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Kinetic and Isotherm Modeling of Adsorption of Ni (II) from Aqueous Solutions onto Powder of Papaya Seeds

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Abstract- The powder of papaya seeds (PPS) is used as an adsorbent for the removal of heavy metal like Ni (II) from aqueous solutions was studied using batch tests. The influence of physico-chemical key parameters such as the initial metal ion concentration, pH, agitation time, particle size and the adsorbent dosage, has been considered in batch tests. The optimum results were determined at an initial metal ion concentration which was 50mg /lit, pH =3, agitation time – 90 min, an adsorbent dose (125 mg/50 ml) and the particle size (0.6 mm). The % adsorption, Langmuir constants [$Q_{0=}$30.58(mg/g) and b=0.5092(L/mg)] Freundlich constants ($K_{f=}$28.13 and n=3.43), Lagergren rate constant (K_{ad} (min^{-1}) =5.38 x 10^{-2}) for Ni (II) 50 mg/lit were determined for the adsorption system as a function of sorbate concentration. The equilibrium data obtained were tested using Langmuir, Freundlich adsorption isotherm models, and the kinetic data obtained were fitted to pseudo first order model.

Index Terms- Adsorption isotherms, Kinetics, Ni (II) ions, Powder of papaya seeds (PPS)

I. Introduction

One of the important toxic metals, Nickel (II) finds its way to the water bodies through effluents from industries. It is present in the effluents of silver refineries, zinc base casting and storage battery industries. As it resists corrosion even at high temperature, it can also be used in gas turbines, rocked engines and desalination plants. It is also used in coinage and costume jewellery. Skin contact with nickel causes a painful disease called "nickel itch" which leads to death, [1].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 [2]. 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 [3]. The toxic nature of fish, crops and algae was also reported [4]. Perinatal toxicity associated with nickel chloride exposure on female rats was also reported [5]. 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 [6] agricultural solid waste [7] peanut hull [8] and Flyash [9].The biosorption of nickel was maximum at a biosorbent concentration of 4 g/l and at pH of 5.0. [10] reported the above results in conclusion of their study on the removal of Ni (II) from aqueous solution using the powdered leaves of *Azadirachta indica*. The modern technology developed by the man, not only depleted the wealth of nature but also created environmental degradation. The problem of water pollution due to heavy metals and their impact on environment is presently the focus of international attention. In choosing a waste water treatment technology, factors like nature of pollutants, permissible limits and economy of the treatment method have to be considered. Recent research of selective and sensitive methods for the determination of metals in water at trace levels. Among available methods, adsorption appears to have least adverse effects. The use of waste material from industries and agriculture for the removal of metal ions which reduces the treatment cost, and also provides a solution for the solid waste management of the industries. Most of the industries cannot afford to use conventional wastewater treatment methods owing to their high cost. In an effort to evolve a useful **u**ser-friendly, **e**co-friendly and **e**conomical process, the present study was taken up. The present study includes the adsorption studies on Nickel (II) using powder of papaya seeds. The efficiency and kinetics of this adsorbent was studied and maximum adsorption and lowest equilibrium time for this adsorbent was recorded. The present work helps the individual organizations to remove the excess concentrations of the Ni (II) from their effluents within their premises without much effort and time.

II. Research Elaborations

A. Adsorbent

Easy availability, economical to use and proven potential for other metals, have been the reasons for selection of this adsorbent Powder of papaya seed was used to adsorb Nickel (II). It was prepared by collecting the seeds from local market. Papaya trees are widely cultivated throughout India. The fruits were popular for their medicinal value. The seeds of the fruits were collected, then cleaned thoroughly with distilled water and soaked for 24 hours in distilled water. The soaked seeds were sun dried and powdered. The powder was screened to select 0.6mm sized particles as they were very effective in the removal of metals.

B. Measurement of pH of the adsorbent

Five grams of adsorbent powder was taken into a 1000 ml beaker. To this 150ml of freshly boiled and cooled water was added and then heated to boiling. The contents were digested for ten minutes and kept 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 in [11].

C. 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 analysis. 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 to this 5 ml of 1% HNO_3 was added to it immediately. Then the contents were made up to 1000 ml with double distilled water.

D. Preparation of Metal Ion Solutions

Spectrophotometric analysis was adopted to estimate Nickel (II) by using dimethylglyoxime (DMG). Different standard solutions containing less than 100 mg /lit 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 up to 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 heavy metal concentrations were expressed in mg/lit while those of the concentration equilibrium, equilibrium time, and adsorption capacity etc., were compared with the Langmuir and Freundlich isotherms.

E. Batch Equilibrium Method

All experiments were carried out at (27^0C) in batch mode. Batch mode was selected because of its simplicity and reliability. The experiments were carried out of taking 50 ml metal ion sample and known amount of the adsorbent in a 100 ml Stoppard conical flask. The flasks were agitated at 160 rpm for predetermined time intervals using a mechanical shaker at room temperature (27^0C). Control experiments were conducted without absorbent to given correction for metal ion adsorption on the walls of the container.

III. RESULTS

A. Effect of pH

Studies were carried out to obtain optimum pH of the adsorption of Ni (II) using 125mg of PPS adsorbent in 50 ml solution of 50mg/lit of Ni (II) Concentration adjusted to different pH values from 2 to 9. The solutions after equilibration were centrifuged and analyzed for Ni (II) content. The results obtained were shown in Fig.1. Maximum removal of 95.96 per cent was found to decrease with increase in pH up to 6.0.Since the aim of the work is to suggest a phenomenon for commercial purpose, it was decided to maintain the pH value at 3.0 for this experiment. Many authors reported maximum adsorption of Ni (II) in the pH range of 3-6.The study on optimum pH value with rice husk and saw dust reported to be 3.5 to 4.0 [12]. The results obtained for the adsorption of Ni (II) on powder of papaya seed adsorbent were in good agreement with the literature.

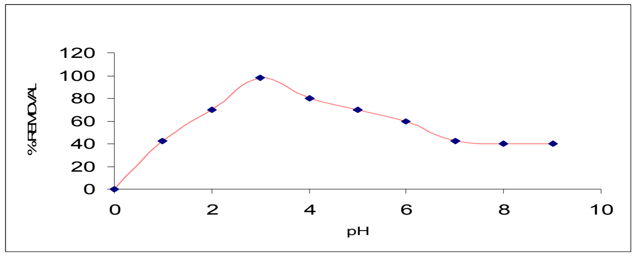

Fig. 1 Relation between pH and % removal of Nickel (II)

B. Effects of equilibrium time and initial metal ion concentration

Equilibrium experiments were carried out by agitating 50 ml of different concentrations of Ni (II) solutions (50, 75 and 100 mg/l) adjusted to pH 3.0 with 125 mg of adsorbent. After equilibrating for different periods, the solutions were centrifuged and analyzed for Ni (II) content. Nickel (II) ion adsorption as a function of time and different concentrations were shown in Table 1. For maximum removal of Nickel (II) by the adsorbent, the solutions should be equilibrated for 90 min. irrespective of the initial concentration. The amounts of Nickel (II) adsorbed were 19.19; 24.98; and 28.91 mg/g for initial Ni (II) concentrations of 50, 75 and 100 mg /lit, respectively. It was evident from Fig.2 that for maximum adsorption the solutions were equilibrated for 120 min., the rate of uptake was rapid in the beginning and became slow in the later stages and reached saturation at 90min. 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 decreased. The formation of monolayer of Ni (II) ions on the outer surface of the adsorbent was inferred, based on the observation that the curves shown in Fig. 2 are single, smoother and continuous. Similar results were reported for Nickel (II) adsorption by [13] for a fruit of *Leucaena glauca* Benth., was 97.62% and the per cent removal decreased with an increase in the initial metal ion concentration.

Table 1	Concentration of Nickel (II) in mg/lit								
	50 mg/lit			75 mg/lit			100 mg/lit		
Agitation time in minutes	Amount of Ni(II) adsorbed q (mg/lit)	qe-q	% Removal	Amount of Nickel (II) adsorbed q (mg/lit)	qe-q	% Removal	Amount of Nickel (II) adsorbed q (mg/lit)	qe-q	% Removal
15	10.48	8.71	52.42	12.37	12.61	41.25	12.32	16.59	30.80
30	14.13	5.06	72.65	17.78	7.20	59.29	20.28	8.63	50.71
45	16.60	2.59	83.04	21.20	3.78	70.68	24.54	4.37	61.36
60	18.05	1.14	90.25	23.65	1.33	78.85	27.14	1.77	67.87
75	18.87	0.32	94.35	24.37	0.61	81.25	28.25	0.66	70.64
90	19.19	-	95.96	24.98	-	83.28	28.91	-	72.28
105	19.19	-	95.96	24.98	-	83.28	28.91	-	72.28
120	19.19	-	95.96	24.98	-	83.28	28.91	-	72.28

Table 1: Effect of agitation time, % of removal and adsorption of Nickel (II) on adsorption

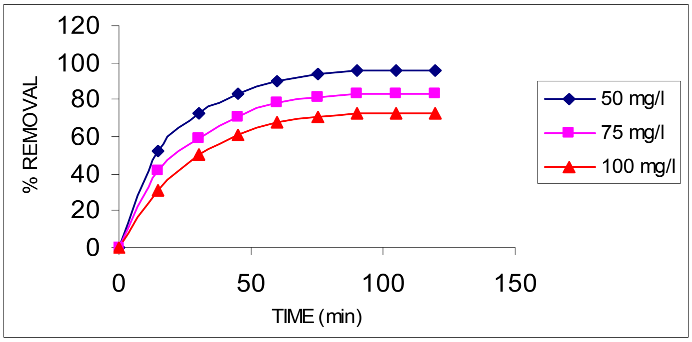

Fig. 2 Effect of time on % removal of Nickel (II) adsorption

C. Effect of adsorbent dosage

Studies on the effect of adsorbent dose, different quantities of the adsorbent ranging from 25 to 175 mg were used. Known quantities of adsorbent were added to 50 ml of Ni (II) solutions of concentration 50mg/lit and the solutions were agitated for 90 min. After equilibrium time, the solutions were centrifuged and analyzed for Nickel (II) Content. The percent removal with various adsorbent dosages was listed in Table 2.It is evident from the Fig.3 that the increase of adsorbent dose, the percent removal of Ni (II) also increased and a complete 100 percent removal was achieved with a dose of 175mg/50 ml. This was attributed to an increase in number of binding sites with increased dosage [14].

Adsorbent dose mg/50ml	% Removal	Equilibrium Concentration Ce(mg/lit)	Amount Adsorbed mg/g
25	31.18	29.89	40.22
50	54.42	22.79	27.21
75	73.82	13.09	24.60
100	89.84	5.08	22.46
125	95.92	2.04	19.18
150	98.08	0.96	16.34
175	100.0	0.00	14.28

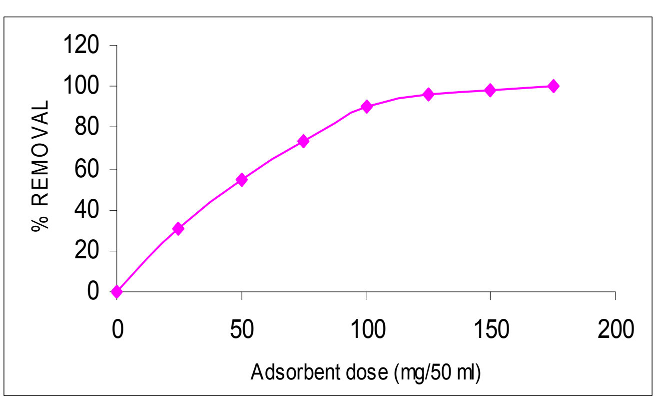

Table 2: Effect of adsorbent dose on the % of removal of Ni (II)

Fig. 3 Effect of adsorbent dose on the %removal of Ni (II)

D. 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

$$\frac{Ce}{qe} = \frac{1}{Q_o b} + \frac{Ce}{Q_0} \qquad -----1$$

Where Ce was the equilibrium Concentration (mg/lit), qe was the amount adsorbed at equilibrium time (mg/g) and Qo and b are Langmuir constants related to adsorption capacity (mg/g) and energy of adsorption (1/mg), respectively. Data for Langmuir plot are given in Table-3 which fitted well in regression analysis of the Langmuir data Ce/qe Vs Ce. The Langmuir constants Q0 and b calculated from the slope and intercept of the Fig.4 were 30.58 mg/lit and 0.5092 mg/1 respectively. Comparison of these values with the literature data indicates that Qo obtained for this adsorbent is less than the Qo obtained by adsorption on activated carbon prepared from biomass by [15]
The essential characteristics of Langmuir are expressed in terms of a dimensionless constant separation factor R_L [16]Equilibrium Parameter that is given by:

$$R_L = \frac{1}{1 + bc_i} \qquad ------2$$

Where Ci was the initial concentration (mg/lit) and b was the Langmuir constant. The value of R_L (Table -4) indicates the nature of isotherm. The characteristic equilibrium parameter R_L of Langmuir isotherm was calculated and the values are 0.037, 0.025 and 0.019 respectively for the metal ion concentrations of 50, 75 and 100mg/lit. As all the values are less than one, it indicates the adsorption of metal ion on to powder of was most favorable. 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:

$$\log x/m = \log k_f + \frac{1}{n}\log Ce \qquad -----3$$

Where (x/m was the amount adsorbed in mg/1it), Ce was the equilibrium concentration (mg/1) and K_f and n were Freundlich constants. K_f [mg/g, 1/mg] was the capacity of the adsorbent and n indicated the favorability of adsorption. The adsorption data were also tested for the validity of Freundlich adsorption isotherm using the equation (3). The plot of log (x/m) Vs Log Ce was linear obeyed the isotherm. The adsorption data also obeyed Freundlich adsorption isotherm; it is evident from the Fig.5 where the plots are linear. Freundlich constants K_f and n calculated are 28.13 are 3.43 respectively. Freundlich constant reported was 39.8 by adsorption of silk cotton hull activated carbon studied by [17]. According to [18] the value of n between 2 and 10 indicated good adsorption. The calculated value of n for the adsorption of nickel was 3.43, inferring very good efficiency for Nickel (II) adsorption by powder of papaya seed adsorbent.

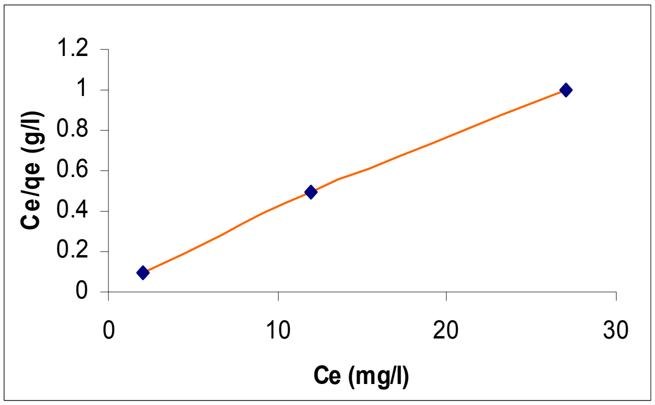

Fig. 4 Langmuir isotherm showing initial concentration vs. equilibrium concentration

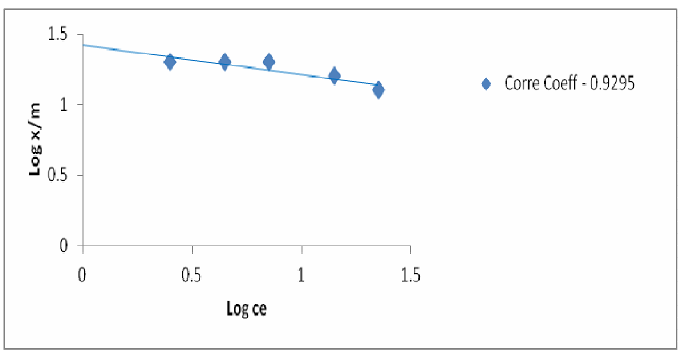

Fig. 5 Freundlich adsorption isotherm for adsorption of Ni (II)

Initial Concentration Ci(mg/lit)	Ce (mg/lit)	qe (mg/g)	Ce/qe(g/lit)
50	2.02	19.19	0.10
75	12.54	24.98	0.50
100	27.72	28.91	0.95

Table 3: Effect of initial concentration on the equilibrium concentration

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

Table 4: Ranges of RL values for comparison

E. Adsorption Kinetics

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

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

Where q and qe 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}). The adsorption data were fitted well in the Lagergren equation (4). The straight line plots of log (qe-q) Vs time for Ni(II) concentrations of 50,75 and 100 mg /lit are shown in Fig. 6.The rate constants of adsorption K_{ad} determined from the slope of the plots are given in Table .5 for Nickel ion adsorption, the initial concentration did not have significant effect on rate constant. (M.Goyal etal.,1999)

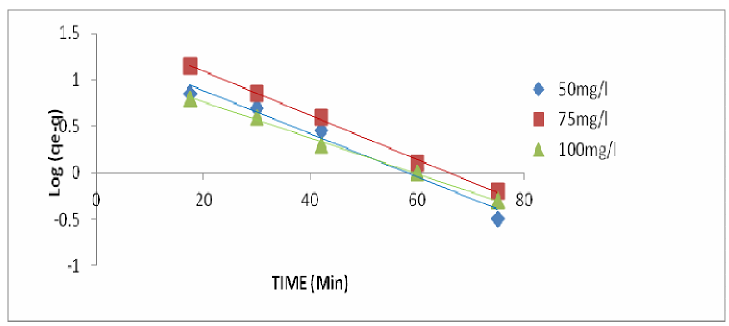

Fig. 6 Lagergren log values plotted for time (min) and log values of equilibrium concentrations on adsorption of Ni (II)

Ni(II) mg/lit	Rate Constant K_{ad} (min^{-1})
50	5.38×10^{-2}
75	5.15×10^{-2}
100	5.31×10^{-2}

Table 5: Rate constants of adsorption calculated for nickel (II)

F. Effects of Particles Size on Lagergren Rate Constant

The effect of particle size on the rate of adsorption was shown in Fig.7 and the rate constant K_{ad} values calculated are given in Table. 6. 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 4.37×10^{-2} 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 (W .J. Weber et al., 1963) 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 is higher than that by larger particles.

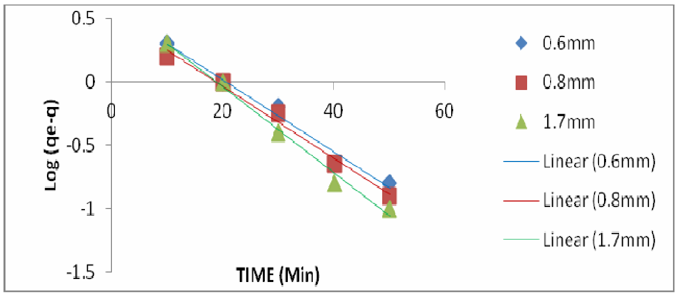

Fig. 7 Relationship between different particle size and time of adsorption

Particle size (mm)	Rate Constant K_{ad} (min^{-1})
0.6	6.01×10^{-2}
0.8	5.28×10^{-2}
1.7	4.37×10^{-2}

Table 6: Lagergren rate constants calculated for different particle sizes

IV. CONCLUSION

A) In this study the heavy metal, namely, nickel (II) was selected for removal from aqueous solutions using adsorption technique. Batch experiments were conducted to study the impacts of practical size, pH, agitation time, adsorbent dose and initial metal ion concentrations. A particle size of 0.6 mm was observed to be highly efficient for nickel (II). The increase of pH showed a negative impact on the adsorption of nickel (II). Maximum adsorption was recorded at pH 3.0 for Ni (II). An increase in the adsorbent dosage gave increased adsorptions for nickel, whereas the adsorption decreased with increase of initial metal ion concentrations.

B) The adsorbent selected for the present study 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 and n values in Freundlich Isotherm indicated that the adsorption of Ni (II) on PPS was favorable. The kinetic data of the adsorption of the metal ions obtained were fitted to pseudo first order model and also obeyed Lagergren equation.

C) The present study provides available and economic procedure(s) for the removal of heavy metal like Ni (II) using the aforesaid adsorbent. The procedure using powder of papaya seeds may be given a thought for removal of metals like Ni (II) in small and medium scale industries for developing countries. Heavy metal removal with the above adsorbent appears to be technically feasible, **u**ser-friendly, **e**co-friendly and **e**conomical process and with high efficiency.

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