Removal of Nickel in Wastewater Using Bagasse Fly Ash

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Abstract- *The bagasse fly ash, an industrial solid waste of sugar industry, was used for the removal of nickel from wastewater. As much as 89% removal of cadmium and nickel is possible in about 60 min, respectively, under the batch test conditions. The removal in a nickel has used for various operating variables that is ph, particle size, initial concentration, adsorbate concentration .20mg of the concentration occur in the maximum adsorption of nickel. It has 2.6 value of ph. A dose of 10g l-1 of adsorbent was sufficient for the optimum removal of both the metal ions. The material exhibits good adsorption capacity and the adsorption data follow the Freundlich model better then the Langmuir model. The adsorption of the metal ions increased with increasing temperature indicating endothermic nature of the adsorption process. We done the kinetic studies with pseudo first order, pseudo second order, intraparticle diffusion and Elovich kinetic model. The optimum level of adsorption can be carried out in the acidic medium at pH 2.6.*

Keywords: Adsorption studies, Bagasse fly ash, Kinetic studies, Langmuir and Freundlich adsorption isotherms.

I. INTRODUCTION

In the world wide concern the heavy metals pollution is affected the environment. The heavy metals are cadmium, zinc and nickel, lead. Even at low concentrations ,these metals are toxic to organisms including humans Nickel(II) ion is one such heavy metal frequently encountered in waste water streams such as non ferrous metal, mineral processing, electroplating porcelain enameling, copper sulfate manufacture, battery and accumulator manufacturing, dyeing operation, electroplating, nuclear power plants, aerospace industries, production of paints.The maximum permissible concentration of nickel in effluents in the soil concentration of nickel is 2.194 mg/kg. Electroplating process wastewater: maximum for any 1 day is 4.1 mg/L and average of daily values for four consecutive monitoring days shall not exceed 2.6 mg/L. The MCLG (maximum contamination level) for nickel has been set at 0.1 ppm (parts per million) because EPA(environmental protection agency) because this level of protection would not cause any of the potential health problems. Higher concentrations of an Ni cause the cancer of an lungs, nose and bone. Dermatitis(Ni itch) is the most frequent effect of exposure to Ni such as coins and jewellery, Acute poisoning of Ni(II) causes head ache, etc. A number of methods available for the removal of metal ions from aqueous solutions are flocculation, sorption, activated carbon adsorption and membrane processes. Some techniques have certain dis-advantages, such as high capital and operational cost of treatment and disposal of the residual metal sludge. Cost of these process are rather expensive, the use of agricultural residues or industrial by-product having biological activities have been received with considerable attention. In recent years, a number of adsorptive materials such as rice husk, saw dust, moss peat, activated carbon, green algae, a sugar industry waste, fly ash, chitin, bone char, lignite, zeolite, Clinoptilolite and all Bio-masses.

II. MATERIALS AND METHODS

All chemicals and reagents used were of analytical grade and were obtained from Raechem chemicals, chennai. Stock solutions of nickel were prepared using nickel nitrate in distilled water. A pH meter was used for pH measurements and rotary shaker used for the agitation purpose.

2.1 Adsorbent development

Baggase fly ash, a solid waste material of the sugarcane, was collected from a local juice shop at Hosur, TN, India. The material was burnt to convert them into ash form, then treated with hydrogen peroxide at 60°C for 24 h to oxidize the adhering organic matter. Adsorbing capacity increases in twice the time, heated at 100°C, powdered, and sieved to produce desired particle size (6-16,16-60,60-100-mesh sizes).

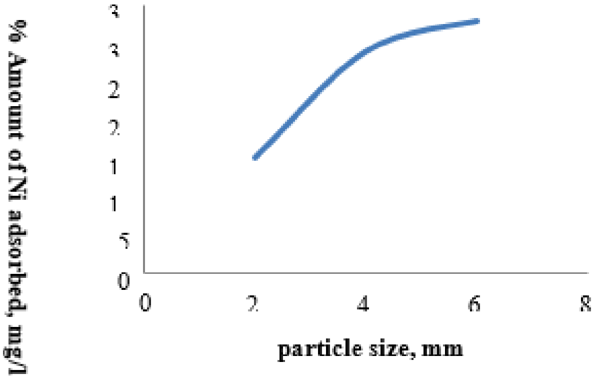
2.2 Batch adsorption:

The experiments were carried out in a series of conical flask having 250 ml capacity covered with aluminium foil to prevent contamination and rotary shaker was used for the uniform rotational speed. The effect of contact time (30,45,60 mins), concentration (30mg/l,40mg/l,50mg/l), solution pH (3,8.5,12.5)i.e acidic, neutral, basic solutions, adsorbent dose (5g/l,10g/l,15 g/l), particle size (6-16,16-60,60-100mm), and temperature (30°C, 45°C and 50°C) were studied. After prescribed contact times, the solutions were filtered and the concentrations of metal ions were determined by atomic absorption spectrometry and uv-visible spectroscopy.

2.2.1 Effect of particle size:

As the mesh size increases particle size decreases. Therefore, surface area is maximum for smaller sized particle. adsorption process is inversely proportional to the particle size. Adsorption in the order of 60-100 >16-60>6-16 mm mesh size. The optimum particle size for the adsorption process is 60-100mm.

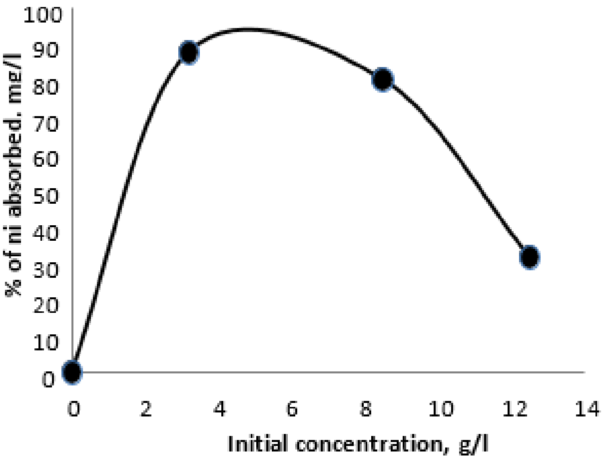
Fig. 2.2.1 effect of particle size on adsorption of Nickel (II)



2.2.2 Effect of Initial Concentration:

The initial concentration provides an important driving force to overcome all mass transfer resistance of nickel between the aqueous and solid parts. The initial concentration of the solution vary from (30-50 mg/l).the adsorption capacity increased up to 60mins after that it decreased gradually and it ranges from (60-75%).according to the results, the adsorption equilibrium reaches at 60 mins. The amount of nickel adsorbed per unit mass of bio-sorbent increased with the initial concentration of the metal ions. The optimum initial concentration was found to be 30 mg/l.

Fig. 2.2.2 Effect of initial concentration on adsorption of Nickel (II)



2.2.3 Effect of contact time:

The contact time parameter was studied at the initial concentration of 50mg/l. The time increases the adsorption process also increases gradually. The amount of nickel absorbed is maximum at 60 mins after that it desorbed little amount of nickel gradually. The optimum time for the removal of nickel using bagasse fly ash was found to be 60 mins.

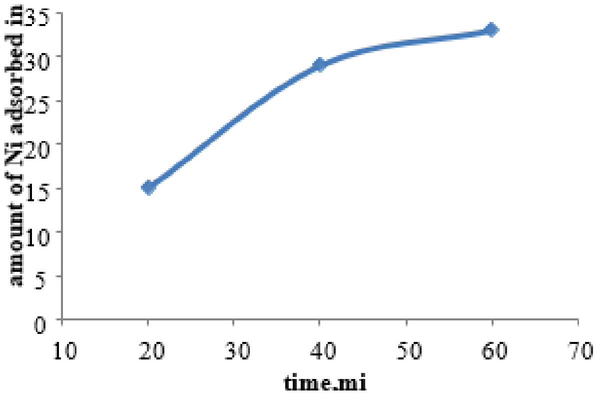


Fig.2.2.3 Effect of contact time on adsorption of Ni (II)

2.2.4 Effect of pH:

The pH of the solution can be varied using the acidic and basic solutions like HCL and NaOH with the 1N of solution. As the pH increases the amount of nickel absorbed decreases. Therefore, pH of the solution is inversely proportional to amount of the nickel absorbed. Basic solution having a minimum amount of nickel removing capacity. The optimum pH for the removal of the nickel in waste water is in acidic medium with the maximum efficiency of 88%.

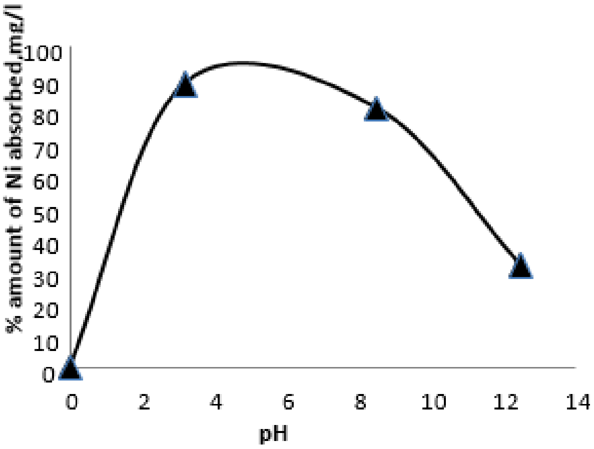


Fig. 2.2.4 Effect of pH on adsorption of Ni (II)

2.2.5 Effect of temperature:

The effect of temperature on the adsorption of metal ions are almost constant at lower concentration while it is increased at higher concentrations . The adsorption followed in the order 30°C <45°C <60°C.In endothermic nature the adsorption process increase with the increasing an temperature. of layers around the adsorbent. Increasing the mobility of the cations and produce number of active sites around the surface of the adsorbent. Temperature is directly proportional to adsorption process.

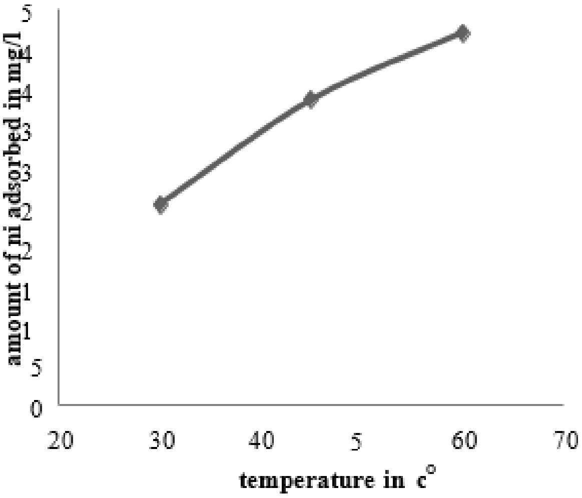


Fig 2.2.5 effect of temperature on adsorption of nickel (II)

2.2.6 Effect of adsorbent dosage:

The effect of bagasse fly ash on the sorption of nickel(II) ion was studied at the pH of 5.6 and 500 mgL-1 initial nickel(II) ion concentration. The sorbent dose was varied between 5 to 15 gL-1. The increase in adsorbent dosage resulted in an increase from 33 to 79% in adsorption of nickel(II) ions. This is because of the availability of more and more binding sites for complexation of nickel (II) ions.

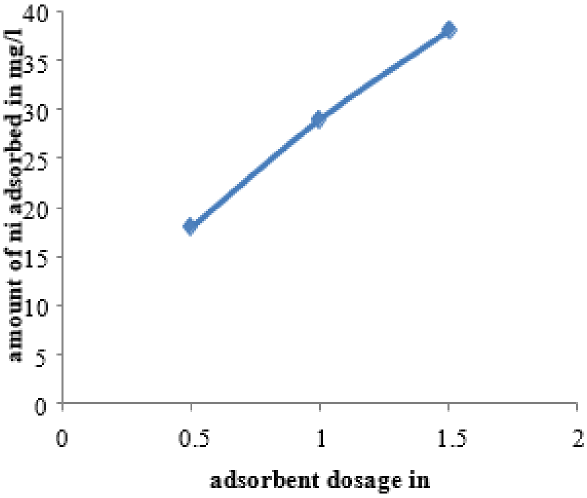


Fig 2.2.6 effect of adsorbent dosage on nickel(II) ion.

III. ADSORPTION ISOTHERM

The purpose of the adsorption isotherm is to relate the adsorbate concentration in the bulk and the adsorbed amount at the interface. the simplest adsorption isotherm is based on the assumption that every adsorption site is equivalent and that the ability of a particle to bind there is independent of whether or not adjacent sites are occupied. Langmuir and Freundlich isotherm are commonly used in the batch adsorption studies. It can be classified as two types of the Freundlich which is the Langmuir Model and the bio mass straightly increases the time of equilibrium. The Freundlich expression is an empirical equation based on sorption on a heterogenous surface. The Langmuir isotherm assumes that a monolayer layer is formed when biosorption take place and there is no interaction between the molecules.The metal adsorbed on adjacent binding sites. The results from the obtained model is Langmuir and Freundlich.

3.1 Langmuir isotherm model:

It relates the coverage or adsorption of molecules on the solid surface has a fixed temperature at gas pressure or concentration .Here we are maintaining the room temperature 28°C as fixed temperature.

$$\theta = \frac{\alpha c}{1 + \alpha c}$$

Table 3.1 adsorption of nickel(II) ion on bagasse waste in various conc. at room temperature

S.No	Initial concentration (mg/l)	Amount adsorbed (mg/l)	Fractional coverage area(Ө)
1	100	25	25
2	200	127	63.5
3	300	234.9	78.3
4	400	354	88.5
5	500	460	92
6	600	568.98	94.83
7	700	674.1	96.3
8	800	775	96.875
9	900	874.8	97.2
10	1000	974.4	97.44

Fig 3.1 langmuir isotherm model relating coverage area with various concentration

3.2 Langmuir equation:

$$\frac{1}{q_e} = \frac{1}{Q_e} + \frac{1}{bQ_eC_e}$$

Where Ce is the equilibrium concentration (mgL-1) , qe is the amount adsorbed at equilibrium (mg g-1),Qe and b are the Langmuir constants related to adsorption capacity and energy of adsorption. The linear plot of 1/qe vs 1/Ce shows that the adsorption obeys the Langmuir model. b and Qe were determined from the slope and intercept of the plot.

Table 3.2 langmuir isotherm model at equilibrium

S No	Initial concentration in mg/L	q_e Amount adsorbed in mg/L	1/qe	1/Ce
1	100	25	0.04	0.01
2	200	127	0.00787	0.005
3	300	234.9	0.004257	0.0033
4	400	354	0.002824	0.0025
5	500	460	0.00217	0.002
6	600	568.98	0.001757	0.00166
7	700	674.1	0.001483	0.00142
8	800	775	0.00129	0.00125
9	900	874.8	0.001143	0.0011
10	1000	974.4	0.001026	0.001

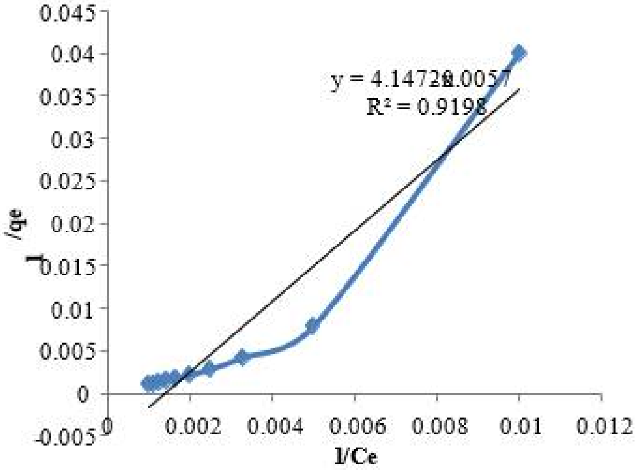


Fig 3.2 langmuir isotherm model for equilibrium Therefore, Qe=0.005 and b=48.2276

3.3 Freundlich isotherm model:

At low pressure, adsorption is directly proportional to the pressure.the logarithmic form of Freundlich isotherm was given by

$$\log q_e = \log K_f + \frac{1}{n} log c_e$$

Where Kf and Ce are the Freundlich constants.

Table 3.3 freunlich isotherm model at equilibrium

S No	Initial concentration(mg/l)	Amount adsorbed q_e(mg)	Log C_e	Log q_e
1	100	25	2	1.3979
2	200	127	2.3010	2.1038
3	300	234.9	2.477	2.3708
4	400	354	2.602	2.5490
5	500	460	2.6989	2.6627
6	600	568.98	2.778	2.7550
7	700	674.1	2.845	2.8287
8	800	775	2.903	2.8893
9	900	874.8	2.9542	2.9419
10	1000	974.4	3	2.9887

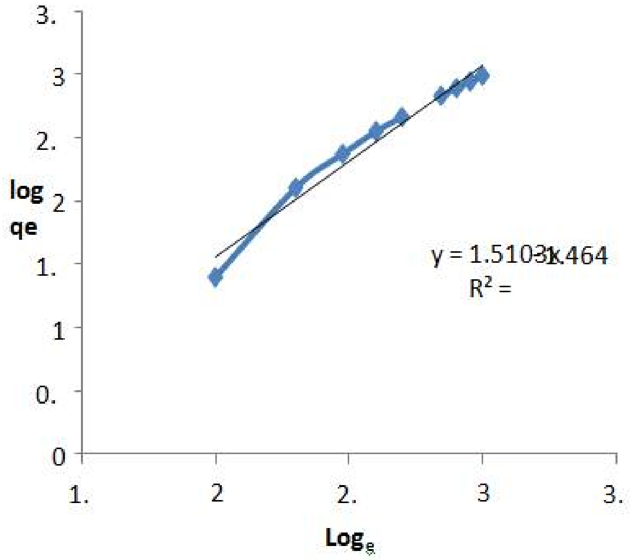


Fig 3.3 freundlich model graph at various concentration

$$\log q_e = \log K_f + \frac{1}{n} log c_e$$

According to the regression line,
Log K_f =-1.471
Taking exponential on both sides, we get K_f = 0.3829

1/n log C_e =1.513 therfore n=0.6609

IV. RESULTS AND DISCUSSION

Kinetic Studies:

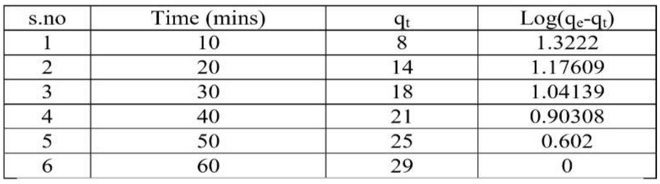
Three most common kinetic models that are pseudo-first order, pseudo-second order and intraparticle diffusion were used for the sorption kinetics of Ni(II) on bagasse fly ash.

4.1 pseudo-first order system:

$$\log(q_e - q_t) = log q_e - \frac{K_1 t}{2.303}$$

Where q_e is the amount of metal ion sorbed (mg g^{-1}) at equilibrium , q_t is the amount of metal ion sorbed at any time (mins) and K_1 is the pseudo-first order reaction rate constant for sorption (min^{-1}). q_e=29 mg/g.

Table 4.1 pseudo-first order kinetics



s.no	Time (mins)	q_t	Log(q_e-q_t)
1	10	8	1.3222
2	20	14	1.17609
3	30	18	1.04139
4	40	21	0.90308
5	50	25	0.602
6	60	29	0

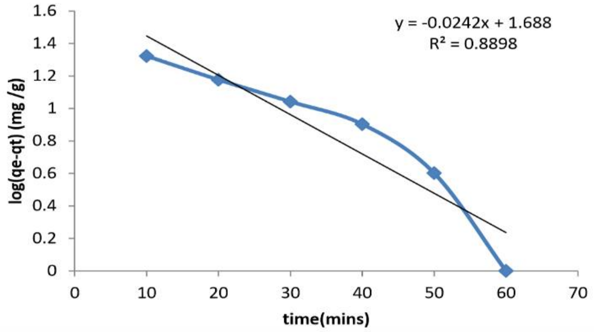


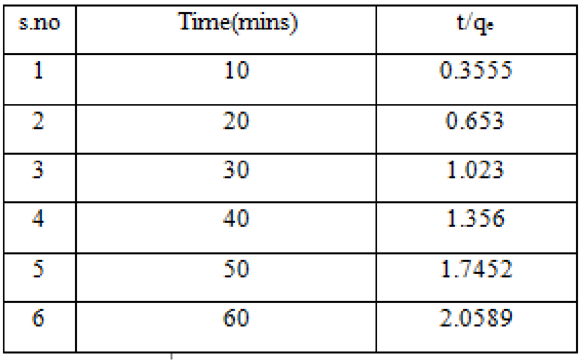
Fig 4.1 time vs log(q_e-q_t) plot for pseudo first order kinetics

4.2 pseudo-second order system :

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e{}^2}$$

Where q_e is the amount of metal ion sorbed (mg g^{-1}) at equilibrium, q_t is the amount of metal ion sorbed(mg g^{-1}) at any given time(mins) and K_2 is the pseudo second order rate constant for sorption (g mg^{-1} min^{-1}).The second order kinetics was obtained by plotting time(t) versus t/q_t.K_2,q_e and R^2 can be calculated using the slope and intercept of the each model respectively.

Table 4.2 pseudo-second order kinetics



s.no	Time(mins)	t/q_e
1	10	0.3555
2	20	0.653
3	30	1.023
4	40	1.356
5	50	1.7452
6	60	2.0589

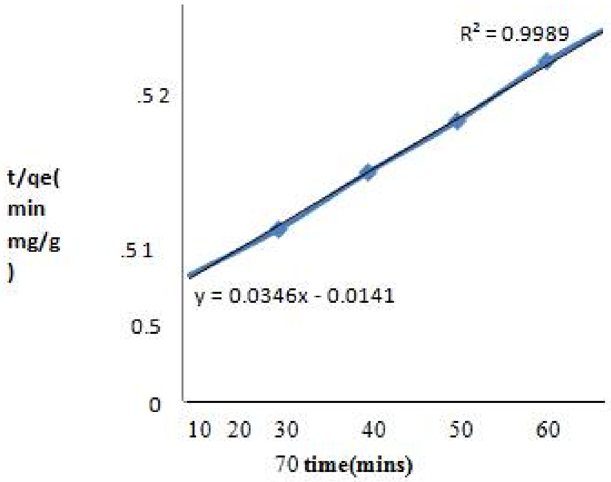


Fig 4.2-time vs t/q_e for pseudo-second order kinetics

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 {q_e}^2}$$

q_e=29.4117 mg/g

K_2=1.617$\times 10^{-5}$ (g $mg^{-1}min^{-1}$)

4.3 Intraparticle diffusion model:

Diffusion of kinetic model Ni(II) ions from its aqueous medium.This model is expressed by the following equation

$$q_t = K_{int} t^{1/2} + c$$

Where c is the intercept and related to the thickness of the boundary layer and K_{int} (mol$L^1min^{-1/2}$) is the intraparticle diffusion rate constant.The values of these constants can be calculated using the slope and intercept of the Graph

Table 5.3 for Intraparticle diffusion model

S No	Time(mins)	$T^{1/2}$	q_t (mg g^{-1})
1	10	3.1622	8
2	20	4.472	14
3	30	5.477	18
4	40	6.324	21
5	50	7.071	25
6	60	7.745	29

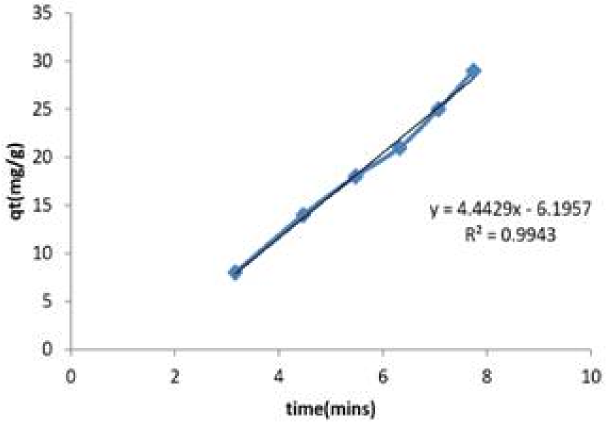


Fig 4.3 time vs q_t for intraparticle diffusion model

$$q_t = K_{int} t^{1/2} + c$$

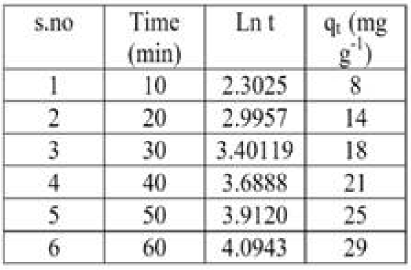
k_{int} = 4.442 c = -6.195

4.4 Elovich model:

The elovich kinetic equation is used to describe thekinetics of the chemisorptions on heterogeneous surfaces and is given as follows.

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t)$$

Where q_t is the amount of Ni(II) sorbed (mol L^{-1}) at time(t),α and β are known as the elovich coefficients, α represents the initial sorption rate(mol L^{-1} min^{-1}) and β is related to the extent of the surface coverage and activation energy for chemisorptions (g min^{-1}) respectively. The elovich coefficient were calculated from the linear plot of q_t versus ln .



s.no	Time (min)	Ln t	q_t (mg g^{-1})
1	10	2.3025	8
2	20	2.9957	14
3	30	3.40119	18
4	40	3.6888	21
5	50	3.9120	25
6	60	4.0943	29

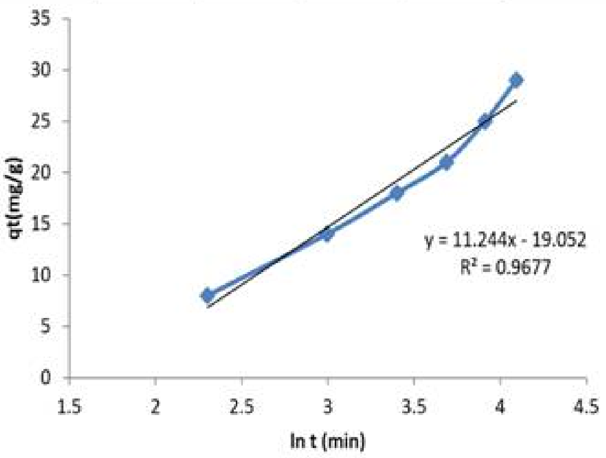


Fig 4.4 ln t vs q_t for elovich kinetic model

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t)$$

β=0.0889 α=2.0655

V. CONTINUOUS OPERATION

5.1 Column study:

A cylindrical glass column having 3.5 cm in diameter and 18 cm in length were filled with 2 g of bagasse fly as ash. The sieved sorbent having 150-200 mesh size was made of the slurry form and filled inside the cotton cloth. The height of the packed column is 10cm.The solution having the fixed concentration (5 g/L^{-1}) with pH 5.6 for Ni(II) of sorbate solution were loaded continuously on the packed bed column and allowed it to percolate through a column using a peristaltic pump.The solution leaving at the end of the column was collected at constant volume and time intervals and the samples were analysed by uv-visible spectrophotometer to determine the amount of sorbate retained on the packed column.

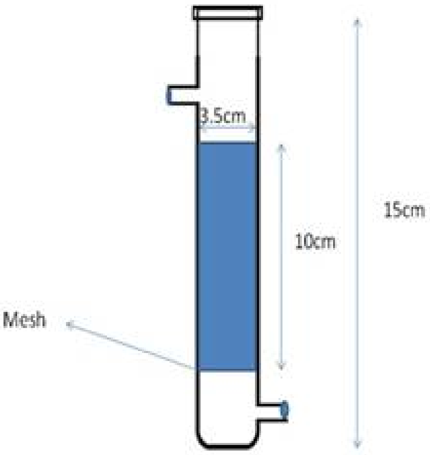


Fig 5.1 packed bed column

Fig 5.2 continous operation using peristaltic pump

5.2Continous operation:

1. Flow rate
2. Ph

5.2.1 Effect of Flow rate:

Flow rate is the important parameter while doing a continous operation study.In industries most of the applications are based on the continous process.flow rate is directly proportional to the adsorption process. There are three different flowrates are 0.3,0.388 and 0.5 ml/s by varying the rpm of the peristaltic pump of 100,125 and 150 rpm.

Table 5.2.1 effect of flow rate

S No	Time (min)	100 rpm	125 rpm	150 rpm
1	20	21	31	39
2	40	33	45	51
3	60	46	54	67
4	80	51	65	81

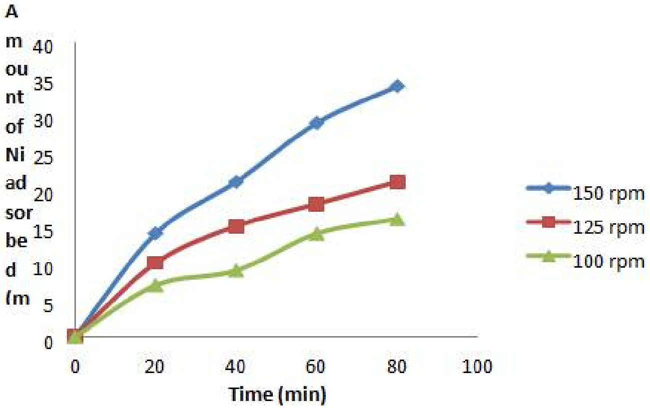


Fig 5.2.1 effect of flow rate

5.2.2 Effect of pH:

The pH of the solution can be varied using the acidic and basic solutions like HCL and NaOH with the 1N of solution. As the pH increases the amount of nickel absorbed decreases. Therefore, pH of the solution is inversely proportional to amount of the nickel absorbed. Basic solution having a minimum amount of nickel removing capacity.The optimum pH for the removal of the nickel in waste water is in acidic medium(6.2) with the maximum efficiency of 69.23%.

Table 5.2.2 effect of pH

S No	Time(min)	Amount of Ni adsorbed in mg/l	
		Acidic	neutral
1	20	46	39
2	40	69	51
3	60	75	67
4	80	90	81

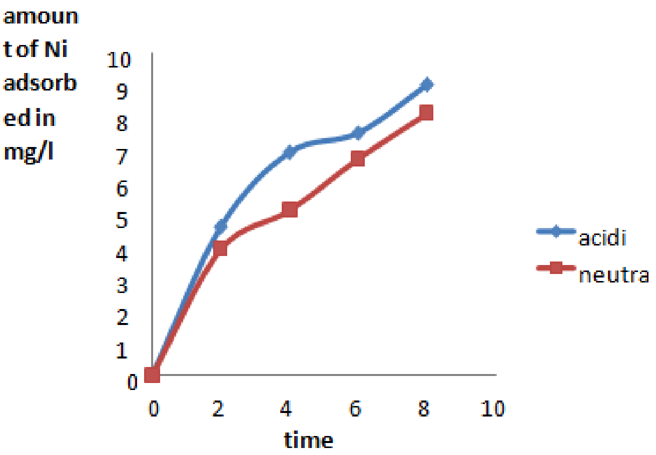


Fig 5.2.2 effect of pH

On the basic medium, it has been coagulated to gel form. Due to the reaction with sodium hydroxide(NaOH) at the pH of 12.6.

5.3 Langmuir equation:

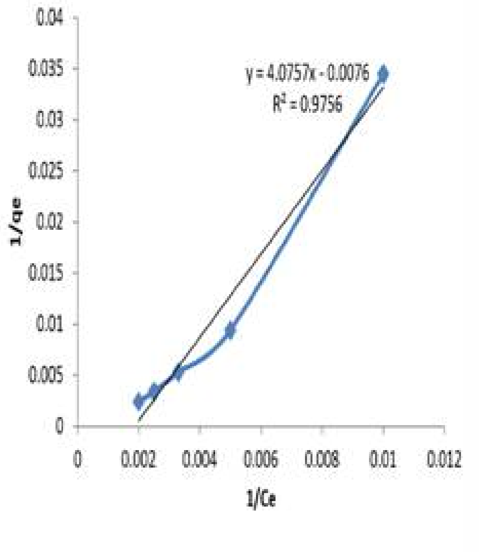
Fig 5.2.3 Basic medium atpH 12.6

$$\frac{1}{q_e} = \frac{1}{Q_e} + \frac{1}{bQ_eC_e}$$

Where C_e is the equilibrium concentration (mgL^{1}) , q_e is the amount adsorbed at equilibrium (mg g^{-1}),Q_e and b are the Langmuir constants related to adsorption capacity and energy of adsorption. The linear plot of $1/q_e$ vs $1/C_e$ shows that the adsorption obeys the Langmuir model. b and Q_e Where Ce is the equilibrium concentration (mgL1) , qe is the amount adsorbed at equilibrium (mg g-1),Qe and b are the Langmuir constants related to adsorption capacity and energy of adsorption. The linear plot of 1/qe vs 1/Ce shows that the adsorption obeys the Langmuir model. b and Qe were determined from the slope and intercept of the plot.

Table 5.3.1 langmuir isotherm model at equilibrium

s.no	Initial concentration in mg/L	q_e Amount adsorbed in mg/L	$1/q_e$	$1/C_e$
1	100	29	0.03448	0.01
2	200	106	0.0094	0.005
3	300	186	0.0053	0.0033
4	400	292	0.0034	0.0025
5	500	405	0.0024	0.002



b=35.056

5.4 Freundlich isotherm model:

At low pressure, adsorption is directly proportional to the pressure.the logarithmic form of freundlich isotherm

$$\log q_e = \log K_f + \frac{1}{n} log c_e$$

Where K_f and C_e are the freundlich constants.

Table 5.4.1 freunlich isotherm model in equilibrium condition

s.no	Initial concentration(mg/l)	Amount adsorbed q_e(mg)	Log C_e	Log q_e
1	100	29	2	1.4623
2	200	106	2.3010	2.0253
3	300	186	2.477	2.2695
4	400	292	2.602	2.4653
5	500	405	2.6989	2.6074

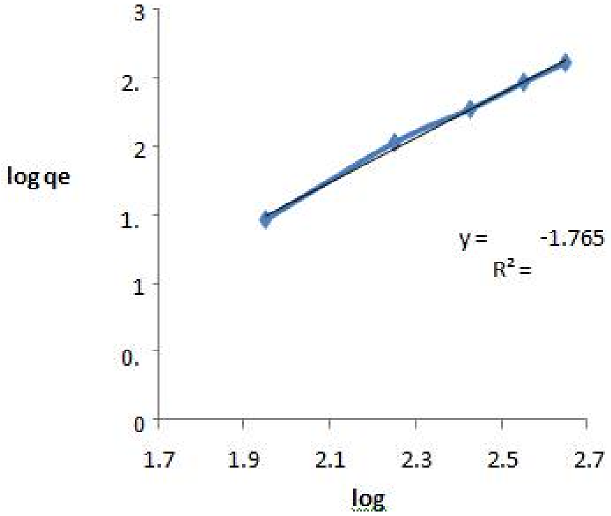


Fig 5.4.1 freundlich model graph at various concentration

$$\log q_e = \log K_f + \frac{1}{n} log c_e$$

According to the regression line,

Log K_f =-1.765

Taking exponential on both sides,we get K_f = 0.17118
1/n log C_e =1.627 therefore n=0.6146

VI. CONCLUSION

The adsorption process was carried using bagasse fly ash in both batch and continous operation.The results shows that the adsorption is maximum at the acidic medium (Ph=2.6) with the removal of 89% of Nickel(II) ion in the batch operation and 90% removal in continous operation. Both the operation follows the freundlich adsorption isotherm model and pseudo second order kinetics.

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