

Physico-Chemical Key Parameters, Langmuir and Freundlich isotherm and Lagergren Rate Constant Studies on the removal of divalent nickel from the aqueous solutions onto powder of calcined brick

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Abstract—The use of powder of calcined brick (PCB) as the low-cost adsorbents was investigated as a replacement for current costly methods of removing nickel ions from aqueous solutions. Batch adsorption studies were conducted to examine the effects of physico-chemical key parameters such as the stirring rate, initial metal ion concentration, pH, agitation time, particle size and adsorbent dosage on the adsorption of Ni(II) by powder of calcined brick powder. The optimum results were determined at an initial metal ion concentration of 50 (mg L⁻¹), stirring rate = 160 rpm pH=4, agitation time – 105 min, an adsorbent dose (75 mg/50 ml) and the particle size (0.6 mm). The % adsorption, Langmuir constants [Q₀=39.63(mg/g) and b=0.138(L/mg)], Freundlich constant K_f= 27.68(mg/g) and n=3.003(L/mg), Lagergren rate constants [K_{ad} (min⁻¹)=4.05 x 10⁻²] for [Ni (II)] 50 (mg L⁻¹), were determined for the adsorption system as a function of sorbate concentration. Equilibrium data were analyzed using the Langmuir and Freundlich isotherms whereas the adsorption kinetics data were evaluated by the pseudo-first-order kinetic model.

Keywords—Adsorption. Ni (II) ions. Powder of calcined brick (PCB). Adsorption kinetics. Adsorption isotherms. Physico-chemical parameters

I. INTRODUCTION

The cosmopolitan problem of heavy metal contamination has been tried world over for more than two decades. The hazardous nature of the heavy metals to biological systems has made the governments to impose stringent standards as the disposal. This has prompted many industries to sponsor special studies on the removal of heavy metals. In the process, several methodologies have been adopted but due to operational difficulties, most of them are not in use. However, still considerable volume of work is generated and added every year. The quest for cost effective and user-friendly mechanisms, that are ultimately ecofriendly, has been going on. One of the important toxic metals, Nickel (II) finds its way into the water bodies through effluents from industries. The nickel salts are known to be acutely and chronically toxic to human. Acute poisoning of Ni (II) causes headache, dizziness, nausea, and tightness of the chest, chest pain, shortness of breath, dry cough, cyanosis, and extreme weakness [1] At higher concentrations it is a potent carcinogen and causes cancer of lungs, nose and bone. Nickel carbonyl [Ni (CO)₄] has been estimated as lethal in humans at atmospheric exposure of 30 ppm for 30 min [2]. The toxic nature of fish, crops and algae was also reported [3]. Perinatal toxicity associated with nickel chloride exposure on female rats was also reported [4].

The conventional methods that are employed to remove heavy metals such as ion exchange, chemical precipitation, reverse osmosis and membrane separation are found to be inefficient and expensive, especially when treating wastewater with low concentration of heavy metals [5]–[7]. Some of these technologies will also produce chemical or biological sludge and cannot be recovered or regenerated [8]. Adsorption, on the other hand, has emerged as a potential alternative to conventional physicochemical technologies in waste-treatment facilities. Adsorption is an effective separation process that has advantages in terms of cost, flexibility and simplicity of design, and ease of operation compared to other techniques. Adsorption also does not result in the formation of harmful substances [9].

In recent years, much attention has been focused on the removal of heavy metals using industrial wastes, agricultural wastes etc. Many authors used natural adsorbents like activated carbon prepared from activated clay [10], agricultural solid waste [11], peanut hull [12] and flyash [13]. Activated carbon is usually being used as adsorbent by chemical industry for wastewater treatment. However, it has shown disadvantage from the economic consideration due to the expensive activated carbon that causes an increase in the operating costs. Thus, some researchers are looking for the other alternative adsorbents which have characteristics similar to activated carbon in removing metal from aqueous solution. Agricultural wastes that are available in large quantities may have a potential to be used as low cost adsorbents, because they represent unused resources that are widely available and environmental friendly [8]. Agricultural wastes such as sugar beet pulp, dried sunflower leaves, sour orange residue and papaya wood are known to be effective in batch adsorption process on the removal of Ni(II) [14]–[17]. The present study aimed to investigate the efficiency of powder of calcined brick as adsorbent for the adsorption of Ni(II) from water. Experiments were conducted to investigate the effects of pH, stirring rate, Ni(II) concentration and contact time on the adsorption efficiency of Ni(II) by powder of calcined brick. Adsorption equilibrium and kinetics had been studied under the optimum adsorption conditions. The Langmuir and Freundlich isotherms

were applied to evaluate the adsorption properties in the batch experiments. In addition, the pseudo-first-order kinetic model was also applied to examine the kinetics of the adsorption process.

II. MATERIALS AND METHODS

Adsorbent : Easy availability, economical to use and proven potential for other metals, have been the reasons for selection of powder of calcined brick powder (PCB) as an adsorbent to adsorb Nickel (II) ions from the aqueous solutions . The calcined bricks were collected from the kiln and powdered. The powder was soaked for 24 hours in distilled water and then thoroughly washed for 4 to 5 times. The powder was sun-dried and sieved to select 0.6 mm sized particles.

Characterization of adsorbents: The adsorbent was treated for achieving best adsorption. The moisture content and pH of the adsorbents were measured.

Measurement of Moisture Content: Ten grams of the adsorbent powder was taken into a petri-dish and overheated for two hours. After heating the plates were instantaneously placed in a desiccator. The powder thus cooled was weighed. The difference between initial weight and final weight was taken as the moisture content.

Measurement of pH of the adsorbent: Five grams of adsorbent powder was taken into a 1000 ml beaker. To this 150 ml of freshly boiled and cooled water was added and then heated till boiling point. The contents were digested for ten minutes and kept aside for ten minutes. The solution was filtered and pH was measured. The metal ion solutions for standard solutions and further dilutions were prepared following the procedures described [18].

Preparation of metal ion solutions: The Nickel (II) was estimated using standard methods. AR grade chemicals and double distilled water were used for all the analyses. The concentrations of the metal ions were estimated using UV-visible spectrophotometer (ELICO SL 150). Standard Nickel Solution: Nickel (II) solution was prepared by using AR Grade nickel ammonium sulphate; 6.7280 g of nickel ammonium sulphate was taken into a 1000 ml volumetric flask. 5 ml of 1% HNO₃ was added to it immediately. Then the contents were made up to 1000 ml with double distilled water.

Analysis of nickel (II) : Spectrophotometric analysis was adopted to estimate Nickel (II), by using dimethylglyoxime (DMG). Different standard solutions containing less than 100 mg/l of Nickel (II) were prepared and 2 ml of 20% w/v sodium tartarate solution 10 ml of 4% w/v potassium persulphate 2.5 ml of 5 M sodium hydroxide solutions and 15 ml of (1+30) HCl solutions were added. Again 0.6 ml of 1% DMG solutions were added to this mixture. The contents were made upto 50 ml. The absorbance was measured after 30 minutes using UV-visible spectrophotometer at 465 nm. A reagent blank was also prepared for Nickel (II) solution. The amount of Nickel present in the sample was obtained from the calibration curve. The results for a heavy metal concentrations were expressed in mg L⁻¹ while those of the concentration equilibrium, equilibrium time, and adsorption capacity etc., were compared with the Langmuir and Freundlich isotherms.

Batch Equilibrium Method: All experiments were carried out at room temperature (27⁰C) in batch mode. Batch mode was selected because of its simplicity and reliability. The experiments were carried out by taking 50 ml metal ion sample (AR grade) in a 100 ml Erlenmeyer flask and after pH adjustments; a known quantity of dried adsorbent was added. The flasks were agitated at 160 rpm for predetermined time intervals using a mechanical shaker until equilibrium conditions were reached. After shaking, the suspension was allowed to settle. The residual biomass adsorbed with metal ion was filtered using whatman 42 filter paper (Whatman International Ltd., Maid Stone, England), filtrate was collected and subjected for metal ion estimation using UV-visible spectrophotometer (ELICO SL 150). The values of percent metal uptake by the sorbent (Sorption efficiency) and the amount of metal ion adsorbed has been calculated using the following relationships

$$\text{Sorption efficiency} = \frac{C_i - C_f}{C_i} \times 100$$

$$\text{Amount adsorbed (q}_e\text{)} = \frac{C_i - C_f}{m} \times v$$

where,

C_i = Initial concentration of metal ion in the solution (mg/lit)

C_f = Final concentration of metal ion in the solution (mg/lit)

m = Mass of adsorbent (g lit⁻¹)

v = Volume of solution (lit)

q_e = Amount of metal ion adsorbed per gram of adsorbent.

Control experiments were carried out and the average values of duplicate runs were obtained and analyzed (Error: ±1-2% for percentage removal and ±0.005-0.01 mg g⁻¹ for amount adsorbed).

The adsorbents selected were very common and eco-friendly. The work mainly helps in bringing sorbents into use to handle the heavy metals. The calcined brick pieces used in this process are only the left over waste pieces at the kilns. This kind of utilization reduces the solid waste problem also.

III. RESULTS AND DISCUSSION

The characteristics of powder of calcined brick powder were discussed in Table 1.

Table 1: Characteristics of PCB

Sl. No	Parameter	Value
1	Bulk Density	1.3207
2	Loss on Ignition	2.70
3	pH	7.67
4	Silica as SiO ₂	61.30
5	Calcium as Ca	0.24
6	Sodium as Na	0.05

EFFECT OF pH :

pH is an important parameter for adsorption of metal ions from aqueous solution because its effects the solubility of metal ions, concentration of counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction. Studies were carried out to obtain optimum pH for the adsorption of nickel (II) using 75mg of adsorbent in 50ml solution of 50mg /lit of nickel (II) concentration adjusted to different pH values from 2.0 to 9.0. The solutions after equilibration were centrifuged. The filtrates were tested for Ni (II) concentrations spectrophotometrically. Fig. 1 shows the effect of pH on adsorption of Ni (II) ion.

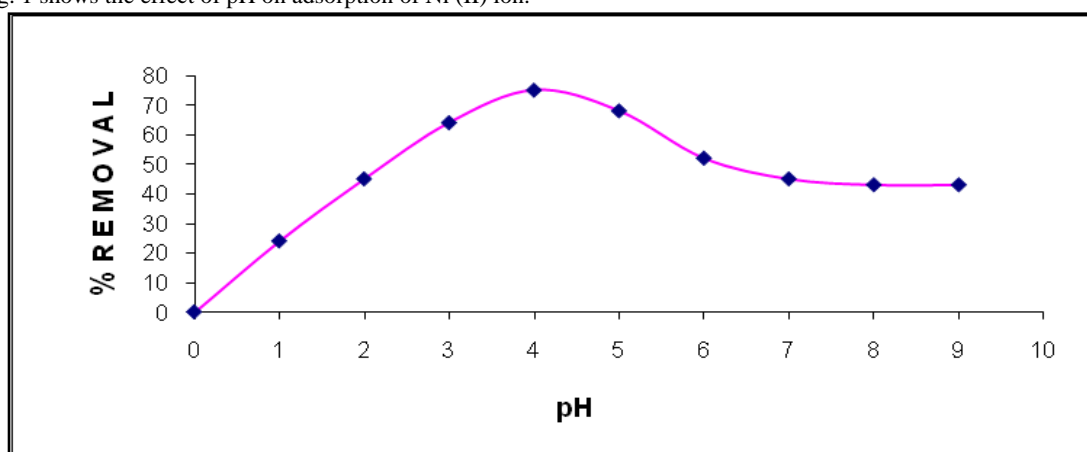


Fig. 1: Effect of pH on the % removal of Ni(II)

Maximum removal of 75.40 % was achieved at pH 4.0 and remained almost constant in the pH range of 7.0 to 9.0. The percentage of adsorption increased with increase in initial pH and decreased with increase in initial pH up to 6.0. The adsorption of metal cations depends on the nature of metal ions, adsorbent surface and species of the metals. At lower pH values Nickel removal was inhibited, possibly because of the competition between hydrogen and nickel ions in the sorption site. With an apparent preponderance of hydrogen ions, it restricts the approach of metal cations as a consequence of the repulsive force. At pH > 6 precipitations started and hence, higher pH was not selected for the present study. Biosorption of nickel Ni²⁺ was maximum at pH =4, as the pH exceeded, the biosorption began to decrease. This is possibly due to the precipitations of Ni (II) ions as a result of hydroxide anions forming nickel hydroxide precipitate. Many authors reported maximum adsorption of Ni(II) in the pH range of 3 to 6. The results obtained for the adsorption of Nickel (II) on the powder of calcined brick were in good agreement with the results of activated carbon [19] where pH was less than 4.5 and adsorption capacity was pH dependent.

EFFECT OF EQUILIBRIUM TIME AND INITIAL METAL ION CONCENTRATION:

To investigate the optimum equilibrium time, Equilibrium experiments were carried out by agitating 50ml of different concentrations of Nickel (II) solutions (50-100) mg/l adjusted to pH 4.0 with 75mg/50ml 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. 2. It was evident that for maximum adsorption, the solutions should be equilibrated for at least 120 min and 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 105min. This was 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 Nickel (II) by the adsorbent, the solutions should be equilibrated for 105 min irrespective of the initial concentration. The amounts of Nickel (II) adsorbed were, 25, 18, 31,18, 34.50 mg/g for Ni(II) concentrations of 50, 75 and 100 mg/l, respectively, showed in Table 2

Table 2: Relationship between initial Ni (II) concentrations and the equilibrium times

Agitation time in minutes	Concentration of Nickel (II) in mg/l								
	50 mg/l			75 mg/l			100 mg/l		
	Amount of Nickel (II) adsorbed q (mg/l)	qe-q	% Removal	Amount of Nickel (II) adsorbed q (mg/l)	qe-q	% Removal	Amount of Nickel (II) adsorbed q (mg/l)	qe-q	% Removal
15	13.01	12.17	39.04	15.25	15.93	32.25	15.76	18.74	26.65
30	18.74	6.44	56.24	22.69	8.49	45.38	24.22	10.28	36.34
45	21.57	3.61	64.72	27.82	3.36	52.88	28.47	6.03	42.71
60	23.11	2.07	69.34	28.28	2.90	56.56	30.92	3.58	46.38
75	24.09	1.09	72.28	29.81	1.37	59.62	32.32	2.18	48.49
90	24.64	0.54	73.92	30.60	0.54	61.29	33.25	1.25	49.88
105	25.18	-	75.40	31.18	-	62.36	34.50	-	51.76
120	25.18	-	75.40	31.18	-	62.36	34.50	-	51.76

The formation of monolayer of nickel (II) ions on the outer surface of the adsorbent was suggested based on the observation that the curves shown in Fig.2 are single, smooth and continuous. Similar adsorption results were reported by [20] for orange peelings.

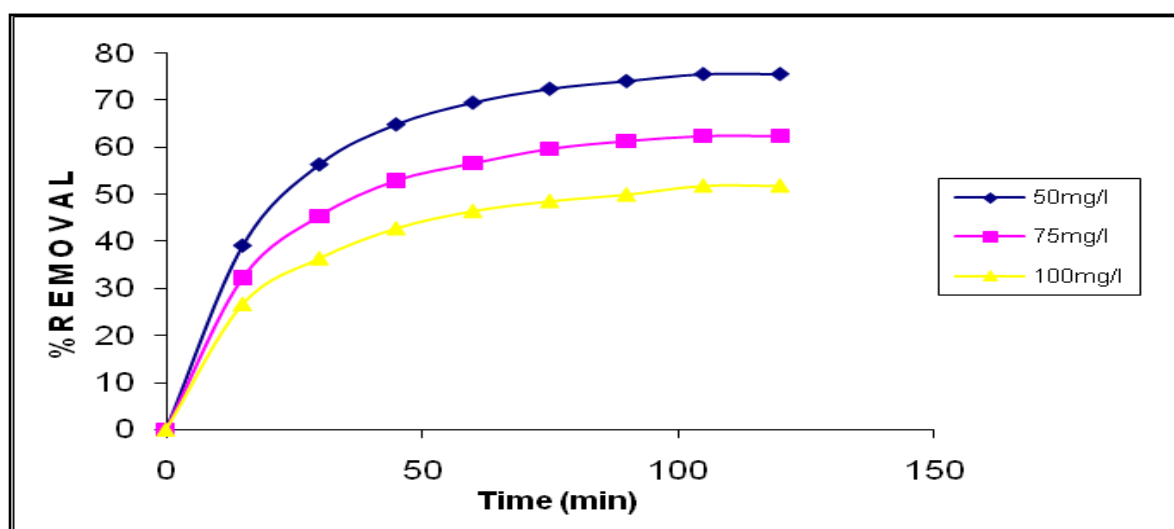


Fig. 2: Effect of time on % removal of Ni(II) at different concentrations

EFFECT OF ADSORBENT DOSAGE:

To investigate the effect of adsorbent dose, various amounts of the adsorbent ranging from 25 to 200 mg were used. Known amounts of adsorbent were added to 50ml of Nickel (II) solutions of concentration 50 mg/l and the solutions were agitated for 105 min. After equilibrium time, the solutions were centrifuged and analyzed for Ni (II) content. The results were given in Table 3.

Table 3: Relationship between adsorbent doses and % removal and equilibrium concentrations

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

From the Fig.3, it was evident that, increase in adsorbent dose increased the percent Ni(II) removal and a complete removal was possible with an amount of 200mg of adsorbent. This was attributed to an increase in number of binding sites as the dosage increased.

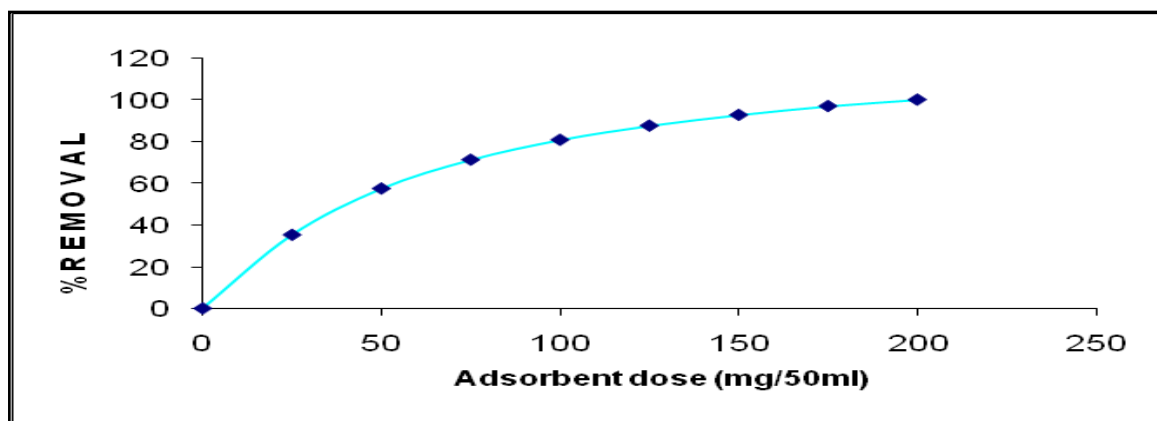


Fig .3 : Relationship between the adsorbent dose and % removal

Effect of Particle Size:

To study the effect of particle size, adsorbent particles of sizes 0.6 mm, 0.8 mm and 1.7 mm were used. In each study 125 mg of adsorbent in 50 ml of 10 mg L⁻¹ of Ni(II) solution was agitated to equilibrium time of 60 min, the adsorbent was separated and the supernatant solution was analyzed for chromium concentration and the values are noted in Table-4, the amounts adsorbed for 0.6 mm, 0.8 mm and 1.7 mm particle size were 3.01, 2.66 and 2.34 mg/g, respectively.

Table 4: Adsorption of Ni (II) ions on different particle sizes (mm) of the adsorbent

Agitation time in minutes	Particle size in mm								
	0.6 mm			0.8 mm			1.7 mm		
	Amount of Ni(II) adsorbed q (mg/lit)	qe-q	% Removal	Amount of Ni(II) adsorbed q (mg/lit)	qe-q	% Removal	Amount of Ni(II) adsorbed q (mg/lit)	qe-q	% Removal
10	1.33	1.68	40.18	1.13	1.53	34.20	0.94	1.40	28.40
20	2.09	0.92	62.75	1.75	0.91	52.50	1.47	0.87	44.22
30	2.48	0.53	74.69	2.12	0.54	63.85	1.82	0.52	54.74
40	2.77	0.24	83.11	2.43	0.23	72.95	2.08	0.26	62.50
50	2.94	0.07	78.02	2.60	0.06	78.02	2.21	0.13	66.46
60	3.01	-	90.58	2.66	-	80.05	2.34	-	70.13
70	3.01	-	90.58	2.66	-	80.05	2.34	-	70.13
80	3.01	-	90.58	2.66	-	80.05	2.34	-	70.13

It is evident from Fig. 4 that increase in particle size decreased the percentage of removal. At a fixed adsorbent dosage, the decrease in particle size increases the metal uptake. The increase in the uptake by smaller particles was due to the greater accessibility to pores and to the greater surface area for bulk adsorption per unit mass of the adsorbent. Similar trend had been observed on removal of Ni(II) by using *Pitchellobium dulce* Benth – A Kinetic Study [21]

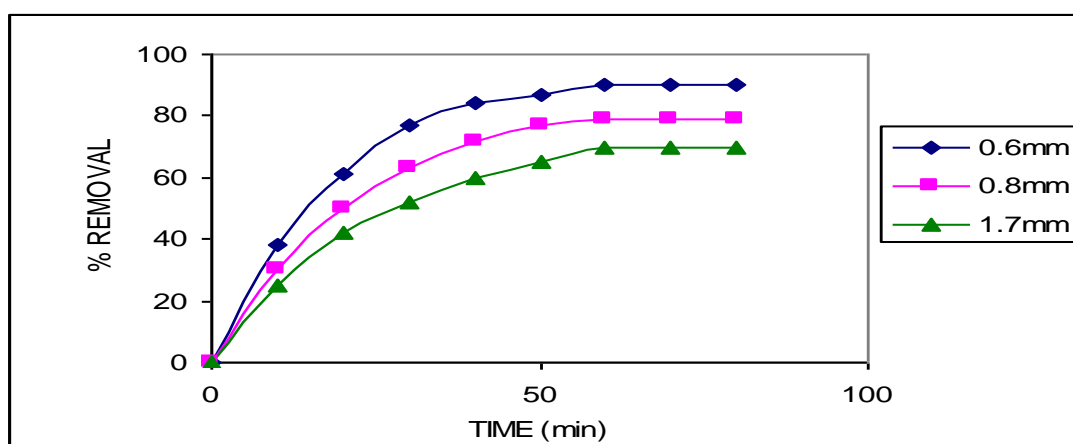


Figure 4: Relationship between particle size, % removal at different times

ADSORPTION ISOTHERM:

Isotherms relate metal uptake per unit weight of adsorbent to equilibrium adsorbate concentration in the bulk fluid phase. The Langmuir isotherm was based on the assumptions that maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface, the energy of adsorption was constant and there was no transmigration of adsorbate in the plane of the surface. The Langmuir isotherm was expressed in the following formula

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad \text{-----1}$$

Where C_e was the equilibrium Concentration (mgL^{-1}) q_e was the amount adsorbed at equilibrium time (mg/g), Q_0 and b are Langmuir constants related to adsorption capacity (mg/g) and energy of adsorption (L/mg), respectively. The data for Langmuir adsorption isotherm were given in Table 5. Regression analysis of the data was shown in Table 5, fitted well in Langmuir adsorption isotherm.

Table 5: Calculated values for the different initial concentrations and equilibrium concentrations to plot Langmuir Adsorption isotherm

Initial Concentration $C_i(\text{mg/l})$	Equilibrium Concentration $C_e (\text{mg/l})$	$Q_e (\text{mg/g})$	$C_e/q_e(\text{g/l})$
50	12.23	25.13	0.486
75	28.23	31.18	0.905
100	48.24	34.50	1.398

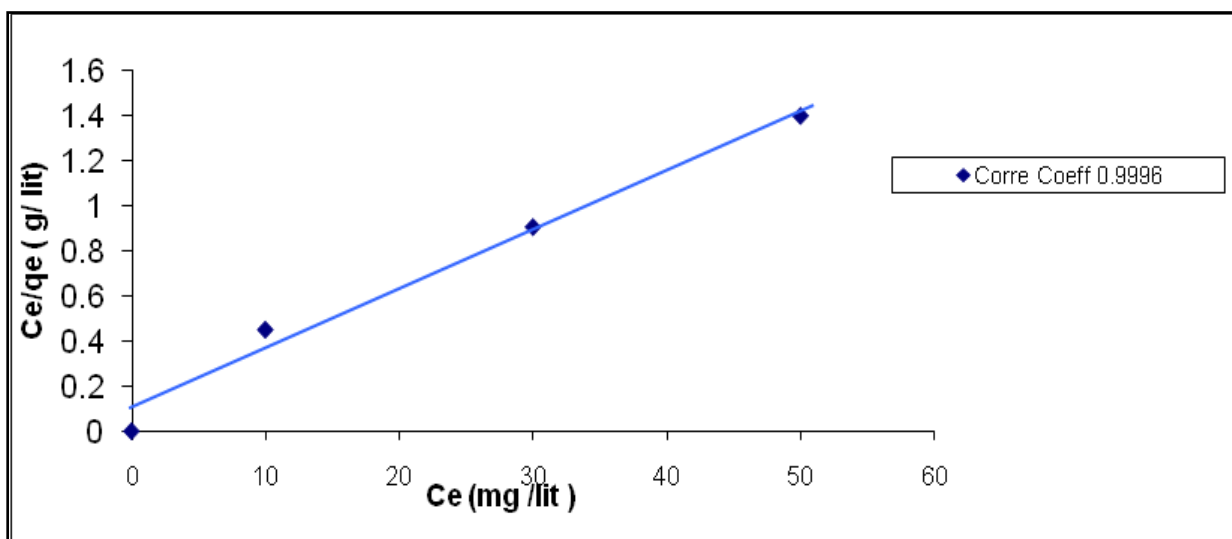


Fig.5: Langmuir isotherm showing initial concentration vs. equilibrium concentration

The Langmuir constants Q_0 and b calculated from the slope and intercept of the plot C_e/q_e vs C_e of Fig. 5, are $39.63 (\text{mg/g})$ and $0.138 (\text{mg/l})$, respectively. Comparison of these values with red mud [22] adsorption capacity Q_0 indicates that, Q_0 obtained for calcined brick powder adsorbent was greater than that of red mud. The essential characteristics of Langmuir are expressed in terms of a dimensionless constant separation factor R_L (Equilibrium Parameters) that is given by:

$$R_L = \frac{1}{1 + bC_i} \quad \text{-----2}$$

Where C_i was the initial concentration (mg L^{-1}) and b was the Langmuir constant. The values of R_L Table. 6, indicate the nature of isotherm.

Table 6. The Ranges of R_L Values for Comparison

R_L	Type of Isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

The characteristic, equilibrium parameter R_L of Langmuir isotherm was calculated and the values were 0.12, 0.08 and 0.06 for the metal ion concentration of 50, 75 and 100 mg/l , respectively, and all the values were between Zero and one, indicating the favorable adsorption of Nickel(II) on the adsorbent. The Freundlich isotherm is generally used for

mathematical description of adsorption in aqueous system and describes heterogeneous surface energies. The equation is expressed in logarithmic form as:

$$\log x/m = \log k_f + \frac{1}{n} \log C_e \quad \text{----- 3}$$

Where (x/m) was the amount adsorbed in mg L⁻¹, C_e was the equilibrium concentration (mg L⁻¹) and K_f and n were Freundlich constants. K_f [mg/g, L /mg] was the capacity of the adsorbent and n indicated the favorability of adsorption. The adsorption data obeyed Freundlich adsorption isotherm the plot of log x/m vs log C_e, from Fig. 6 is linear and Freundlich constants K_f and n obtained are 27.68 and 3.003, respectively. Freundlich constant K_f for Fly ash in natural and acid treated forms was 1472 and 2904 respectively [23].

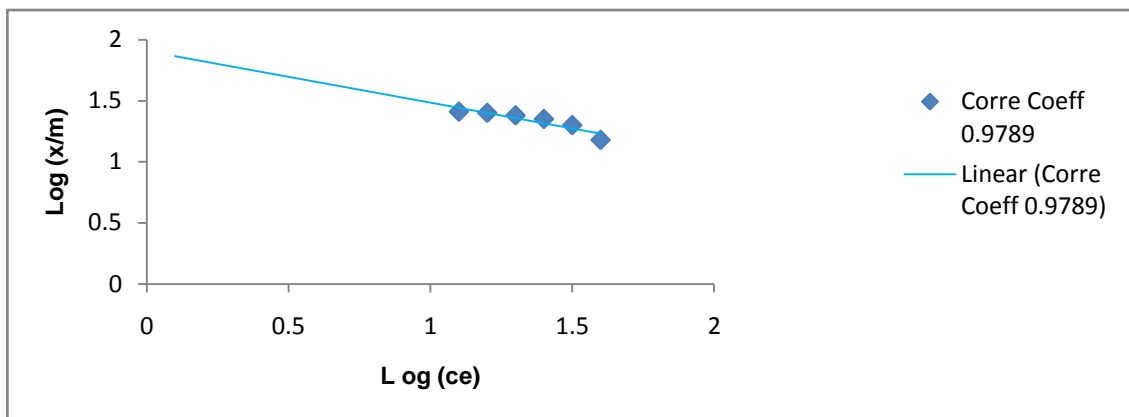


Fig. 6: Freundlich adsorption isotherm for the equilibrium concentration and adsorption rate

According to [24], the value of n between 2 and 10 indicate good adsorption. The calculated n value for the adsorption of Nickel was 3.00 showing good efficiency for Nickel adsorption by powder of calcined brick adsorbent.

ADSORPTION KINETICS: Effects of Ni (II) Concentration on Lagergren Rate Constant

The kinetics of Ni (II) adsorption followed the first order rate. Equation given by Lagergren was:

$$\log(q_e - q) = \log q_e - \frac{K_{ad}}{2.303} t \quad \text{----- 4}$$

Where q and q_e were the amounts of metal ion adsorbed (mg/g) at time t (min) and at equilibrium time, respectively and K_{ad} was the rate constant of adsorption (min⁻¹). From the Fig.7 it was evident that, the linear plots of log (q_e-q) Vs time at different concentrations show the applicability of the Lagergren equation

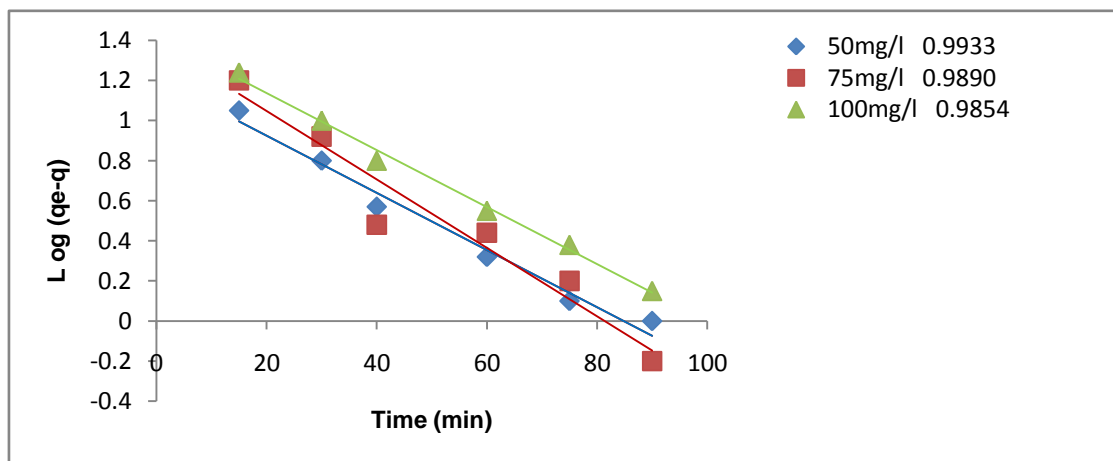


Fig.7: Lagergren equation showing relationship between Log concentrations and time of adsorption for different concentrations of nickel(II)

The adsorption data were fitted in the Lagergren equation (4) the straight line plots of log (q_e-q) vs time for Nickel(II) concentrations of 50,75 and 100 mg/l are shown in the slope of the plots were given in the Table 7. For Nickel Ion adsorption, the initial concentration did not have significant effect on rate constant. [10]

Table -7 Lagergren rate constant for different initial Concentrations of nickel(II)

Ni(II) mg/l	Rate Constant K_{ad} (min^{-1})
50	4.05×10^{-2}
75	4.26×10^{-2}
100	3.98×10^{-2}

The results indicated that the metal ion concentration has no significant effect on the rate. These values are comparable with the results obtained by [25].

Effect of Particles Size on Lagergren Rate Constant

Table 8 . Lagergren rate constants calculated for different particle sizes (mm)

Particle size (mm)	Rate Constant K_{ad} (min^{-1})
0.6	6.01×10^{-2}
0.8	5.21×10^{-2}
1.7	4.37×10^{-2}

The effect of particle size on the rate of adsorption was shown in Fig 8. And the rate constant K_{ad} values calculated are given in Table 8. For the adsorption of Ni (II), increase in particle size from 0.6 mm to 1.7 mm decreased the rate of adsorption from 6.01×10^{-2} to $4.37 \times 10^{-2} \text{ min}^{-1}$. The higher rate of metal uptake by smaller particles was due to greater accessibility to pores and greater surface area for bulk adsorption per unit weight of the adsorbent have stated that the breaking up of larger particles to form smaller ones opens some tiny sealed channels that will be available for adsorption and therefore the rate of uptake by smaller particles was higher than that larger particle.

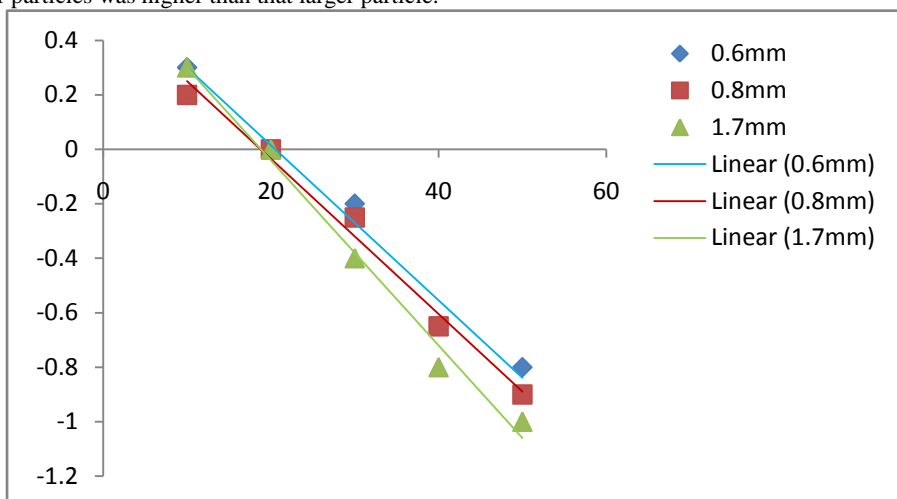


Fig. 8. Relationship between different particle size and time of adsorption.

IV. CONCLUSION

It is clear from the results that heavy metal like divalent nickel removal with the above adsorbent appears to be technically feasible, eco-friendly and has high efficacy. Also it helps in reduction of waste generation. In the present study the adsorbent proved to be good adsorbent which was evident with the adsorption data obeying the Langmuir and Freundlich isotherms. The equilibrium parameter R_L in Langmuir isotherm, the Langmuir constants for nickel (II) are $Q= 39.63 \text{ mg/g}$ and $b= 0.138 \text{ L/mg}$, by PCB and Freundlich adsorption constants K_f for nickel (II) is 27.68, and $n=3.003$ by PCB indicated that the adsorption of Ni (II) on PCB was favorable. The kinetics of the adsorption of the metal ions also obeyed Lagergren equation. This results shows that PCB has a considerable potential as an adsorbent for the removal of nickel (II) from aqueous solutions.

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