Adsorption Batch Studies on Calcined Brick Powder in Removing Chromium and Nickel Ions

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Abstract: *The adsorption studies on the removal of Cr (VI) and Ni (II) ions from aqueous solution using calcined brick powder (CBP) were carried out under various experimental conditions. The uptake of chromium and nickel ions on CBP was studied at different pH values, adsorbent dosages, contact time and initial metal ion concentration. The maximum efficiency of 81.00% was achieved at pH 2.0 for Cr (VI) and at pH 4.0 the removal efficiency was 75.40% for Ni (II) at equilibrium conditions. Adsorption capacity of CBP exhibits good adsorption characteristics. The isotherms were in conformity with both Langmuir and freundlich isotherms and the constants are also evaluated.*

Keyword: *Calcined Brick Powder (CBP), adsorption isotherms*

1. INTRODUCTION

Water, the most vital resource for all kinds of life on this planet is adversely affected by various human activities. Water pollution by heavy metals is now a unique challenge to the environmentalists in recent years. The incredible use of heavy metals over past few decades has inevitably resulted in an increased influx of metallic substances in aquatic environment.

Adsorption is a unique process for the removal of both organics and inorganics from water and wastewater; also it is competitive and effective process for the removal of trace quantities of heavy metals. It is considered to be reliable process that can be used to remediate a mixture of contaminants with low concentration (Chermisinoff, 1978). The cost effective removal of toxic heavy metals from waste waters can be done with low cost adsorbents. Various industrial solid wastes, agricultural wastes and miscellaneous products have been found to have adsorption affinity for heavy metals. In the present investigation powdered calcined brick powder (CBP) was used as an adsorbent.

Chromium in particular has received a great deal of attention due to its perilous nature. The most predominant forms of chromium are Cr (VI) and Cr (III). But Cr (VI) is most hazardous. The anthropogenic sources include, burning of oil and coal, production of ferrochromium, chromate, chromium steels, fungicides, cement, pigments, catalysts, and oxidants. It is also used in metal plating, tanneries, and oil well drilling (Abbasi, 1985 and 1998). These sources annually release around106 tones of chromium in the form of fly ash, industrial effluents, particulates, dust and fumes into air, soil and water. It can generate serious disorders and diseases when accumulated at high levels and it can be ultimately lethal (Kaufman et al., 1976).

Nickel Salts are acutely and chronically toxic to man. It is Present in the effluents of silver refineries, zinc based Castings, storage battery industries, desalinate plants, gas turbines, coinage and costume jewelry. Acute poisoning of Ni (II) causes headache, nausea, dizziness, chest pain, dry cough, shortness of breath etc. At higher concentration it is a carcinogen, causes cancer of lungs, Nose and bone. Skin contact with nickel causes a painful disease called 'NICKEL ITCH', which leads to death (Abbasi S.A. and R. Soni, 1990).

2. MATERIAL AND METHOD

Calcined Brick Powder (CBP): CBP a common building material made of clay is abundant in availability. Waste pieces of bricks, which are left unused after construction of a building can be used as adsorbents and waste management, may be another achievement in the process. Kiln burnt new calcined brick waste pieces were collected and ground to fine powder, and washed with distilled water for 4 to 5 times after soaking it in distilled water for 24 hours. It is dried under sunlight and the powder is sieved into different particle sizes such as 0.6mm, 0.8mm, and 1.7mm. Particle of 0.6 mm was used for characterization as it is more effective in metal adsorption.

Standard stock solutions of Cr (VI) and Ni (II) ions were prepared and used.

3. BATCH MODE STUDIES

Entire experiments were carried out in batch mode studies by taking 50 ml of respective metal ion solution (simulated sample) and known amount of the adsorbent in conical flasks of 100 ml capacity. The flasks were agitated at 160 rpm for predetermined time intervals using a mechanical shaker at room temperature (27ºc). Effects of pH, agitation time, initial metal ion concentration, adsorbent amount and particle size were studied on the removal of metal ions. After required contact time, the contents of the flask were filtered by using whatman filter paper. The filtrate was used for Chromium and nickel ions estimation respectively using spectrophotometer by following standard methods. (APHA, 1992; and Stewart E., 1974). Control experiments were carried out without absorbent to give correction for metal ion adsorption on the walls of the container and were found negligible.

4. RESULT AND DISCUSSION

Optimum pH:

The pH of aqueous solution is an important parameter in adsorption process where the removal efficiency depends on pH value. Experiments were conducted to explore optimum pH. To find out optimum pH for the removal of Cr (VI), 200mg of the CBP adsorbent in 50ml solutions of 10 mg/l of Cr (VI) concentration and adjusted to different pH Values ranging from 2.0 – 9.0 were equilibrated for 80 minutes. The solutions were centrifuged and analyzed for Cr (VI) content. The results obtained are shown in Fig -1. Maximum removal of 81% was achieved at pH 2.0 (Singh and Lal, 1992).

Also studies were carried out to obtain optimum pH for the adsorption of nickel (II) using 75 mg of adsorbent in 50 ml solution of 50 mg/l of nickel (II) concentration adjusted to different pH values from 2.0 to 9.0. The solutions at equilibration were centrifuged and analyzed for Ni (II) content. The results obtained are shown in Fig – 2 maximum removal of 75.40 per cent was achieved at pH 4.0, and remained almost constant in the pH range7.0-9.0.In the absence of adsorbent, precipitation started at pH above 6.0, in the presence of adsorbent it started at 6.0. Since the aim of work is to establish a new method for commercial use to industries, it was decided to maintain the pH at 4.0, for all the subsequent experiments.
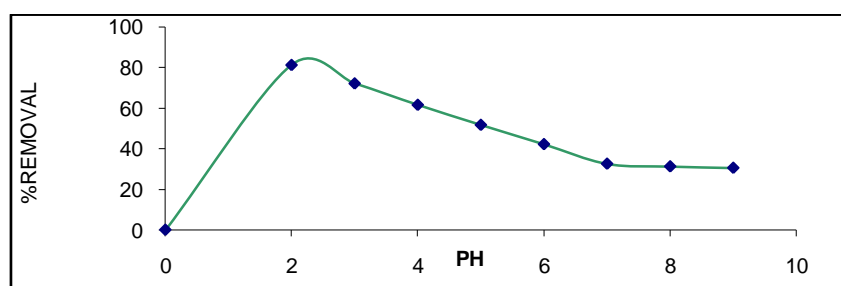

Fig-1. *(Cr (VI)-10 mg/l, adsorbent dose-200mg/50ml, Particle size-0.6mm)*
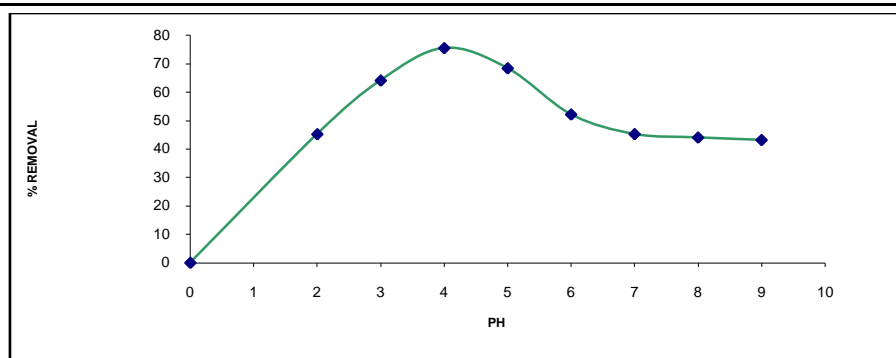
Fig 2. *(Ni (II) conc-50mg/l, adsorbent dose-75 mg/50ml, particle size-0.6mm)*

Effects of Equilibrium Time and Initial Metal Ion Concentration

Equilibrium experiments were carried out by agitating 50ml of different concentrations of Cr (VI) solutions (10 – 30 mg/l) adjusted to pH 2.0 with 200 mg of adsorbent. After equilibrating for different time periods, the solutions were centrifuged and analyzed for Cr (VI) content. Cr (VI) adsorption as a function of time and different concentrations are shown in Fig- 3. It is evident that the equilibrium time is independent of initial concentration. The rate of uptake was rapid in the beginning and became slow in the later stages and reached saturation. During the initial stages of the adsorption process, the adsorbate metal ions preferentially occupied many of the active sites at a random manner resulting in rapid uptake of Cr (VI) ions. As the time passed, the active sites were blocked and hence the rate was slowed. For maximum removal of Cr (VI) by the adsorbent, the solutions should be equilibrated for 60min irrespective of the initial concentration. Data was given in table-1. The curves observed in Fig-3 are single, smooth and continuous indicating the formation of monolayer coverage of the adsorbate on the surface of the adsorbent. Similar trend has been reported for bituminous coal and photo film waste (Narayana Nagesh and Krishnaiah, 1989 and Selvaraj et al., 1998.).

Table 1. *Cr (VI) (adsorbent dose-200mg, pH-2.0, particle size-0.6mm)*

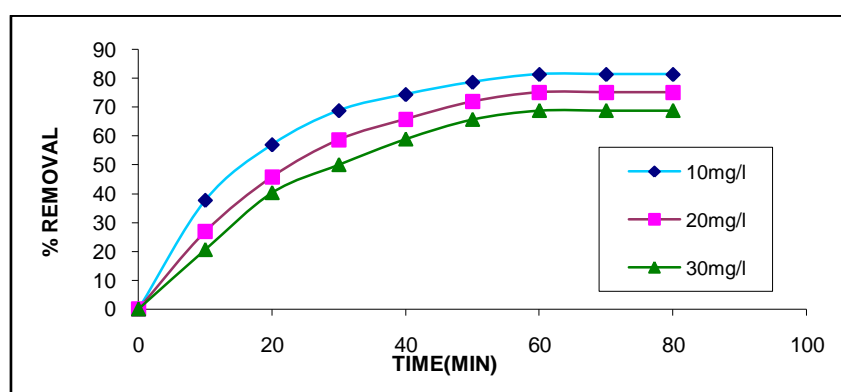| Cr (VI) mg/l	Agitation time /min	10	20	30	40	50	60	70	80
10	% Removal	37.69	56.98	68.80	74.40	78.66	81.37	81.37	81.37
	q (mg/g)	0.94	1.47	1.72	1.86	1.96	2.03	2.03	2.03
	q_e - q	1.09	0.56	0.31	0.17	0.07	-	-	-
20	% Removal	26.81	45.78	58.65	65.79	71.87	75.07	75.07	75.07
	q(mg/g)	1.34	2.28	2.93	3.28	3.59	3.75	3.75	3.75
	q_e – q	2.41	1.47	0.82	0.47	0.16	-	-	-
30	% Removal	20.60	40.33	50.04	58.92	65.71	68.80	68.80	68.80
	q(mg/g)	1.54	3.02	3.75	4.41	4.92	5.16	5.16	5.16
	q_e – q	3.62	2.14	1.41	0.75	0.24	-	-	-

Fig 3. *Cr (VI) (adsorbent dose-200mg, pH-2.0, particle size-0.6mm)*

q_e for 10mg/l=2.03 mg/g, for 20mg/l=3.75mg/g , for 30mg/l=5.16mg/g

Equilibrium experiments were also carried out by agitating 50 ml of different concentrations of Nickel (II) solutions   (50-100 mg/l) adjusted to pH 4.0 with 75 mg/50 ml of adsorbent. After equilibrating for different periods, the solutions were centrifuged and analyzed for Ni (II) content. Ni (II) adsorption as a function of time and different concentrations are shown in Fig - 4. It is evident that for maximum adsorption, the solutions should be equilibrated for at least 120 min and found that the equilibrium time is independent of initial concentration. The rate of uptake was rapid in the beginning and became slow in the later stages and reached saturation at 105 min. This is due to the fact that the metal ion occupied the sites in a random manner because of maximum availability of sites. As the time passed, the active sites were blocked and hence the rate was slowed. For maximum removal of Ni (II) by the adsorbent, the solutions should be equilibrated for 105 min irrespective of the initial concentration. The amounts of Ni (II) adsorbed were, 25.18, 31.18 and 34.50 mg/g for Ni (II) concentrations of 50mg/l, 75 mg/l and100 mg/l respectively which were showed in Table-2.

The formation of monolayer of nickel (1I) ions on the outer surface of the adsorbent is suggested based on the observation that the curves shown in Fig-4 are single, smooth and continuous. Similar results were reported for Ni (II) (Kannan and Inbaraj, 2006) adsorption by orange peelings.

Table 2. *Ni (II) (Adsorbent dose – 75 mg/50ml, initial pH – 4.0, particle size – 0.6 mm)*

| Ni(II) mg/l	Agitation time (min)	15	30	45	60	75	90	105	120
50	%Removal	39.04	56.24	64.72	69.34	72.28	73.92	75.40	75.40
	q (mg/ g)	13.01	18.74	21.57	23.11	24.09	24.64	25.18	25.18
	q_e-q	12.17	6.44	3.61	2.07	1.09	0.54	-	-
75	%Removal	32.52	45.38	52.88	56.56	59.62	61.29	62.36	62.36
	q (mg/ g)	15.25	22.69	27.82	28.28	29.81	30.60	31.18	31.18
	q_e-q	15.93	8.49	3.36	2.90	1.37	0.54	-	-
100	%Removal	26.65	36.34	42.71	46.38	48.49	49.88	51.76	51.76
	q (mg /g)	15.76	24.22	28.47	30.92	32.32	33.25	34.50	34.50
	q_e-q	18.74	10.28	6.03	3.58	2.18	1.25	-	-
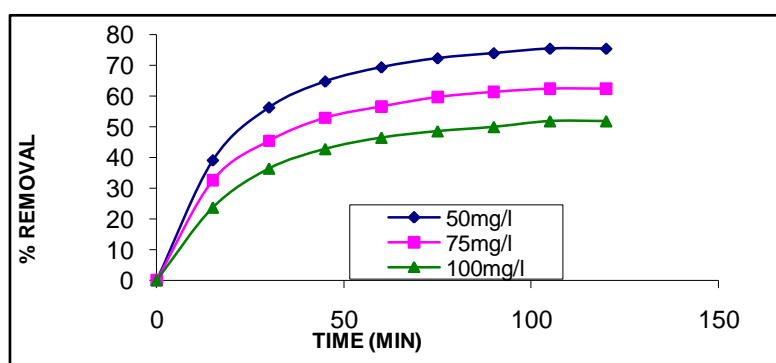
Fig 4. *Ni (II) (Adsorbent dose – 75 mg/50ml, initial pH – 4.0, Particle size – 0.6 mm)*

q_e for 50 mg/L = 25.18 mg/g, 75 mg/L = 31.18 mg/g, 100 mg/L = 34.50mg/g

Effects of Adsorbent Dosage

To investigate the effect of adsorbent dose on Cr (VI) metal ions, various amounts of the adsorbent ranging from 50 – 400 mg were used. Known amounts of adsorbent were added to 50ml of Cr (VI) solutions of concentration 10 mg/l and the solutions were agitated for equilibrium time and the solutions were centrifuged, analyzed for Cr (VI) content. The Percent removal with various adsorbent dosages is listed in Table- 3. Complete removal was possible with dose of 400 mg/50 ml of metal solution. The increase in percentage of adsorption with the increase in dosage is due to the availability of more surface area of the adsorbent for adsorption.

To investigate the effect on Ni (II) ions, various amounts of the adsorbent ranging from 25 to 200 mg was used. Known amounts of adsorbent were added to 50 ml of Ni (II) solutions of concentration 50 mg/l and the solutions were agitated for equilibrium time; the solutions were centrifuged and analyzed for Ni (II) content. The results are given in Table-4. From The data it is evident that, increases in adsorbent dose increase the percent Ni (II) removal and a complete removal was possible with an amount of 200 mg of adsorbent. This is attributed to an increase in number of binding sites with increase in adsorbent dosage

Table 3. *(Cr (VI) -10mg/l, Agitation time – 60 min, PH – 2.0, Particle size – 0.6 mm)*

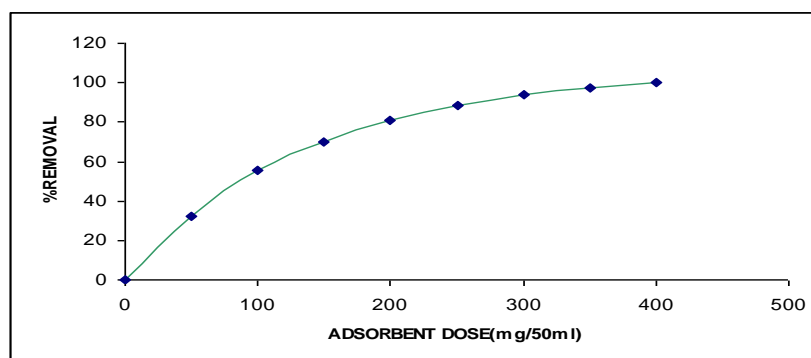| Adsorbent dose mg/50ml	% Removal	Equilibrium concentration Ce (mg/l)	Amount adsorbed mg/g
50	31.90	7.01	2.99
100	55.50	4.45	2.77
150	70.20	2.98	2.34
200	81.25	1.85	2.03
250	88.20	1.18	1.76
300	93.70	0.63	1.56
350	97.30	0.27	1.39
400	100.00	0.00	1.25

Fig 5. *Cr (VI)-effect of adsorbent dose*

Table 4. *Ni (II) - 50mg / l Particle size 0.6mm Agitation time – 105 Initial pH – 4.0*

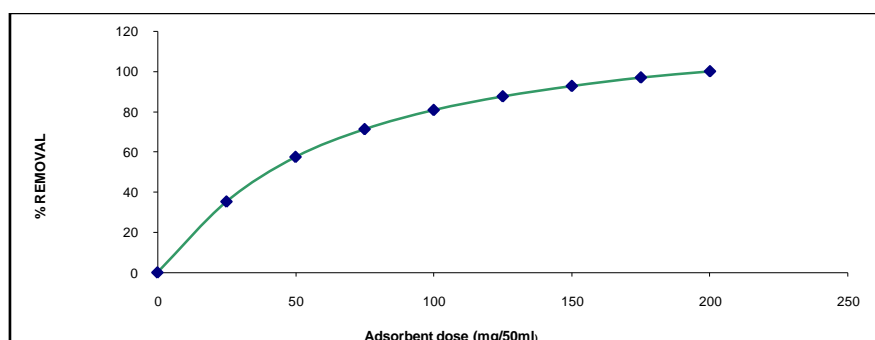| Adsorbent dose mg/50ml	% Removal	Equilibrium Concentration Ce(mg/l)	Amount adsorbed (mg/g)
25	35.24	32.38	35.24
50	57.44	21.28	28.72
75	71.24	14.38	23.74
100	80.76	9.62	20.19
125	87.54	6.23	17.50
150	92.70	3.65	15.45
175	96.92	1.54	13.84
200	100.00	0.00	12.50

Fig 6. *Ni (II) effect of adsorbent dose*

Adsorption Isotherms

Langmuir Isotherm is for monolayer adsorption on adsorbent surface containing finite number of identical sites. Data for Cr (VI) Langmuir isotherm are given in Table -5

Table 5. *(Initial P^H – 2.0, Adsorbent dose – 200mg/ 50ml, Particle size – 0.6 mm)*

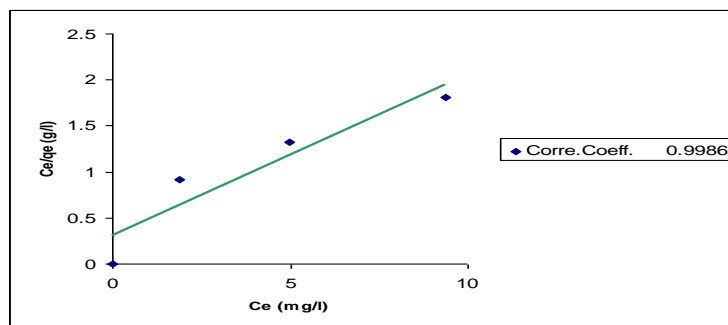| Initial concentration Ci (mg/l)	Equilibrium concentration Ce (mg/l)	qe (mg/g)	Ce/qe (g/l)
10	1.863	2.03	0.917
20	4.986	3.75	1.329
30	9.358	5.16	1.810

Fig 7. *Cr (VI)-Langmuir isotherm*

The plot of Ce/qe vs Ce is linear as shown in Fig -7. It indicates that the adsorption of Cr (VI) obeys Langmuir Isotherm. The langmuir adsorption capacity Qo and energy of adsorption b are found to be 5.68 and 0.584 respectively. Langmuir adsorption capacity of 5.73 mg/g was reported for the adsorption of Cr(VI) on distillery sludge(Manonmani, 2002).Values that decide the nature of adsorption were calculated by using langmuir constant b are 0.146, 0.078 and 0.053 for 10, 20 and 30 mg/l of chromium (VI) concentrations respectively. The values fitted well in $0<R_L<1$, confirming the favorable adsorption of chromium (VI) on the CBP adsorbent. The adsorption data were also tested for the validity of freundlich adsorption isotherm using the standard equation .The plot of log (x/m) vs log Ce is linear (Fig-8)obeying the isotherm. For Cr (VI), the freundlich constants Kf and n calculated from the Fig-8 are 1.46 and 3.29 respectively.
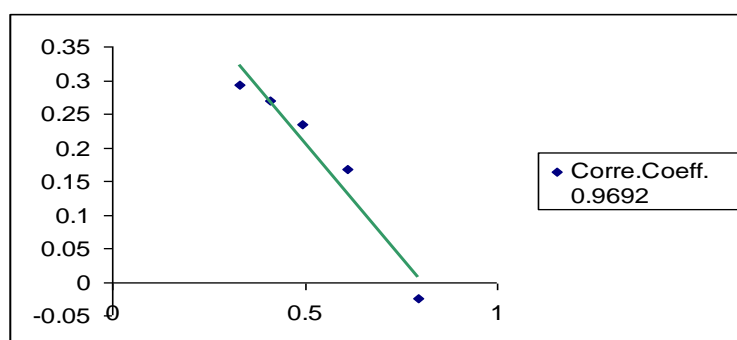

Fig 8. *Cr (VI)-Freundlich isotherm*

For nickel the langmuir constants Qo and b calculated from the slope and intercept of the plot ce/qe vs ce of Figure -9, are 39.63 (mg/g) and 0.138 (l/mg) respectively .Comparison of these values with red mud (Zouboulis and Kydros,1993) indicates that Qo obtained for calcined brick powder adsorbent is greater than that of redmud.The characteristic, equilibrium parameter RL of Langmuir isotherm for nickel was calculated and the values are 0.12, 0.08 and 0.06 for the metal ion concentration of 50, 75 and 100 mg/l, respectively and all the values are between zero and one, indicating the favorable adsorption of Ni (II) on the CBP adsorbent.

Table 6. *Ni(II)(Agitation time – 105 Initial pH – 4.0 Ni (II) - 50mg / l Particle size 0.6mm)*

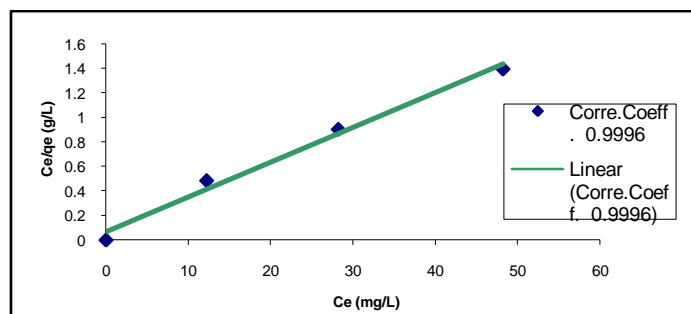| Initial concentration Ci (mg/l)	Equilibrium Concentration Ce (mg/l)	qe (mg/g)	Ce/qe (g/l)
50	12.23	25.13	0.486
75	28.23	31.18	0.905
100	48.24	34.50	1.398

Fig 9. *Ni (II)-Langmuir   isotherm*

Also the adsorption data were tested for the validity of freundlich adsorption isotherm using the equation. The plot of log (x/m) vs log Ce is linear obeying the isotherm. freundlich constants kf and n obtained for Ni(II) are 27.68 and 3.003 respectively.

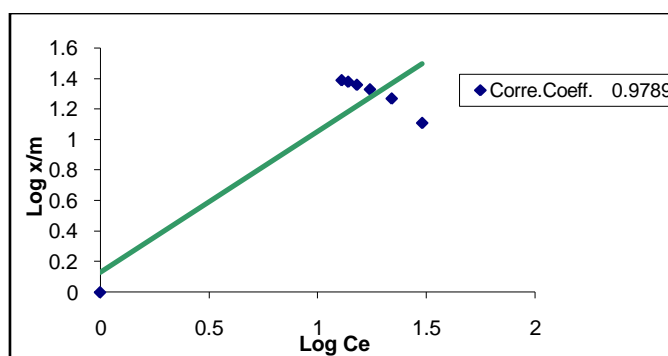**Fig 10.** *Ni (II)-freundlich Isotherm*

According to Mc Kay et al., (1982) the n value between 2 and 10 represents good adsorption. The present n value for the adsorption of   Cr (VI) is 3.29 and Ni (II) is 3.00 on the CBP adsorbent which confirms the validity of freundlich isotherm.

5. CONCLUSION

In this study adsorbent used is a solid waste calcined brick powder which is available in large quantities and can be used as an alternative to existing commercial adsorbents for removal of Cr (VI) and Ni (II).The removal of these carcinogenic toxicants was found to depend on dosage, pH, initial concentrations of Cr (VI) and Ni (II) ions and also contact time. The adsorption capacity of CBP adsorbent for Chromium (VI) is more than Nickel (II). Contact time for the maximum adsorption required is 60 min at pH 2.0 for Cr (VI) and 105 min at pH 4.0 for Ni (II). The equilibrium sorption data are satisfactorily fitted with Freundlich and Langmuir equations. The calculated values of the dimensionless separation factor from the Langmuir constant also confirm favorable sorption of Cr (VI) and Ni (II) onto calcined brick powder. Heavy metal removal with aforesaid CBP adsorbent appears to be technically feasible and eco friendly too. Also it helps in reduction of waste generation.

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