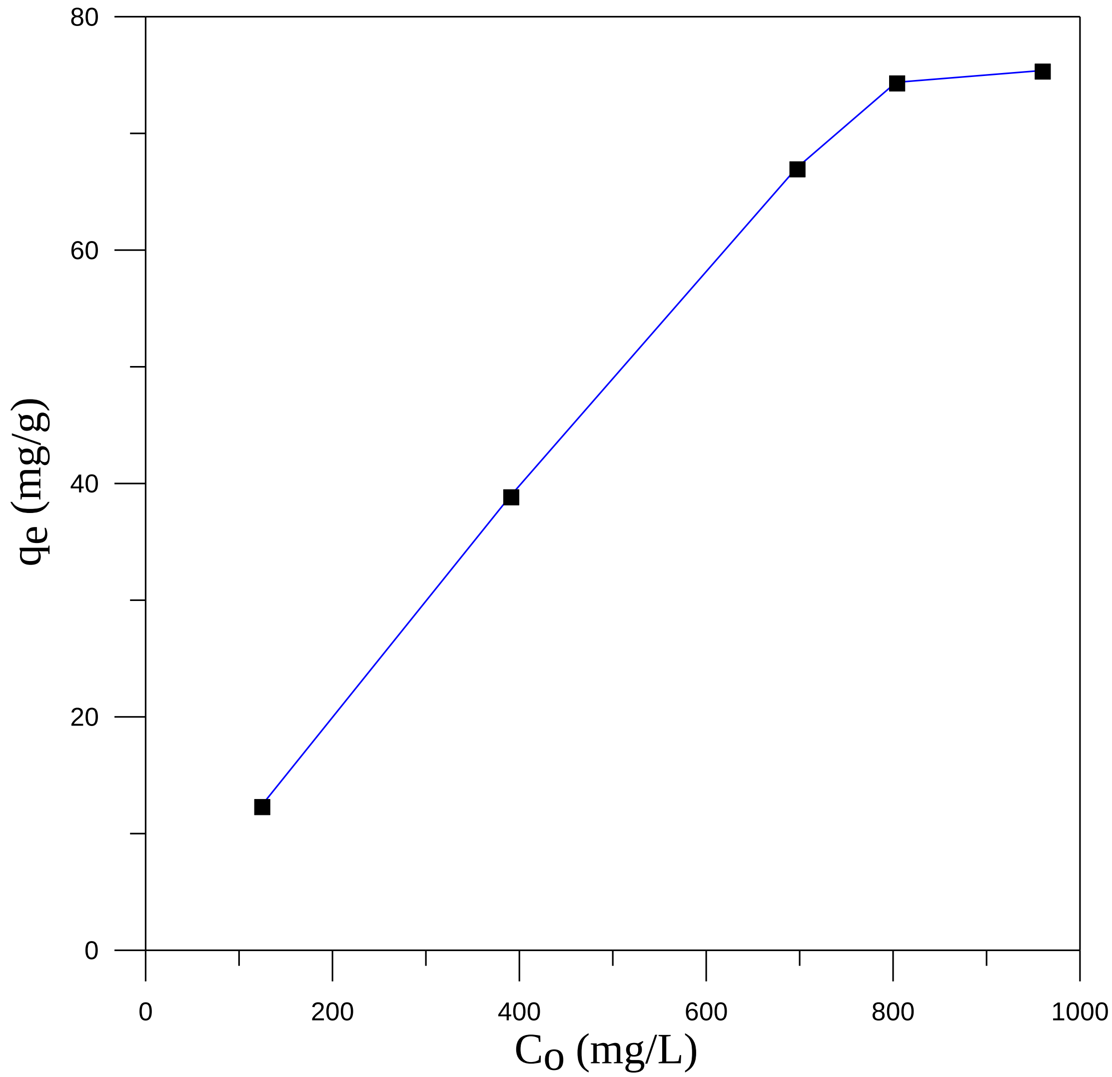

Figure 3.51 Effect of initial concentration on the adsorbent amount of **Al** metal ions by using CKD, at pH (5.89-8.57), 5 min., 130 rpm, temp 30 ^{o}C and 10 g CKD / L.

Table 3.20 Effect of initial concentration on the percent removal of **Co** metal ions by using CKD, at pH (8-10.94), 4 hour, 130 rpm , temp 30 ^{o}C and 10 g CKD / L.				
Initial Conc. **C_o (mg / L)**	Residual conc. **C (mg / L)**	Adsorbent amount **q (mg / g)**	% Percent Removal **$(C_o\text{-}C)/C_o$*100**	Distribution coefficient **$(C_o\text{-}C)$/ C* v/m**
150.40	0.08348	15.03165	99.94449	90.03146
165.22	0.648323	16.45717	99.6076	12.69211
704.65	164.53	54.012	76.65082	0.16414
956.17	313.21	64.296	67.24327	0.10264

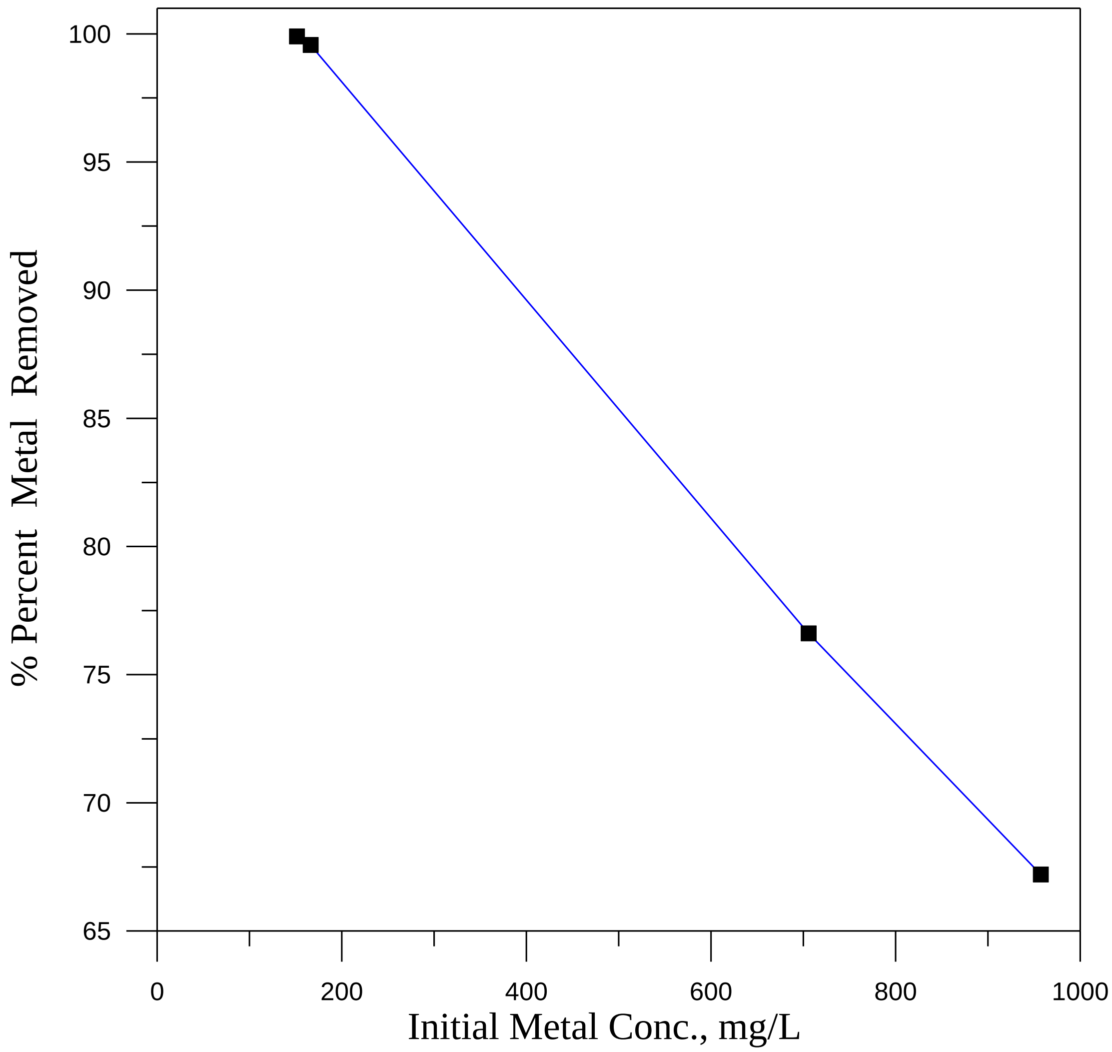

Figure 3.52 Effect of initial concentration on the percent removal of Co metal ions by using CKD, at pH (8-10.94), 4 hour, 130 rpm, temp 30 ^{o}C and 10 g CKD / L.

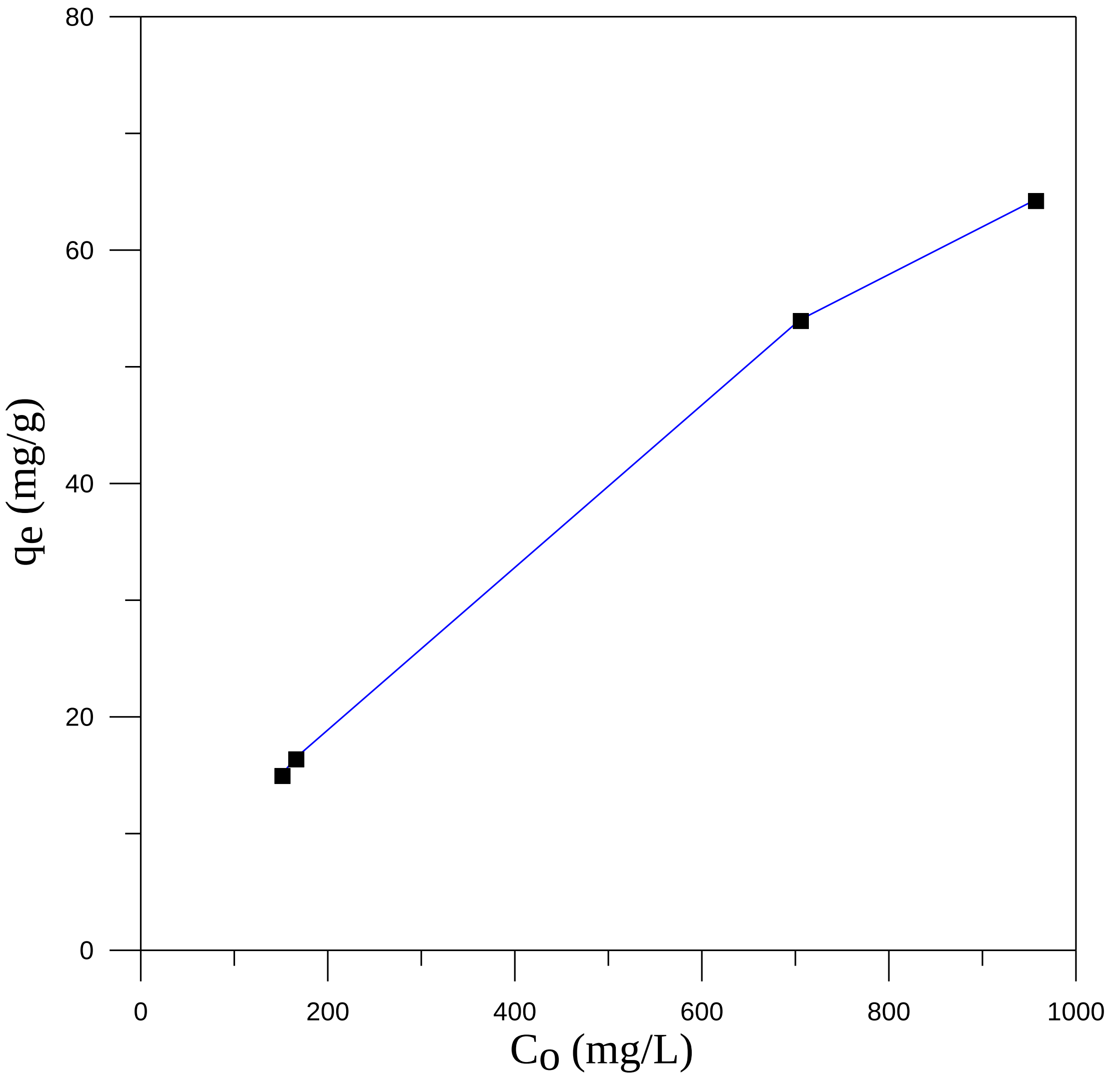

Figure 3.53 Effect of initial concentration on the adsorbent amount of Co metal ions by using CKD, at pH (8-10.94), 4 hour, 130 rpm, temp 30 ^{o}C and 10 g CKD / L.

Table 3.21 Effect of initial concentration on the percent removal of **Cd(II)** metal by using CKD, at pH (6.17-12.19), 1hour, 130 rpm , temp 30 ^{o}C and 10 g CKD / L.

Initial Conc. **C_o (mg / L)**	Residual conc. **C (mg / L)**	Adsorbent amount **q (mg / g)**	% Percent Removal **$(C_o-C)/C_o*100$**	Distribution coefficient **$(C_o-C)/ C* v/m$**
258.51	0.34365	25.81664	99.86707	37.5624
393	0.71743	39.22826	99.81745	27.33943
700	2.0080	69.7992	99.71314	17.38028
911.41	108.71	80.27	88.07233	0.369193
1000	133.52	86.648	86.648	0.324476
1500	411.25	108.875	72.58333	0.132371

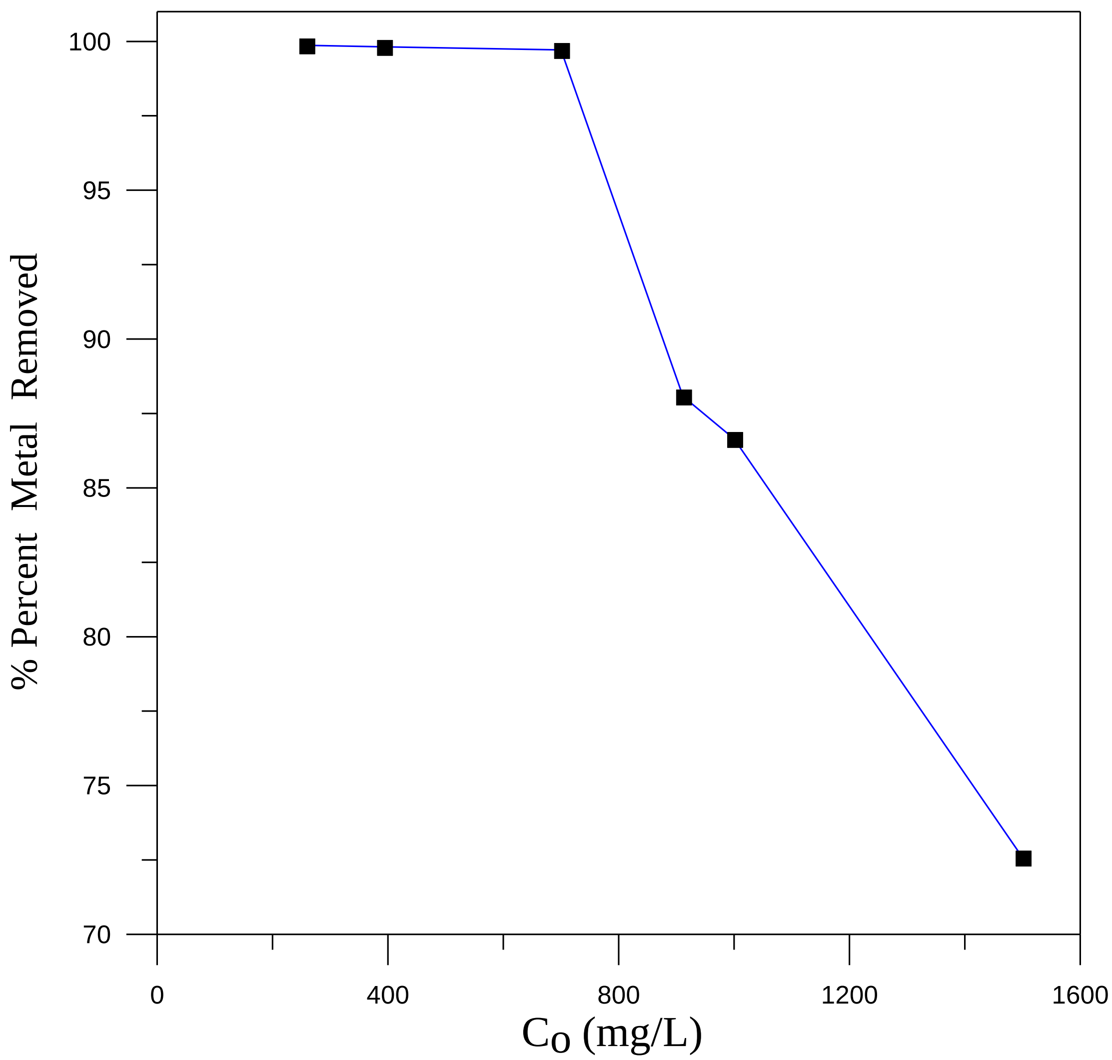

Figure 3.54 Effect of initial concentration on the percent removal of Cd(II) metal by using CKD, at pH (6.17-12.19), 1hour, 130 rpm, temp 30 ^{o}C and 10 g CKD / L.

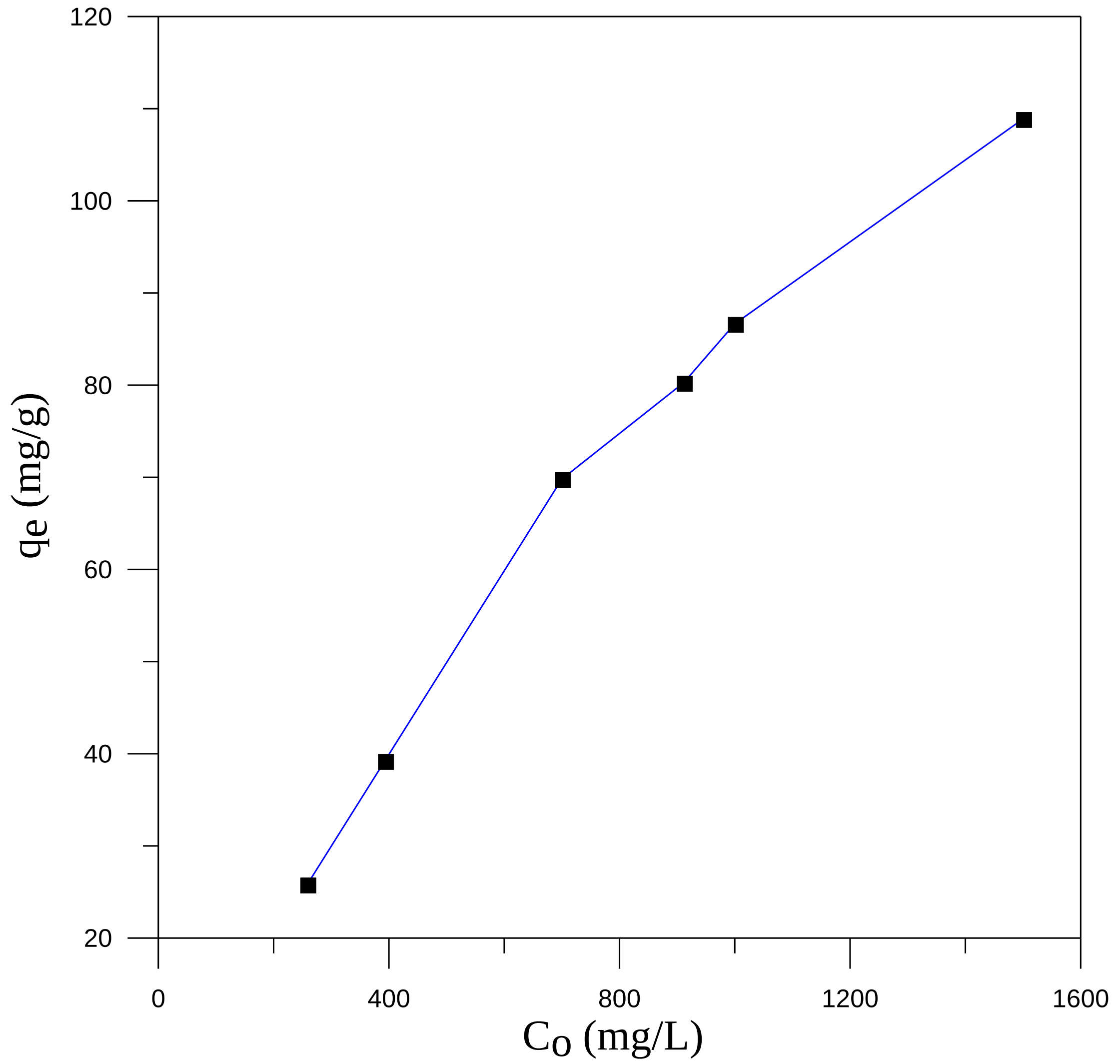

Figure 3.55 Effect of initial concentration on the adsorbent amount of Cd(II) by using CKD, at pH (6.17-12.19), 1hour, 130 rpm, temp 30 ^{o}C and 10 g CKD / L.

3.7 Effect of temperature

The temperature is an important parameter so the effect of temperature was studied using different temperatures 30, 40, 60 °**C**. All experiments were done by using 0.5 g of CKD added to 50 ml of metal ions solution having initial concentration 484.88, 390.09, 165.22 and 393.57 mg/l for Zn(II), Al(III), Co(II) and Cd(II), respectively, 130 rpm agitation rate and average particle size 3μ during the adsorption process.

Figures. (4.56 and 4.57) show the experimental results obtained from a series of studies for metal ions adsorption with an initial metal ions concentration of 484.88, 390.09, and 165.22, 393.57 mg/l for Zn(II), Al(III), Co(II) and Cd(II), respectively at pH 6-8 in which temperature was varied from 30 to 60 °C. The adsorption of metal ions has been found to increase with an increase in temperature from 30 to 60 °C. The increase in adsorption capacity of CKD with temperature indicates an endothermic process. The increase in adsorption with temperature may be attributed to either increase in the number of active surface sites available for adsorption on the adsorbent or the desolvation of the adsorbing species and the decrease in the thickness of the boundary layer surrounding the adsorbent with temperature, so that the mass transfer resistance of adsorbate in the boundary layer decreases. At higher temperatures the possibility of diffusion of solute within the pores of the adsorbent may not be ruled out as reported by earlier workers for the adsorption of cations on GAC. Since diffusion is an endothermic process, greater adsorption will be observed at higher temperature. Thus, the diffusion rate of ions in the external mass transport process increases with temperatures. The above results were further substantiated by the various thermodynamic parameters evaluated for adsorption.

The thermodynamic parameters, such as free energy (ΔG), enthalpy change (ΔH), and entropy change (ΔS) were determined using the following equations and presented in Table 4.22

$$K_e = \frac{C_{AC}}{C_e} \qquad (4)$$

where, K_e is the equilibrium constant, C_{Ac} and C_e are the equilibrium concentration (mg/l) of the metal ion on adsorbent and in the solution, respectively. The free energy change (ΔG) was calculated from the relation:

$$\Delta G = -RT \ln K_e \qquad (5)$$

where, T is temperature in Kelvin (273 K) and R is gas constant (8.314×10−3 kJ/mol K). Enthalpy change (ΔH) was calculated from the following equation

$$\Delta G = \Delta H - T\Delta S \qquad (6)$$

$$\log K_e = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \qquad (7)$$

ΔH and ΔS were obtained from the slopes and intercepts of Vant Hoff plots of log K_e versus $1/T$ (Fig. 3.57). Positive values of ΔH thermodynamically substantiate the assumption that the adsorption of metal ions on the CKD is endothermic. The negative values of ΔG indicate feasibility and spontaneous nature of adsorption of metal ions on the adsorbent. ΔS is estimated to be very small in the experimental Conditions. Therefore, the entropy change occurring from adsorption is though to be negligible.

Explanation of the effect of temperature on percent removal

The effect of temperature on sorption data was linked to the thermodynamics of the sorption process. The experiment was conducted at temperatures from 30 to 60 ^{o}C by using a mechanical shaker with hot bath. Inside temperature of all bottles fluctuated between 30 and 60 ^{o}C throughout the batch period for individual metal ion solution experiments without showing any significant variation. This may be attributed to the stability of CKD at these temperatures since this material has been burnet under high temperature.

The effect of temperature on trend heavy metal ions Zn(II), Al(III), Co(II) and Cd(II) on CKD are indicated in tables 3.22 (3.23 and 3.24), (3.25 and 3.26), (3.27 and 3.28), (3.29 and 3.30) and figures (3.58), (3.59), (3.60), (3.61) respectively .

Table 3.22 Equilibrium constants and thermodynamic parameters for the adsorption of heavy metal ions on CKD.

Metal	Temperature (^{o}C)	Equilibrium Constant K_e(mg/L)	ΔG (KJ/mol)	ΔS (KJ/mol K)	ΔH (KJ/mol)
Zn(II)	30	118.3992	-12.02654	0.15491	10562.3
	40	193.7231	-13.70474	0.15491	10910.9
	60	415.4562	-16.6927	0.15491	11608.1
Al(III)	30	383.6598	-14.98828	0.286218	21359.5
	40	3288.484	-21.07375	0.286218	22064.4
	60	5954.936	-24.06427	0.286218	23474.2
Co(II)	30	253.8421	-13.94776	0.297014	23006.32
	40	748.0083	-17.22038	0.297014	23765.61
	60	3914.444	-22.90273	0.297014	25284.18
Cd(II)	30	547.5831	-15.88449	0.21967	15327.1
	40	1137.176	-18.31045	0.21967	15832.9
	60	3394.772	-22.50839	0.21967	16844.6

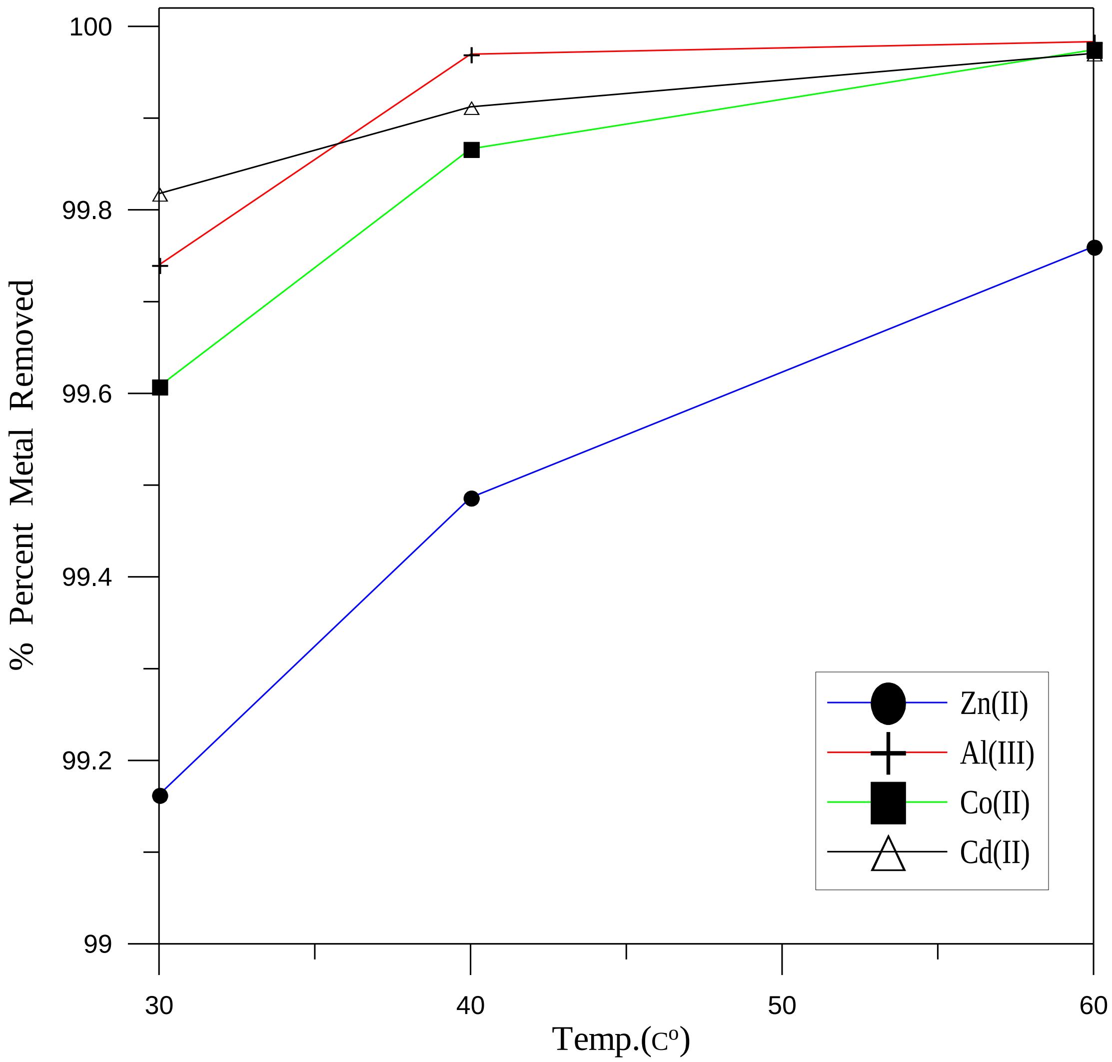

Figure 3.56 Plot of Percent Metal removed vs. Temperature show the effect of temperature variation on percent heavy metal ion removed from solution by using CKD.

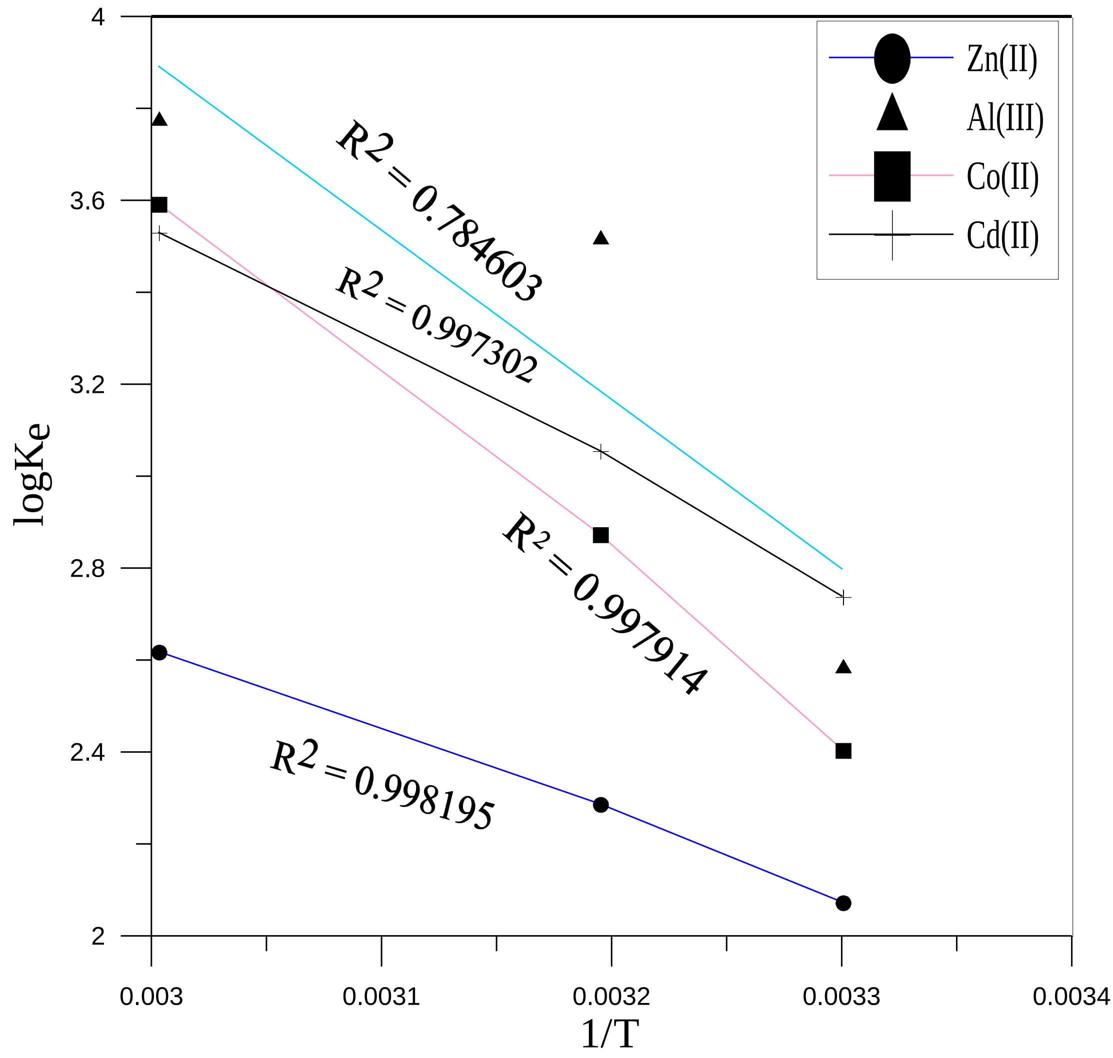

Figure 3.57 Plot of $\log K_e$ vs. $1/T$ for heavy metal ions by using CKD.

Table 3.23 Effect of different temp - values on **Zn** metal ion removal within initial concentration **484.88 mg/L** by using CKD, at pH (8-10.17), 40 min., 130 rpm and 10 g CKD / L.				
Temperature (**^{o}C**)	Residual conc. **C (mg / L)**	Adsorbent amount **q (mg / g)**	% Percent Removal	Distribution coefficient
30	4.0610	48.0819	99.16247	11839.92
40	2.4901	48.23899	99.48645	19372.31
60	1.1643	48.37157	99.75988	41545.62

Table 4.24 Equilibrium constants and thermodynamic parameters for the adsorption of **Zn** metal ion on CKD within initial concentration **484.88 mg/L** by using CKD, at pH (8-10.17), 40 min., 130 rpm and 10 g CKD / L.					
Temperature (**^{o}C**)	Residual conc. **C** (mg/L)	Equilibrium Constant K_e(mg/L)	ΔG (KJ/mol)	ΔS (KJ/mol K)	ΔH (KJ/mol)
30	4.0610	118.3992	-12.02654	0.15491	10562.3
40	2.4901	193.7231	-13.70474	0.15491	10910.9
60	1.1643	415.4562	-16.6927	0.15491	11608.1

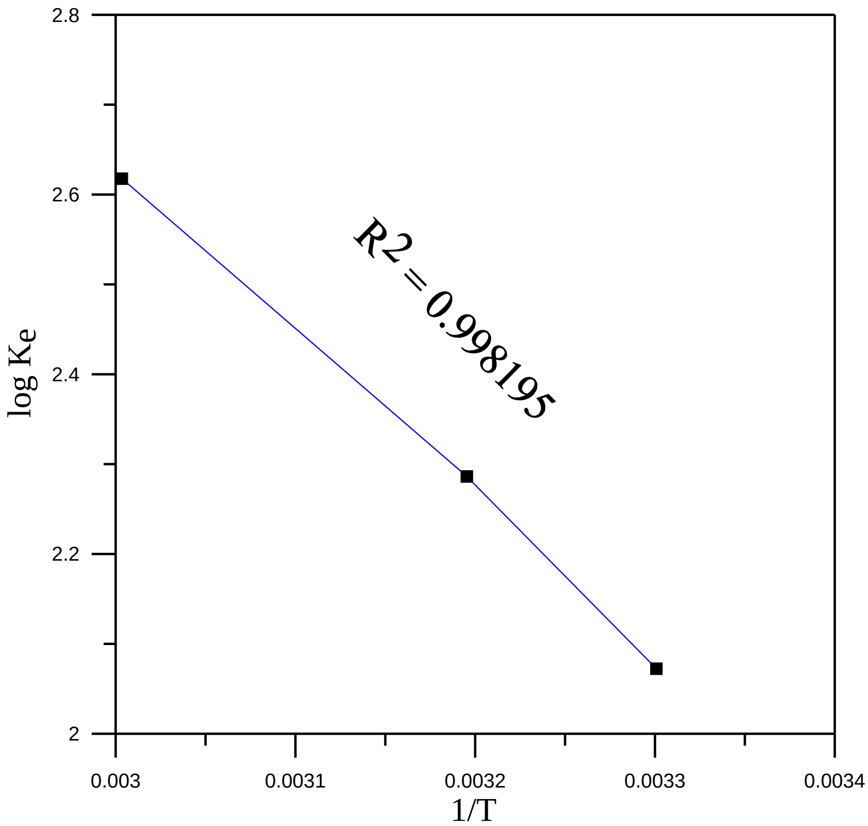

Figure 3.58 Plot of $\log K_e$ vs. 1/T for **Zn** metal ion on CKD within initial concentration **484.88 mg/L** by using CKD, at pH (8-10.17), 40 min., 130 rpm and 10 g CKD / L.

Table 3.25 Effect of different temp - values on **Al** metal ions removal within initial concentration **390.09 mg/L** by using CKD, at pH (5.89-8.57), 5 min., 130 rpm and 10 g CKD / L.				
Temperature C°	Residual conc. **C (mg / L)**	Adsorbent amount **q (mg / g)**	% Percent Removal **$(C_o$-$C)/C_o$*100**	Distribution coefficient **$(C_o$-$C)/ C$* v/m**
30	1.014117	38.90759	99.99638	2762577
40	0.118587	38.99714	99.99524	2100546
60	0.065496	39.00245	99.98321	595457.3

Table 3.26 Equilibrium constants and thermodynamic parameters for the adsorption of **Al** metal ion on CKD within initial concentration **390.09 mg/L** by using CKD, at pH (5.89-8.57), 5 min., 130 rpm and 10 g CKD / L.					
Temperature (**°C**)	Residual conc. **C** (mg/L)	Equilibrium Constant K_e(mg/L)	Δ*G* (KJ/mol)	Δ*S* (KJ/mol K)	Δ*H* (KJ/mol)
30	1.014117	383.6598	-14.98828	0.286218	21359.5
40	0.118587	3288.484	-21.07375	0.286218	22064.4
60	0.065496	5954.936	-24.06427	0.286218	23474.2

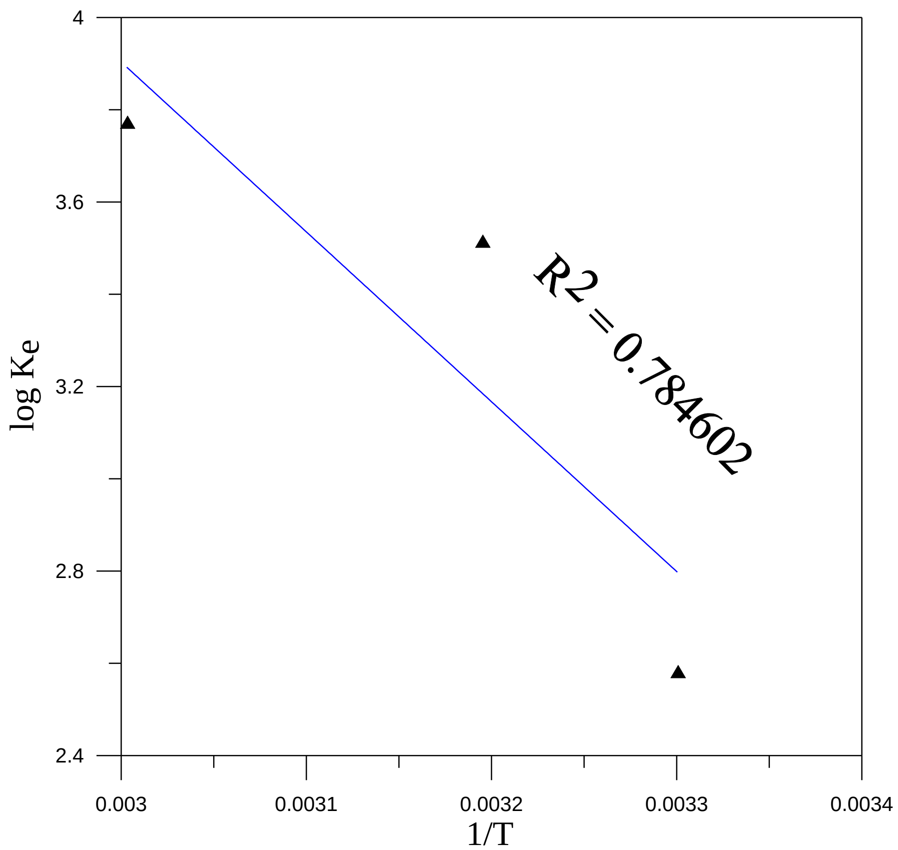

Figure 3.59 Plot of $\log K_e$ vs. 1/T for **Al** metal ion on CKD within initial concentration **390.09 mg/L** by using CKD, at pH (5.89-8.57), 5 min., 130 rpm and 10 g CKD / L.

Table 3.27 Effect of different temp - values on **Co** metal removal within initial concentration **165.22 mg/L** by using CKD, at pH (8-10.94), 4 hour, 130 rpm and 10 g CKD / L.

Temperature $^{\circ}C$	Residual conc. **C (mg / L)**	Adsorbent amount **q (mg / g)**	% Percent Removal **$(C_o$-$C)/C_o$*100**	Distribution coefficient **$(C_o$-$C)/$ C* v/m**
30	0.648323	16.45717	99.97075	341828.8
40	0.220585	16.49994	99.98754	802328.4
60	0.042197	16.51778	99.97446	391416.6

Table 3.28 Equilibrium constants and thermodynamic parameters for the adsorption of **Co** metal ion on CKD within initial concentration **165.22 mg/L** by using CKD, at pH (8-10.94), 4 hour, 130 rpm and 10 g CKD / L.

Temperature (^{o}**C**)	Residual conc. **C** (mg/L)	Equilibrium Constant K_e(mg/L)	ΔG (KJ/mol)	ΔS (KJ/mol K)	ΔH (KJ/mol)
30	0.648323	253.8421	-13.94776	0.297014	23006.32
40	0.220585	748.0083	-17.22038	0.297014	23765.61
60	0.042197	3914.444	-22.90273	0.297014	25284.18

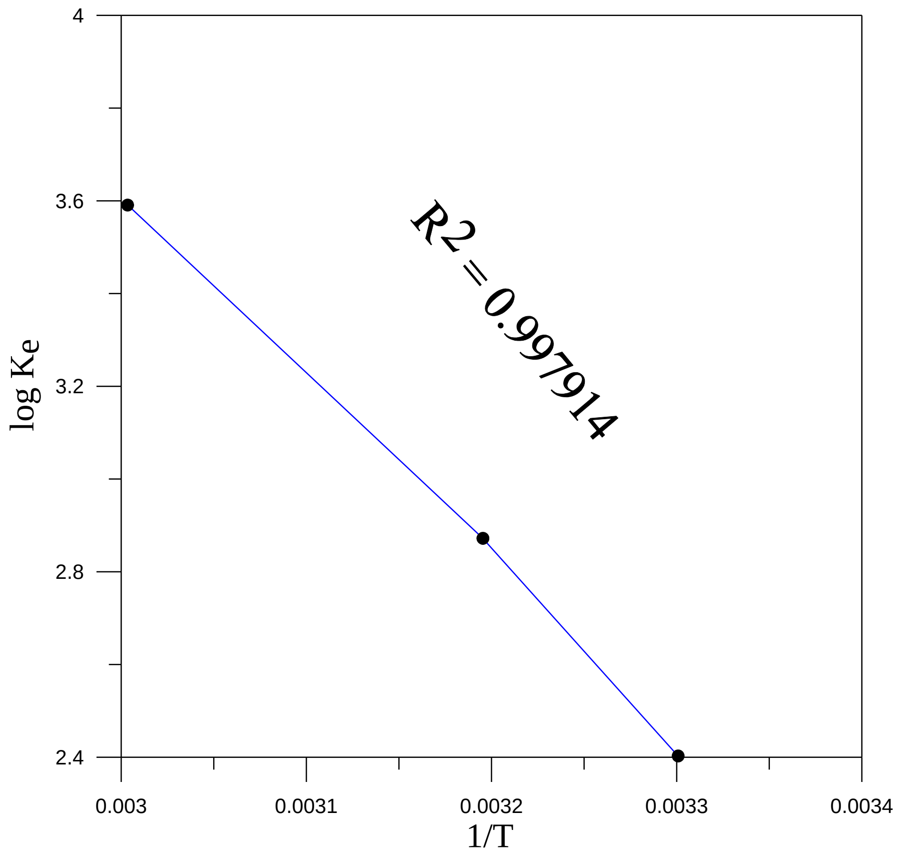

Figure 3.60 Plot of $\log K_e$ vs. 1/T for **Co** metal ion on CKD within initial concentration **165.22 mg/L** by using CKD, at pH (8-10.94), 4 hour, 130 rpm and 10 g CKD / L.

Table 3.29 Effect of different temp - values on **Cd** metal ions removal within initial concentration **393.57 mg/L** by using CKD, at pH (6.17-12.19), 1hour, 130 rpm and 10 g CKD / L.

Temperature $^{\circ}C$	Residual conc. **C (mg / L)**	Adsorbent amount **q (mg / g)**	% Percent Removal **$(C_o-C)/C_o*100$**	Distribution coefficient **$(C_o-C)/ C* v/m$**
30	0.71743	39.28526	99.81771	54758.31
40	0.34579	39.32242	99.91214	113717.6
60	0.11590	39.34541	99.97055	339477.2

Table 3.30 Equilibrium constants and thermodynamic parameters for the adsorption of **Cd** metal ion on CKD within initial concentration **393.57 mg/L** by using CKD, at pH (6.17-12.19), 1hour, 130 rpm and 10 g CKD / L.

Temperature (**^{o}C**)	Residual conc. **C** (mg/L)	Equilibrium Constant K_e(mg/L)	ΔG (KJ/mol)	ΔS (KJ/mol K)	ΔH (KJ/mol)
30	0.71743	547.5831	-15.88449	0.21967	15327.1
40	0.34579	1137.176	-18.31045	0.21967	15832.9
60	0.11590	3394.772	-22.50839	0.21967	16844.6

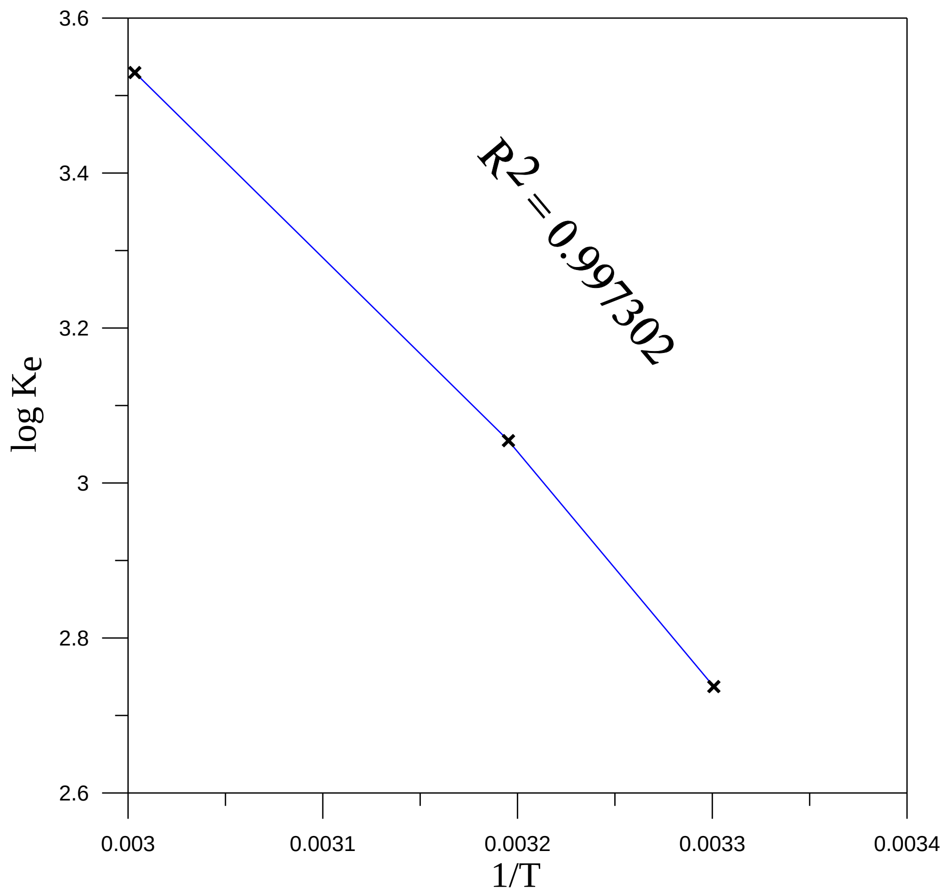

Figure 3.61 Plot of $\log K_e$ vs. 1/T for **Cd** metal ion on CKD within initial concentration **393.57 mg/L** by using CKD, at pH (6.17-12.19), 1hour, 130 rpm and 10 g CKD / L.

3.8 Adsorption isotherms

The adsorption studies were conducted at fixed initial concentration of heavy metal ions by varying adsorbent dosage. The equilibrium data obtained were analyzed in the light of Langmuir and Freundlich isotherms.

The Freundlich equation is given by [51].

$$q_e = K_f C_e^{\frac{1}{n}} \qquad (1)$$

Taking the logarithmic form of the equation

$$Log(q_e) = Log(K_f) + \tfrac{1}{n} Log(C_e) \qquad (2)$$

Langmuir equation is given by [52].

$$q_e = \frac{abC_e}{(1 + bC_e)} \qquad (3)$$

The linearized expression of this equation is

$$\frac{1}{q_e} = \frac{1}{a} + \frac{1}{abC_e} \qquad (4)$$

This equation is called the **"Double-Reciprocal Langmuir Equation"** and more suitable for situations in which the distribution of equilibrium concentrations tend to be skewed towards the lower end of the range of the equilibrium concentrations.

where q_e is the amount of heavy metal ions adsorbed per unit mass of adsorbent in mg/g, C_e the equilibrium concentration of heavy metal ions in mg/l, K_f and n are Freundlich constants, '***a***' is a Langmuir constant which is a measure of adsorption capacity expressed in mg/g, '***b***' is also Langmuir constant which is a measure of energy of adsorption expressed in l/mg. The parameters '***a***' and '***b***' have been calculated from the slope and the intercept of the plots.

Fig. (3.67) gives the Freundlich adsorption isotherm i.e. the plot of **log** q_e versus **log*Ce***. The values of K_f and **1/*n*** obtained from intercept and slope of the plot are given in table 3. The Langmuir adsorption isotherm plot for $1/q_e$ versus **1/*C*e** is shown in fig. 3.62) and the plots show two distinct regions, one for low 1/*C*e values up to about 25 l/mg and another for higher 1/*C*e values. The essential characteristics of Langmuir isotherm can be described by a separation factor or equilibrium constant R_L, which is defined as,

$$R_L = \frac{1}{1 + bc_i} \qquad (5)$$

where C_i is the initial concentration of heavy metal ions (mg/l) and b is Langmuir constant which indicates the nature of adsorption. The separation factor $\boldsymbol{R_L}$ indicates the isotherm shape and whether the adsorption is favourable or not, as per the criteria given below.

$\boldsymbol{R_L}$ values	Adsorption
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

The values of Langmuir constants **‘*a*’**, **‘*b*’** and $\boldsymbol{R_L}$ are presented in table (3.31.) Since $\boldsymbol{R_L}$ values lie between 0 and 1 for all four adsorbants studied, it is seen that the adsorption of heavy metal ions is favourable [53].

Adsorption capacity as indicated by value of **‘*a*’** is seen to be maximum for CKD, i.e. Zn(II) (233.18 mg/g), Cd(II) (92.35 mg/g), Al(III) (62.64 mg/g), and Co(II) (58.77 mg/g) with much lower capacities. The energies of adsorption, as indicated by **‘*b*’** are seen to be highest for Al(III) (5.26 L/mg), Co(II) (4.12L/mg), Cd(II) (1.12 L/mg), and Zn(II) (0.013 L/mg) in that order.

A comparison of the Freundlich adsorption isotherms for the metal ions presented in table (3.36.) show that ***n*** in that order Cd(II) > Co(II) > Al(II) > Zn(II). The values of **n** lie between 1 and 10 indicating favourable adsorption [54]. $\boldsymbol{K_f}$ seen to be Zn (II) > Cd(II) > Al(II) >Co (II) .This gives a similar inference as that obtained from Langmuir isotherms.

When the coefficient of determination (r^2) is used as a criterion for this study, Zinc, Aluminum, Cobalt and cadmium ions sorptions fit the Langmuir plot. Zinc, Aluminum, Cobalt and cadmium ions sorption isotherms also agreed with the Freundlich model. However, the general trend observed in sorption profiles in figs. (3.68) and (3.71) revealed that the sorption data were better interpreted with the Langmuir equation. On the other hand, For Zinc and cadmium ions sorption equilibrium in Freundlich model, correlation coefficients were lowest ($r2 < 0.90$).

The adsorption isotherm studies clearly indicated that the adsorptive behavior of heavy metal ions on CKD satisfies not only the Langmuir assumptions but also the Freundlich assumptions, i.e. multilayer formation on the surface of the adsorbent with an exponential distribution of site energy.

On the basis of regression analysis of the experimental data on the adsorptive behaviour of metal ions on CKD, it may be inferred that the adsorption behaviour of metal ions on CKD is in good agreement with Langmuir model. These can be attributed to three main causes (i) the formation of monolayer coverage on the surface of CKD with minimal interaction among molecules of substrate (ii) immobile and localized adsorption and (iii) all sites having equal adsorption energies. The shapes of isotherms suggest that there are high-energy adsorption sites to favour strong adsorption at low equilibrium concentrations for the CKD.

The Freundlich adsorption isotherm presented for heavy metal ions Zn(II), Al(III), Co(II) andCd (II) on CKD in tables(3.37), (3.38), (3.39), (3.40) and figures (3.68) ,(3.69), (3.70)and (3.71) respectively .

The Langmiur adsorption isotherm presented for heavy metal ions Zn(II), Al(III), Co (II) and Cd(II) on CKD in tables(3.32), (3.33), (3.34), (3.35) and figures (3.63) ,(3.64), (3.65)and (3.66) respectively .

3.8.1 Langmuir adsorption isotherms

Table 3.31 values of langmuir isotherm constants for adsorption of heavy metal ions by using CKD

Metal ions	**slop**	a(mg/g)	**intercept**	b(L/mg)	R^2	R_L
Zn(II)	0.328784528	233.1785	0.004288560825	0.013044	0.992037	0.0950
Al(III)	0.003033405	62.63779	0.01596480332	5.262996	0.982052	0.0015
Co(II)	0.004133276	58.77456	0.01701416256	4.116386	0.997344	0.0016
Cd(II)	0.009701566	92.35398	0.01082790419	1.116098	0.986492	0.0034

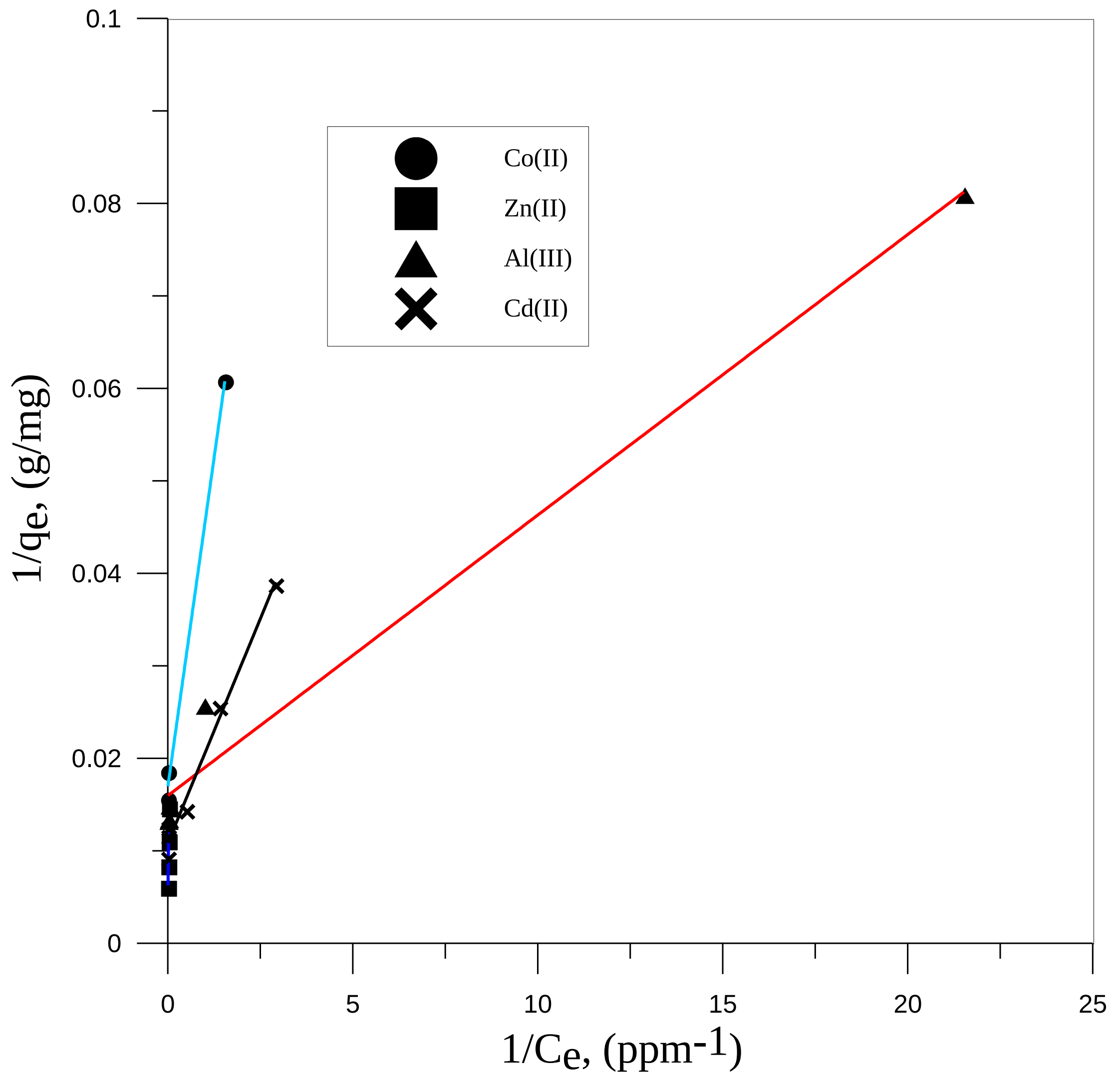

Figure 3.62 **Langmuir adsorption isotherm of heavy metal ions by using CKD at 30 °C.**

Table 3.32 Langmuir Adsorption isotherms of Zn(II) by using CKD at 30 ºC			
Equilibrium conc. C_e (mg / L)	$1/C_e$	Amount heavy metal adsorbed q_e (mg / g)	$1/ q_e$
0.29002	3.448038	38.426	0.026024
4.0610	0.246245	48.0819	0.020798
32.112	0.031141	68.4838	0.014602
46.912	0.021317	90.6328	0.011034
91.227	0.010962	120.0773	0.008328
165.86	0.006029	165.994	0.006024

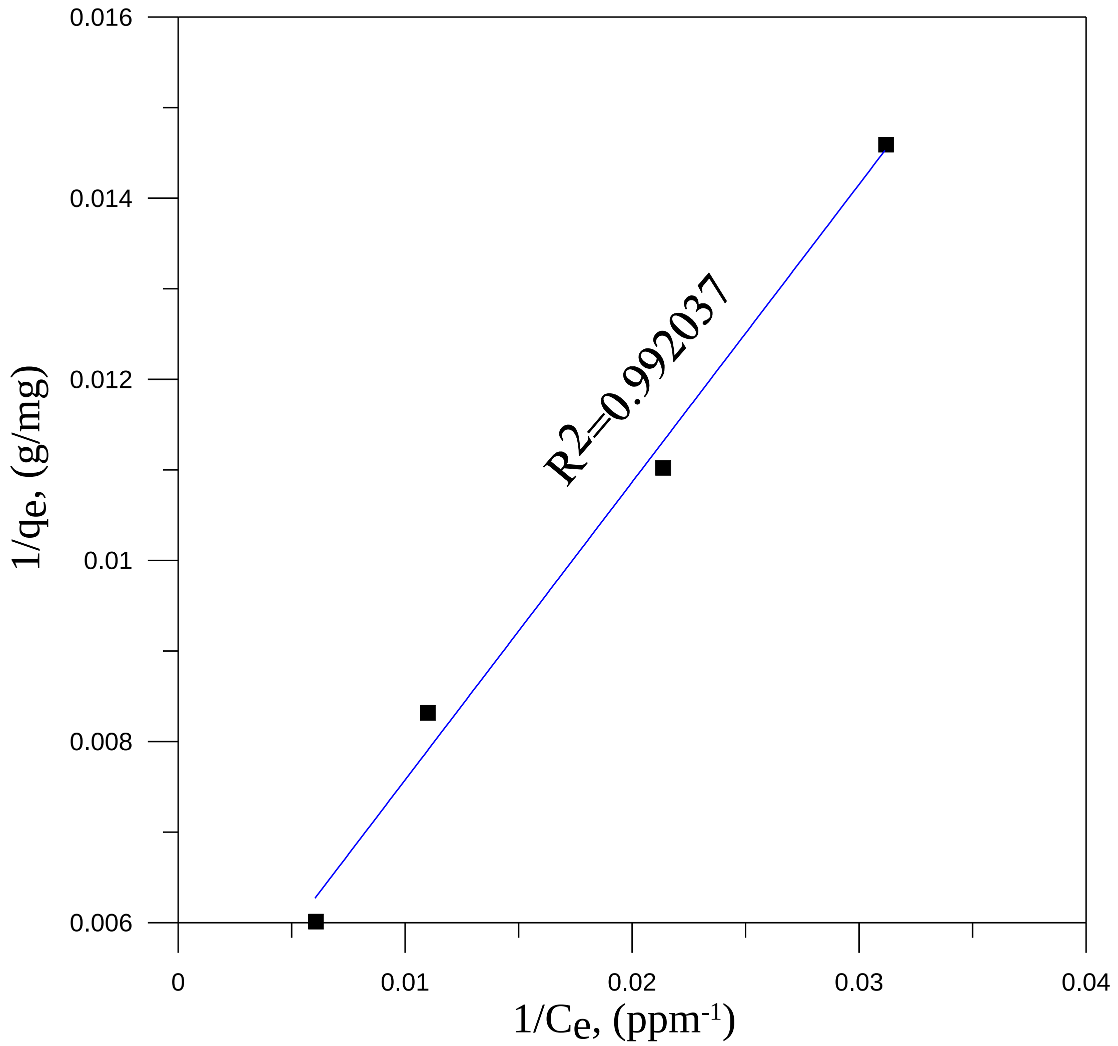

Figure 3.63 Langmuir Adsorption isotherms of Zn(II) by using CKD at 30 ºC

Table 3.33 **Langmuir Adsorption isotherms of Al(III) by using CKD at 30 °C**			
Equilibrium conc. C_e (mg / L)	$1/C_e$	Amount heavy metal adsorbed q_e (mg / g)	$1/ q_e$
0.04647	21.51926	12.35535	0.080937
1.014117	0.98608	38.90759	0.025702
26.316	0.038	67.0114	0.014923
59.377	0.016842	74.3723	0.013446
205.06	0.004877	75.389	0.013265

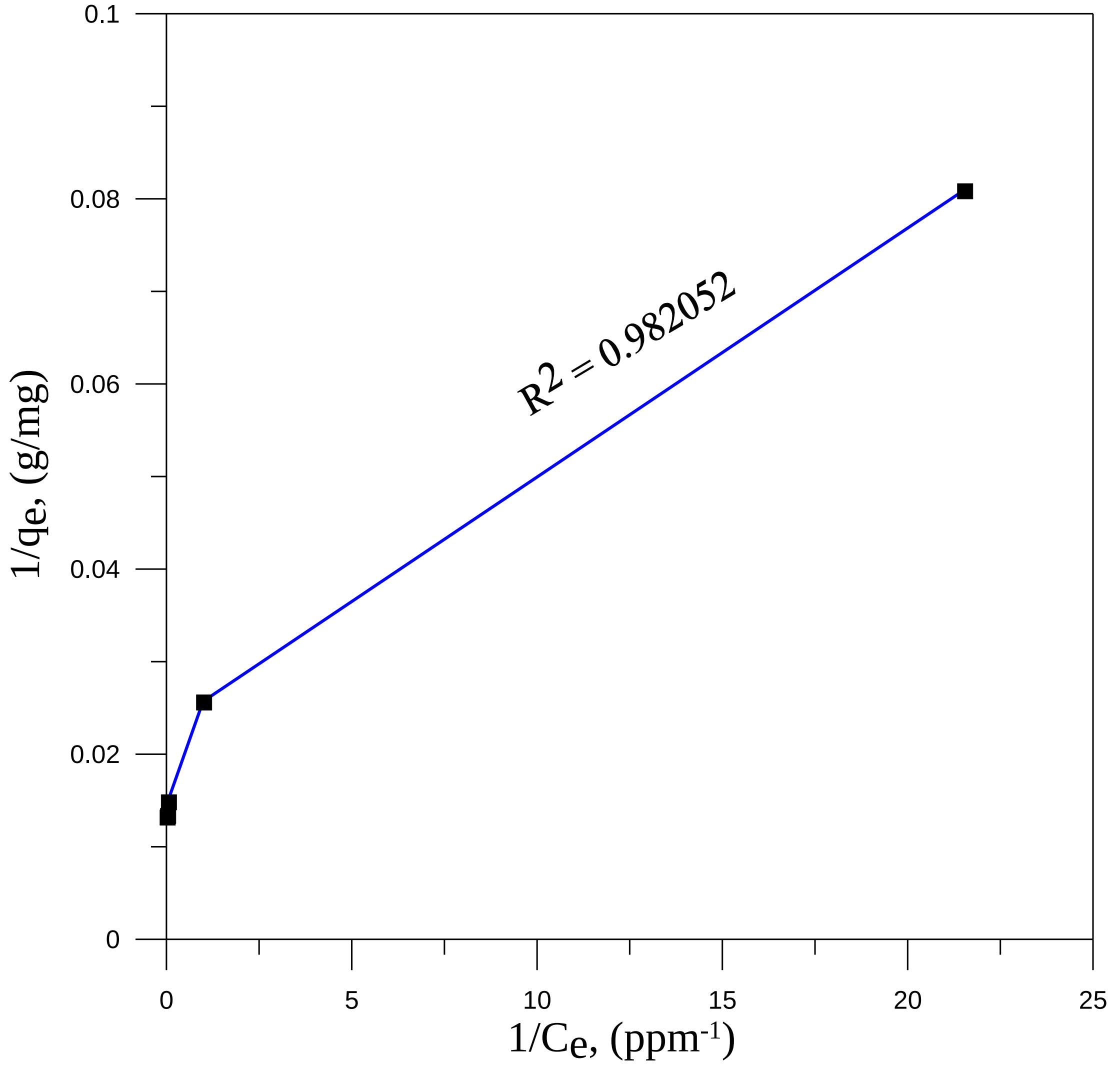

Figure 3.64 **Langmuir Adsorption isotherms of Al(III) by using CKD at 30 °C**

Table 3.34 **Langmuir Adsorption isotherms of Co(II) metal by using CKD at 30 ^oC.**			
Equilibrium conc. C_e (mg / L)	$1/C_e$	Amount heavy metal adsorbed q_e (mg / g)	$1/ q_e$
0.08348	11.97892	15.03165	0.066526
0.648323	1.542441	16.45717	0.060764
164.53	0.006078	54.012	0.018514
313.21	0.003193	64.296	0.015553

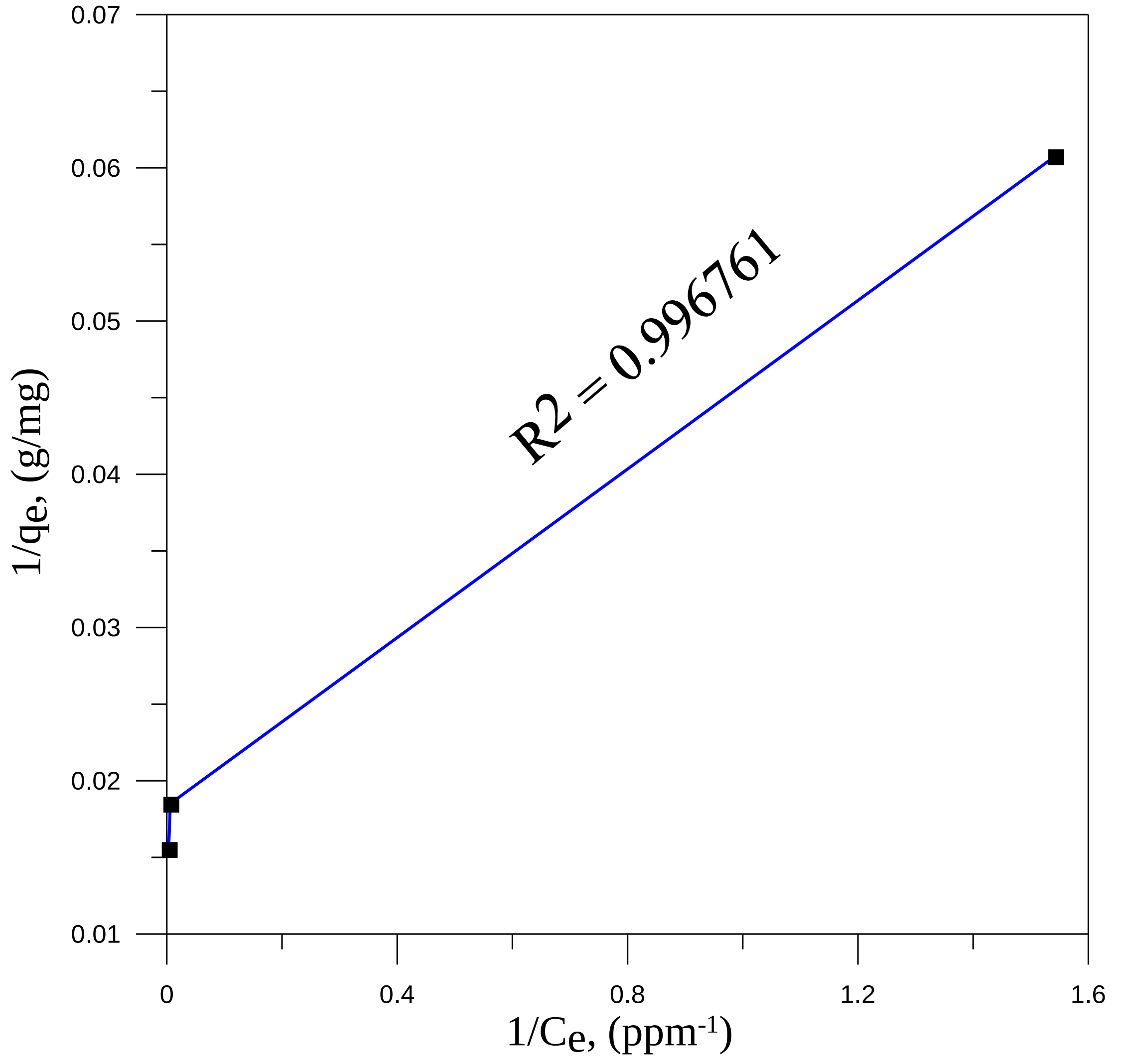

Figure 3.65 Langmuir Adsorption isotherms of Co(II) by using CKD at 30 ^oC

Table 3.35 Langmuir Adsorption isotherms of Cd(II) by using CKD at 30 °C.			
Equilibrium conc. C_e (mg / L)	$1/C_e$	Amount heavy metal adsorbed q_e (mg / g)	$1/ q_e$
0.34365	2.909937	25.81664	0.038735
0.71743	1.393864	39.22826	0.025492
2.0080	0.498008	69.7992	0.014327
108.71	0.009199	80.27	0.012458
133.52	0.00749	86.648	0.011541
411.25	0.002432	108.875	0.009185

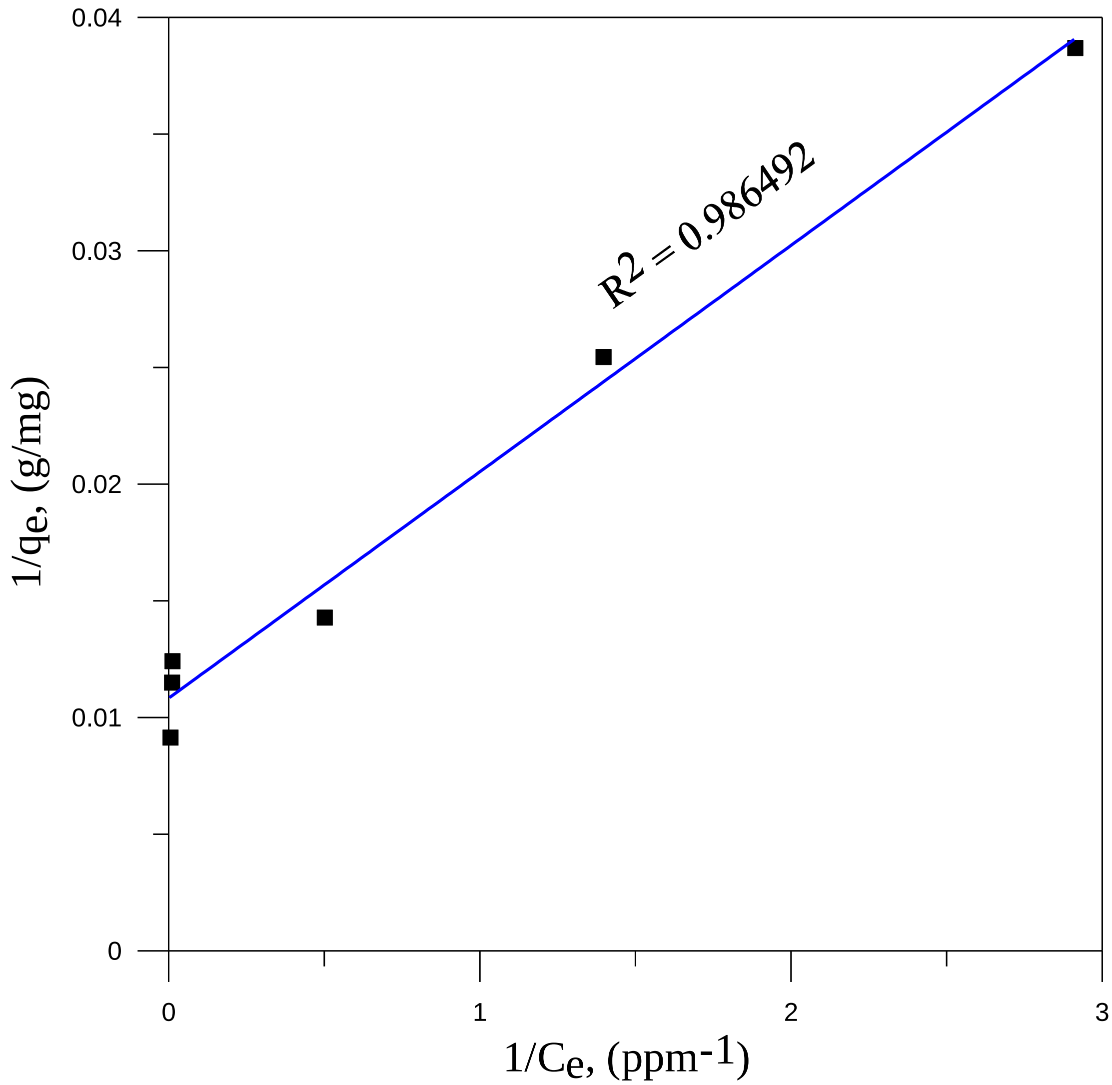

Figure 3.66 Langmuir Adsorption isotherms of Cd(II) by using CKD at 30 °C.

3.8.2 Frendlich adsorption isotherms

Table 3.36 values of freundlich isotherm constants for the adsorption of heavy metal ions by using CKD

Metal ions	**slop**	K_f	**intercept**	n	R^2
Zn (II)	0.2169544939	42.1260480	1.624550719	4.609262	0.862792
Al (III)	0.2168382642	29.5201782	1.470118976	4.611732	0.925075
Co (II)	0.1859835242	21.0527929	1.32330972	5.37682	0.974276
Cd (II)	0.1610804879	41.1513419	1.614384002	6.208077	0.818879

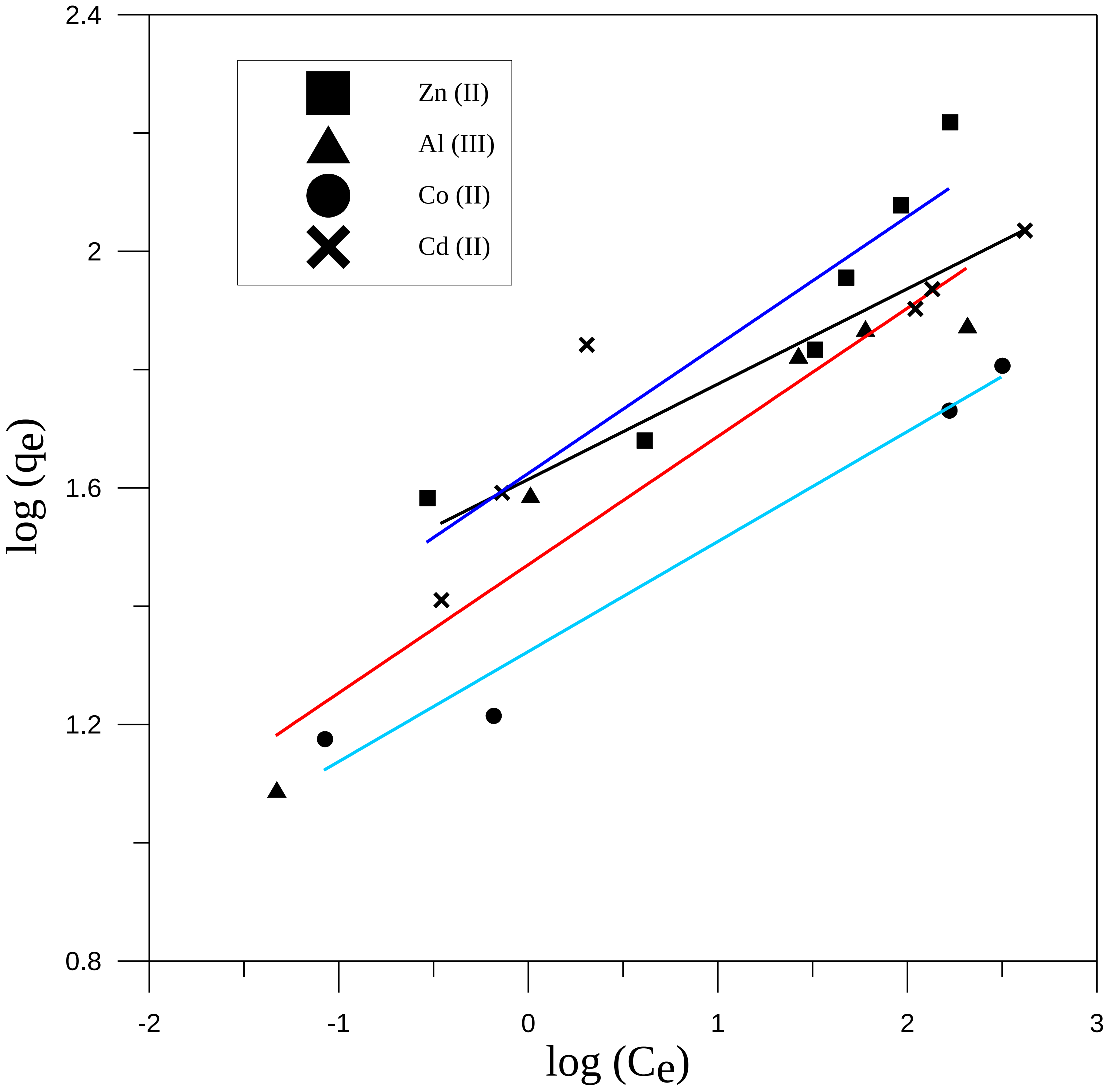

Figure 3.67 Frendlich adsorption isotherm of heavy metal ions by using CKD at 30 °C.

Table 3.37 Frendlich adsorption isotherm of Zn(II) by using CKD at 30 ^{o}C

Equilibrium conc. C_e (mg / L)	$Log(C_e)$	Amount heavy metal adsorbed q_e (mg / g)	$Log(q_e)$
0.29002	-0.53757	38.426	1.584625
4.0610	0.608633	48.0819	1.681982
32.112	1.506667	68.4838	1.835588
46.912	1.671284	90.6328	1.957285
91.227	1.960123	120.0773	2.079461
165.86	2.219742	165.994	2.220092

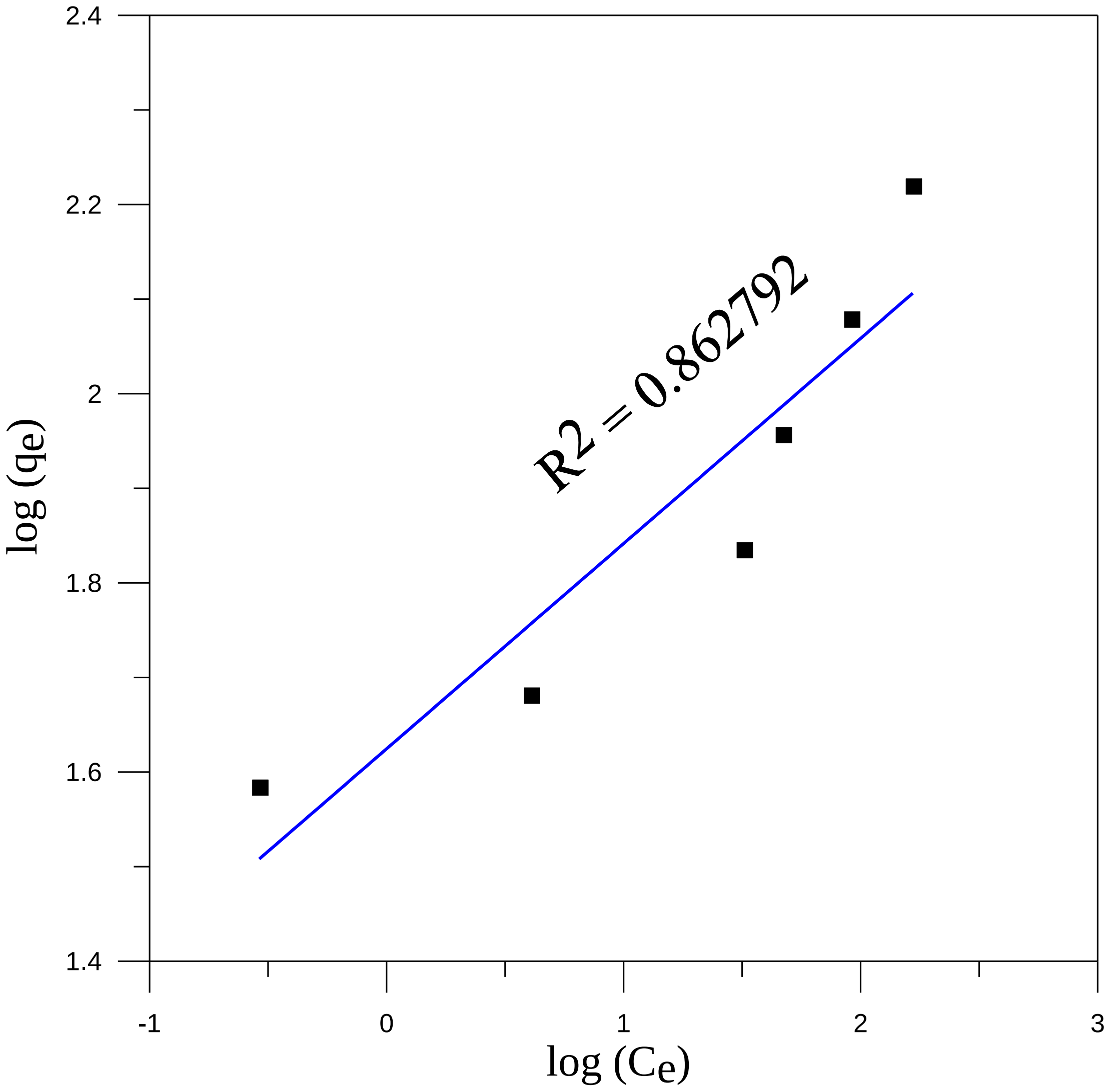

Figure 3.68 Frendlich adsorption isotherm of Zn(II) by using CKD at 30 ^{o}C

Table 3.38 Frendlich adsorption isotherm of Al(III) by using CKD at 30 °C			
Equilibrium conc. C_e (mg / L)	Log(C_e)	Amount heavy metal adsorbed q_e (mg / g)	Log(q_e)
0.04647	-1.33283	12.35535	1.091855
1.014117	0.006088	38.90759	1.590034
26.316	1.42022	67.0114	1.826149
59.377	1.773618	74.3723	1.871411
205.06	2.311881	75.389	1.877308

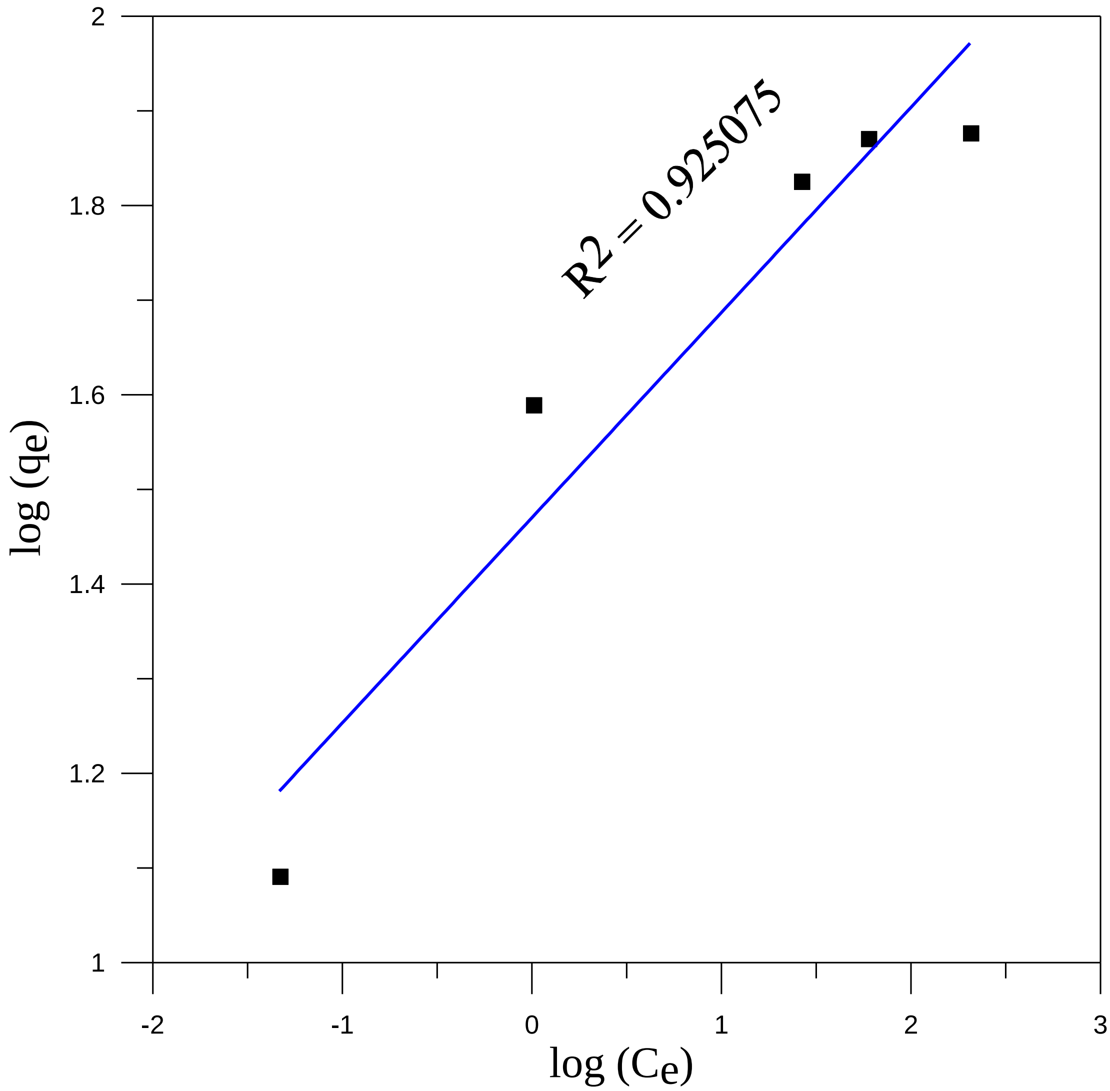

Figure 3.69 Frendlich adsorption isotherm of Al(III) by using CKD at 30 °C

Table 3.39 Frendlich adsorption isotherm of Co(II) by using CKD at 30 ^oC.			
Equilibrium conc. C_e (mg / L)	$Log(C_e)$	Amount heavy metal adsorbed q_e (mg / g)	$Log(q_e)$
0.08348	-1.07842	15.03165	1.177007
0.648323	-0.18821	16.45717	1.216355
164.53	2.216245	54.012	1.73249
313.21	2.495836	64.296	1.808184

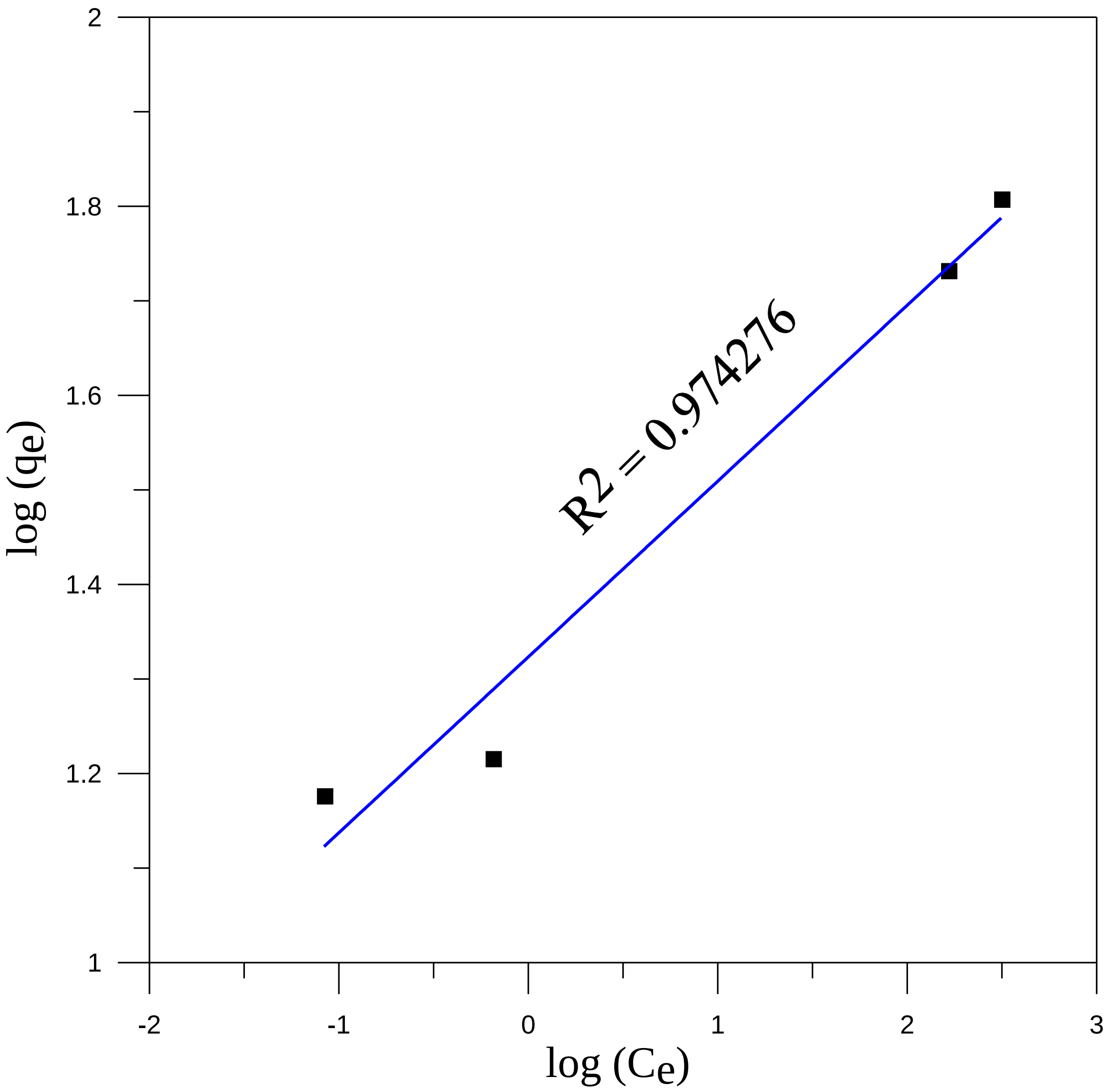

Figure 3.70 Frendlich adsorption isotherm of Co(II) by using CKD at 30 ^oC

Table 3.40. Frendlich adsorption isotherm of Cd(II) by using CKD at 30 °C.

Equilibrium conc. C_e (mg / L)	$Log(C_e)$	Amount heavy metal adsorbed q_e (mg / g)	$Log(q_e)$
0.34365	-0.46388	25.81664	1.4119
0.71743	-0.14422	39.22826	1.593599
2.0080	0.302764	69.7992	1.84385
108.71	2.036269	80.27	1.904553
133.52	2.125546	86.648	1.937759
411.25	2.614106	108.875	2.036928

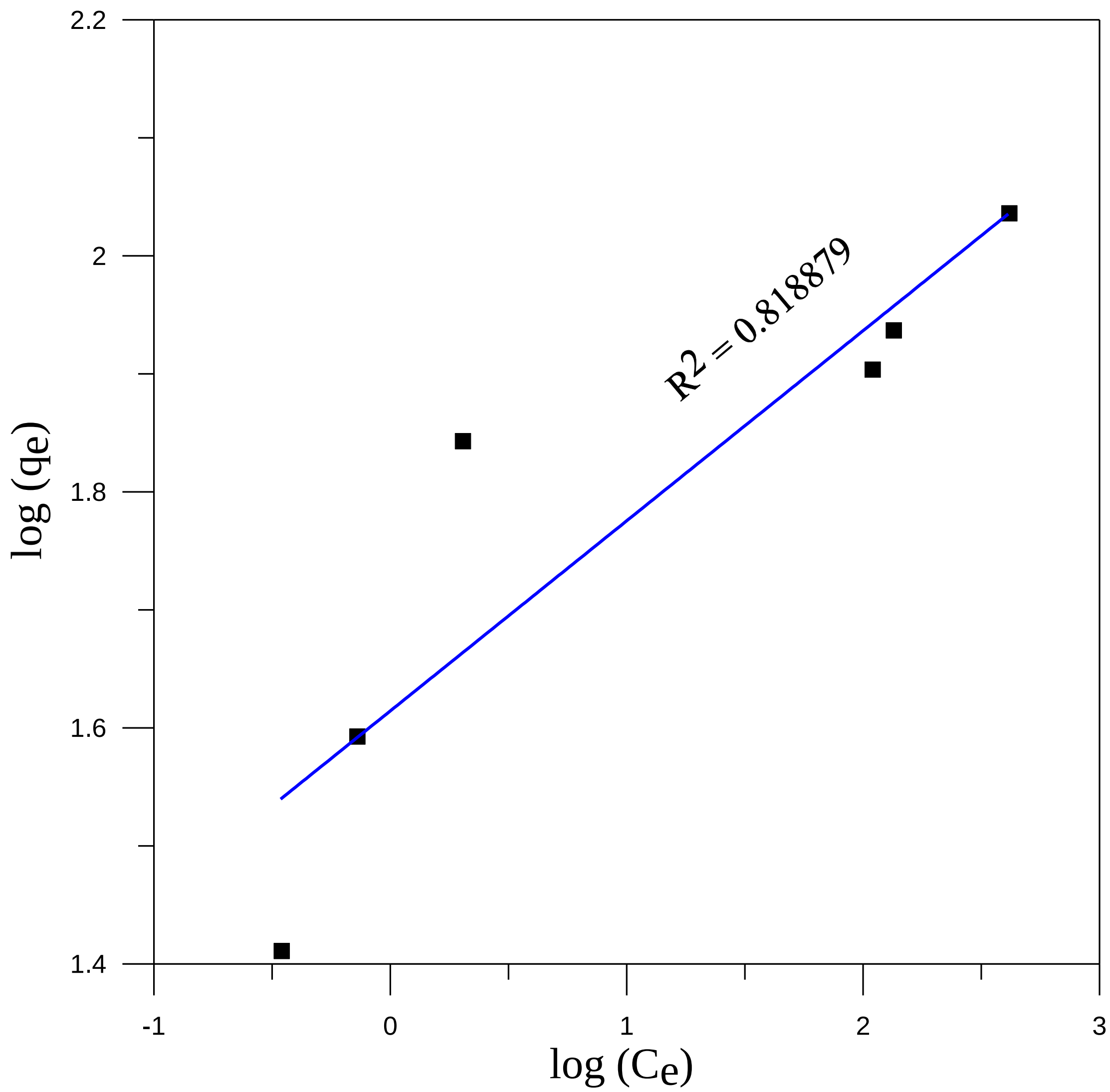

Figure 3.71 Frendlich adsorption isotherm of Cd(II) by using CKD at 30 °C.