REMOVAL OF NiI(II) FROM SPIKED SOLUTIONS USING NATURAL ADSORBENT – A METHOD OF FLOW TECHNIQUES

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ABSTRACT

Discharge of heavy metals from metal process industries is known to have adverse effects on the environment. Conventional treatment technologies for removal of heavy metals from aqueous solutions are non-economical and generate huge quantities of chemical sludge. Bio-sorption of heavy metals by chemically inactive non-living biomass of microbial of plant origin is an innovative and technology of these pollutants from aqueous solutions.

The operating conditions such as pH, dose required, initial metal concentrations and treatment performance are presented, recovery adsorbent was also discussed. The efficiency of fixed bed system depends on the initial concentration of influent rate and bed height. The effects of parameters on the adsorption of Ni(II) on PPP were examined. A simpler approach to fixed bed adsorption has been proposed by Hutchin which is called bed – depth - service time (BDST). Model service time with parameters, initial concentrations, flow rate and bed heights. A bed height of 3.0 cm having 2.0 g adsorbent was used, to study the effects of initial metal ion concentration. The metal ion concentration varied from 20 - 40 ppm and flow rate of 10 ml/min, at required pH. The effects of flow rate on adsorption of Ni(II) was studied with 20 ppm of Ni(II) solution was allowed to pass through the column of an adsorbent 3.0 cm at different flow rates. Effects of metal initial concentration of 20 ppm, flow rate of 10 ml/min, bed heights contains different weights were used to study.

Key words: *Pongami Pinneta* Pricarp (PPP), Heavy metals, Wastewater treatment, Removal, Advanced techniques

Introduction

Nickel used in electroplating industry, in the making of coins, chemical reagents, alloys preparation, nickel compounds, house wear utensils, machine parts, preparation of stainless steel, spare parts in automobiles, leather and textile industries.

However, the number of sites, evaluated for nickel is not known. Nickel and its compounds are naturally present in the earth's crust and releases to the atmosphere occur from natural discharges such as windblown dust and volcanic eruptions, as well as from anthropogenic activities. It is estimated that 8.5 million kg of nickel are emitted into the atmosphere from natural sources such as windblown dust, volcanoes and vegetation each year. Five times that quantity is estimated to come from anthropogenic sources. The burning of residual and fuel oil is responsible for 62 % of anthropogenic emissions, followed by nickel metal refining, municipal incineration, steel production, other nickel alloy productions and coal combustion. These components releases, which totaled 3,081 metric tons, were distributed as follows: 82.2 % to land, 6.0 % to air, 2.2 % to water, and 0.8 % to underground injection.

Nickel (II) is well known toxic heavy metal, which pose serious threat to the fauna and flora of receiving water bodies when discharged from industrial wastewaters. Nickel (II) present in the effluents of silver refineries, electroplating, zinc base casting and storage battery industries. Kadirvelu *et al*., 2000a. As it resists corrosion even at high temperature, it can also be used in gas turbines, rocked engines and distillation plants. It is also used in coinage and costume jewelry. Skin contact with nickel causes a painful disease called 'nickel itch' which leads to death, reported Abbasi and Soni, 1990. In India acceptable limit of nickel in drinking water is 0.01 mg/lit and for discharge of industrial wastewater is 2.0 mg/ lit, Kadirvelu, 1998. At higher concentrations, nickel (II) causes cancer to the lungs, nose and bones. Dermatitis (nickel itch) is the most frequent effect of exposure to nickel, such as coins and costume jewelry. Nickel carbonyl [$Ni\ (Co)_4$] has been estimated as lethal in humans at atmospheric exposures of 30 ppm for 30 min, Namasivayam and Ranganathan, 1994. Acute poisoning of nickel (II) causes headache, dizziness, nausea, tightness of the chest, chest pain, shortness of breath, dry cough, cyanosis and extreme weakness. Parker, 1980. The toxic nature of fish, crops and algae was also reported David, 1977. Perennial toxicity associated with nickel chloride exposure on female rats was also reported, Kate Smith *et al*., 1993.

The main object of present work was to evaluate the feasibility of using natural adsorbents from waste materials for the removal of nickel (II) from aqueous solutions and industrial wastewaters by using batch mode and fixed bed study. The influence of experimental conditions such as contact time, metal ion concentration, adsorbent dosage and pH effects were studied. Experimental results are analyzed to provide an adsorption mechanism. This method was applied for the removal of Ni (II) from synthetic aqueous solutions and industrial wastewaters.

Column Study

The efficiency of a fixed bed system depends on the initial concentration of the influent, flow rate and bed height. The effects of these parameters were examined. A simpler approach to fixed bed absorbent has been proposed by Hutchin's (Equation-1) (1973) which is called Bed-Depth-Service-Time (BDST) model which correlates service time 't' with the parameters are initial metal ion concentration, flow rate and bed height.

Effects of Metal Ion Concentration on Ni (II) Adsorption

A bed height of 3.0 cm of the weight 2.2 g of the adsorbent was used to study the effects of initial metal ion concentration. The initial Ni (II) concentrations were varied from 20 to 40 mg/l at constant bed height of 3.0 cm and flow rate of 10 ml/min and adjusted pH 5.0. The efficiency of the fixed bed method depends on the shape of the breakthrough curves obtained by plotting (C_t / C_o) vs effluent volume or time. *Breakthrough volume is defined as the maximum volume of effluent required to reach $C_t / C_o = 0$ or $C_t / C_o = 0.5$ (ml) (50% breakthrough)*. The plots of C_t / C_o vs effluent volume for different Ni (II) concentrations are shown in Fig- 1. The plots are traditional 'S' shape but the steepness of the curve varies with the concentrations of nickel (II). The breakthrough volumes at $C_t / C_o = 0$ for nickel (II) concentrations of 20, 30 and 40 mg/ l were found to be 750, 600 and 500 ml respectively. The time for 50 percent breakthrough ($t_{0.5}$) decreased from 200.0 to 105.0 min for the Ni (II) concentrations of 20 mg / lit to 40 mg / lit. The results are shown in Table- 1.

Table -1

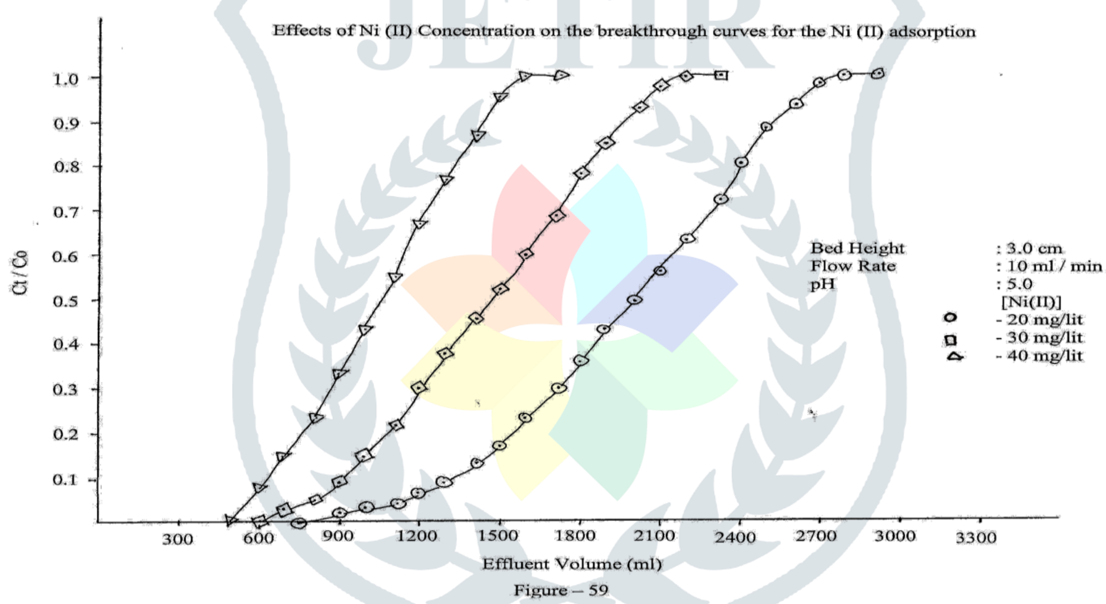
Breakthrough Volumes for nickel (II) Adsorption for different Concentrations

Particle size : 0.800 mm Initial pH : 5.0

Bed height : 3.0 cm Flow rate :10 ml/min

Initial Concentration (mg / lit)	Breakthrough volume		Time for 50 % breakthrough $t_{0.5}$ (min)
	C_t / C_o = 0 (ml)	C_t / C_o = 0.5 (ml)	
20	750	2000	200
30	600	1500	142
40	500	1050	105

Fig-1



Effects of Flow rate on Nickel (II) Adsorption

The effects of flow rate was examined by changing the flow rates from 5 to 15 ml/min, keeping the bed height and initial Ni (II) concentrations kept constant at 3.0 cm and 20 mg/ l respectively and adjusted pH 5.0. Fig- 2 shows the sigmoidal "S" type plot of C_t / C_o vs volume and Table- 2 gives the breakthrough volumes and corresponding times required for saturation of half of the column. The difference between breakthrough volumes at C_t / C_o = 0 for 5 and 15 ml were found to be 1050 and 550 ml respectively, showing that the breakthrough volume was decreased by 500 ml when flow rate was increased. For the removal of metal ions like Ni (II) slower flow rates are suggested.

Table – 2

Breakthrough Volume for Ni (II) Adsorption for different Flow Rates

[Ni (II)] : 20 mg / l Bed height : 3.0 cm Particle size : 0.800 mm Initial pH : 5.0

Flow rate (ml/ min)	Breakthrough Volume		Time for 50 % breakthrough $t_{0.5}$ (min)
	$C_t / C_o = 0$ (ml)	$C_t / C_o = 0.5$ (ml)	
5	1050	2300	460.00
10	750	2000	200.00
15	550	1650	156.67

Fig-2

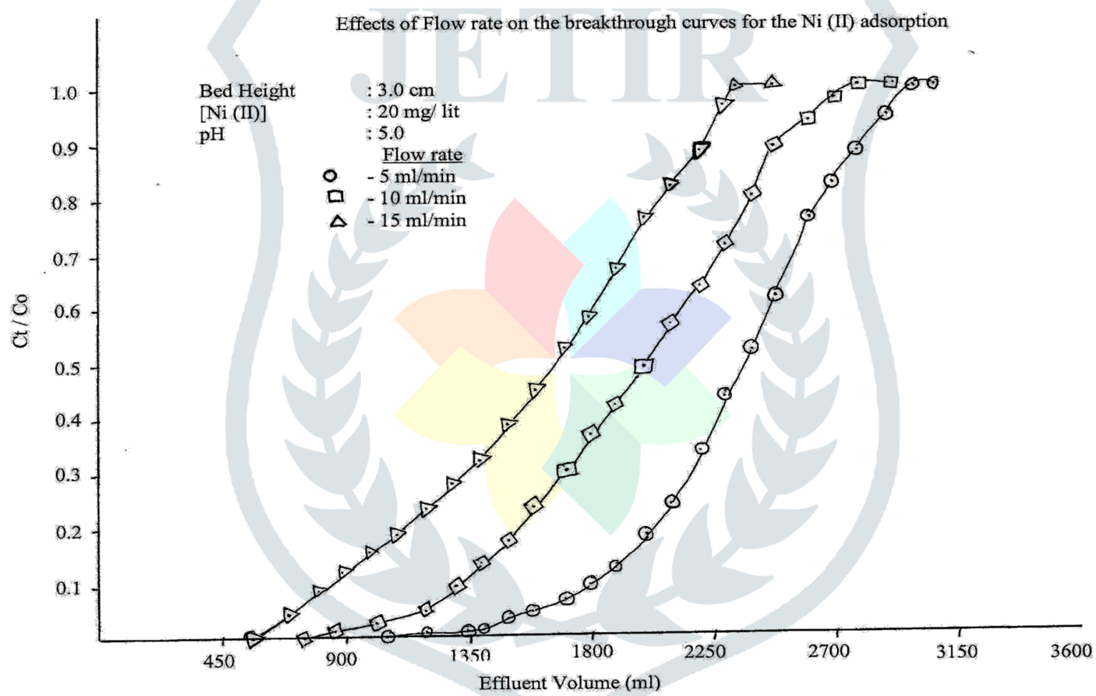


Figure – 60

Effects of Bed height on Nickel (II) removal

The studies were conducted by varying the bed heights from 2.2 to 3.8 cm having the adsorbent weights 1.62, 2.20 and 2.84 g, keeping flow rate and initial nickel (II) concentrations kept constant at 10 ml/ min and 20 mg/ lit respectively and adjusted pH 5.0. The 'S' shape plots of C_t / C_o vs volume are given in Fig - 3. The breakthrough volumes recorded in Table- 3, it is evident that increase in the bed height from 2.2 to 3.8 cm has resulted in an increase in breakthrough volumes at $C_t / C_o = 0$ from 400 to 1100 ml.

Table -3

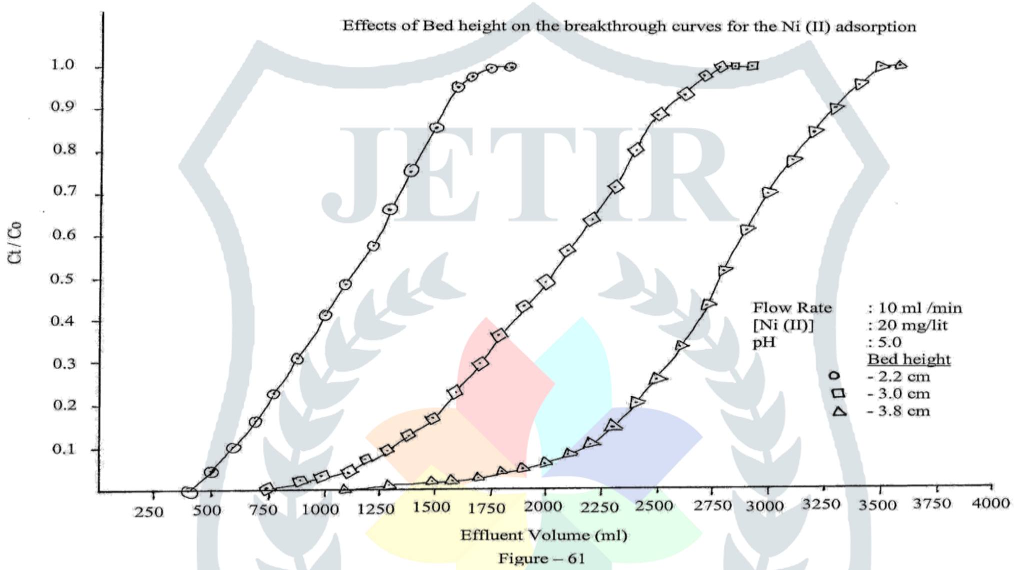
Breakthrough volumes for Ni (II) adsorption for different bed heights

[Nickel (II)] : 20 mg / l Flow rate : 10 ml / min

Initial pH : 5.0 Particle size : 0.800 mm

Bed height (cm)	Breakthrough volume		Time for 50 % break through $t_{0.5}$ (min)
	$C_t / C_o = 0$ (ml)	$C_t / C_o = 0.5$ (ml)	
2.2	400	1060	106
3.0	750	2000	200
3.8	1100	2780	278

Fig-3



Application of BDST model

As predicted from Hutchin's equation (1973) for BDST (Equation-1), the plot of $C_o t$ vs ln $[(C_o/C_t) - 1]$ should be a straight line. The data for BDST equation are given in Tables- 4, 5 and 6 for different Ni (II) concentrations, different flow rates and different bed heights respectively. The plots of $C_o t$ vs ln $[(C_o/C_t) - 1]$ are linear (Fig- 4, 5 and 6) obeying Hutchin's equation. The constants K_a and N_o, namely the rate constant of adsorption and adsorption capacity respectively were obtained from the slope and intercepts of the plots (Fig - 4, 5 and 6) and are listed in Table-7. It is evident from the values that increase in initial concentration of Ni (II) solution from 20 to 40 mg/ lit, increased the adsorption capacity from 4020 to 4400 mg/ lit and decreased the rate constant from 1.39×10^{-3} to 1.11×10^{-3} lit / min / mg. Similar behavior has been observed by Ranganathan and Namasivayam 1998.

At fixed influent concentration and bed heights, smaller flow rate of 5 ml/ min showed better adsorption capacity of 9600 mg/ l than 10 and 15 ml/min. The $K_a$values in Table -7 shows that higher flow rates saturate the bed more quickly than slower flow rates. From the results obtained for different bed heights, it is evident that increase in bed height form 2.2 to 3.8 cm the breakthrough volumes at $C_t / C_o = 0$ increased from 400 to 1100 ml and N_o from 2220 to 5360 mg/ l. Increase in bed height increased the adsorption capacity. This is due to the fact that the number of adsorption sites increases with increase in adsorbent doses.

Table - 4

Data for BDST Equation for Ni (II) Adsorption at different Concentrations

Flow rate : 10 ml/ min
Particle size : 0.800 mm

Bed height : 3.0 cm
Initial pH : 5.0

[Ni (II)] (mg / l)	Time (min)	C_o t (mg/l)(min)	$\ln\left(\frac{Co}{Ct}-1\right)$
20	170	3400	0.847
	180	3600	0.575
	190	3800	0.282
	200	4000	0.040
	210	4200	- 0.241
	220	4400	- 0.532
	230	4600	- 0.895
30	110	3300	1.266
	120	3600	0.800
	130	3900	0.489
	140	4200	0.201
	150	4500	- 0.252
	160	4800	- 0.662
	170	5100	- 1.161
40	70	2800	1.735
	80	3200	1.208
	90	3600	0.708
	100	4000	0.241
	110	4400	- 0.242
	120	4800	- 0.512
	130	5200	- 0.840

Fig-4

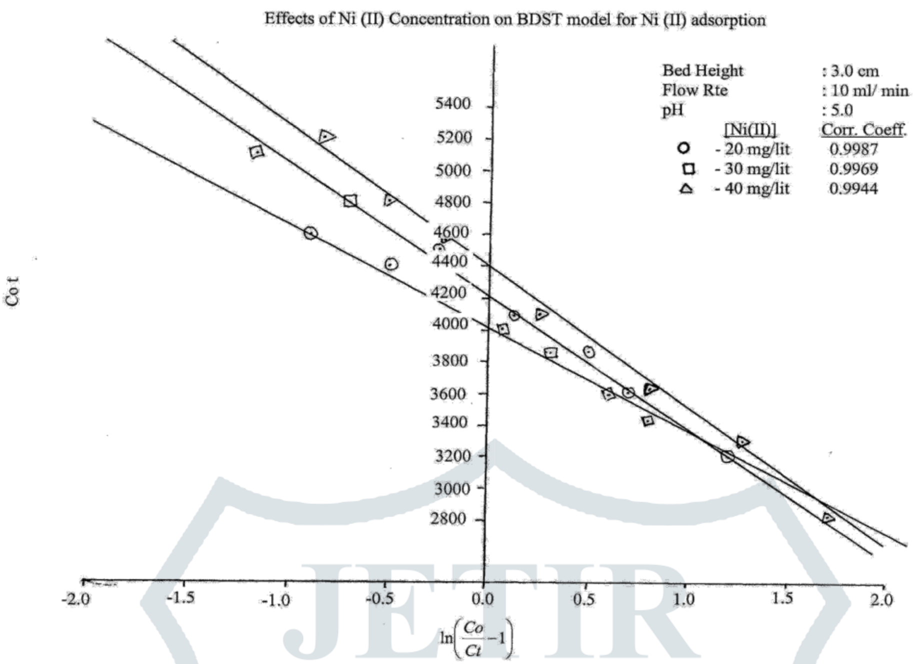


Figure – 62

Table – 5

Data for BDST equation for Nickel (II) Adsorption at different Flow Rates

[Ni (II)] : 20 mg / l Initial pH : 5.0

Bed height : 3.0 cm Particle size : 0.800 mm

Flow rate (ml / min)	**Time (min)**	C_o t (mg/l)(min)	**ln** $\left(\frac{Co}{Ct} - 1\right)$
5	400.00	8000.0	1.586
	420.00	8400.0	1.208
	440.00	8800.0	0.708
	460.00	9200.0	0.323
	480.00	9600.0	- 0.080
	500.00	10000.0	- 0.447
	520.00	10400.0	- 1.099
15	86.67	1733.40	0.995
	93.33	1866.70	0.754
	100.00	2000.00	0.489
	106.67	2133.40	0.201
	113.33	2266.70	- 0.080
	120.00	2400.00	- 0.322
	126.67	2533.40	- 0.663

Fig-5

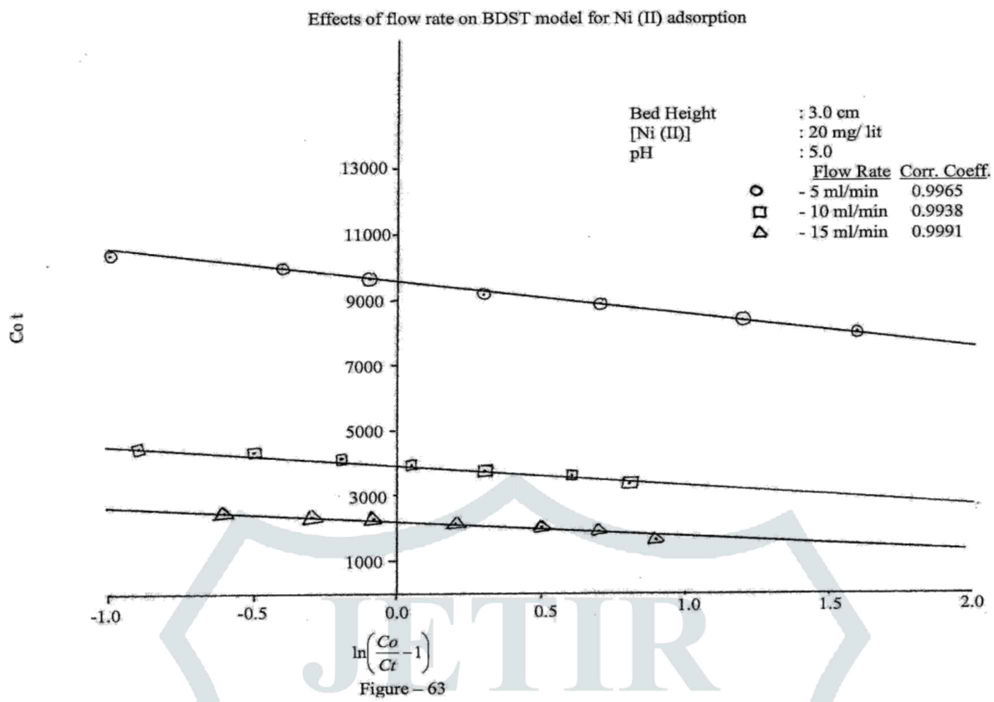


Table - 6

Data for BDST Equation for Ni (II) adsorption at different bed heights

[Ni (II)] : 20 mg / l Flow rate : 10 ml / min Initial pH : 5.0 Particle size : 0.800 mm

Bed height (cm)	**Time (min)**	C_o t (mg/l)(min)	**ln** $\left(\frac{Co}{Ct}-1\right)$
2.2	80	1600	1.208
	90	1800	0.800
	100	2000	0.364
	110	2200	0.040
	120	2400	- 0.282
	130	2600	- 0.663
	140	2800	- 1.099
3.8	240	4800	1.325
	250	5000	1.046
	260	5200	0.666
	270	5400	0.282
	280	5600	- 0.080
	290	5800	- 0.447
	300	6000	- 0.847

Fig-6

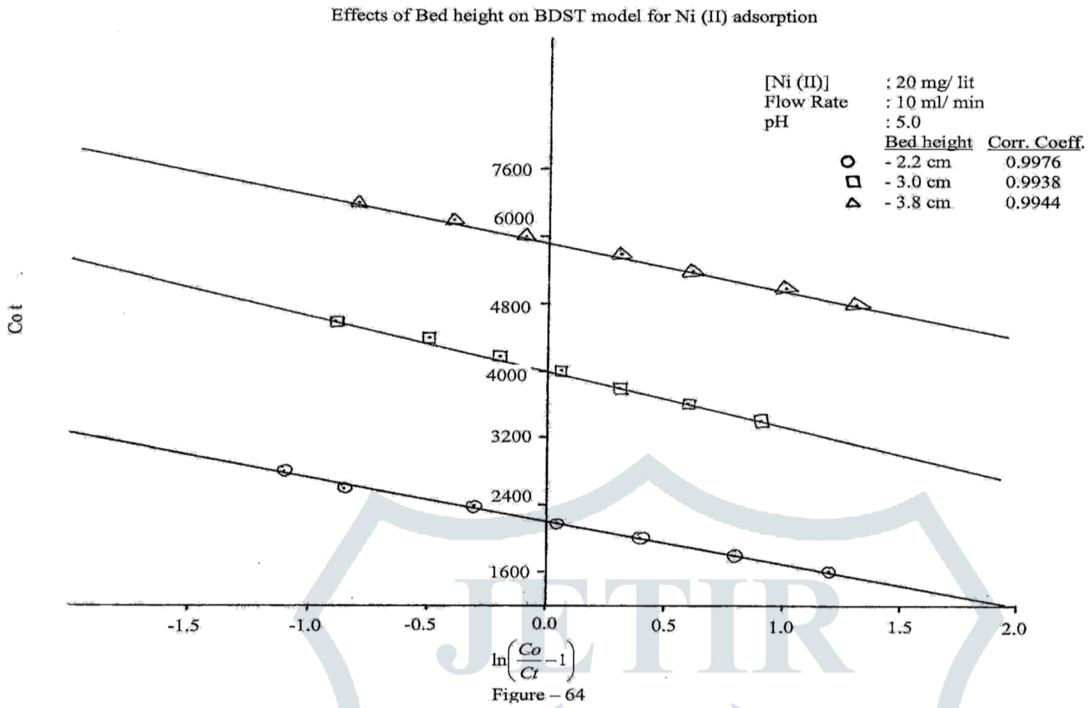


Table –7

BDST constants for Nickel (II) adsorption

BDST constants	Concentration (mg / l)			Flow rate (ml / min)			Bed height (cm)		
	20	**30**	**40**	**5**	**10**	**15**	**2.2**	**3.0**	**3.8**
K_a(lit/min/ mg) x 10^{-3}	1.39	1.19	1.11	1.01	1.56	2.25	3.10	2.01	1.86
N_o(mg / lit)	4020	4200	4400	9600	3900	2200	2220	4000	5360

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