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Scavenging of Ni(II) Metal Ions by Adsorption on PAC and Babhul Bark

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The removal of toxic nickel metal ions by adsorption, using powder activated charcoal (PAC) and non-conventional adsorbent modified Indian powder babhul bark (PBB), was studied at room temperature. The adsorption isotherms were obtained in a batch reactor. It is observed that, the process of uptake followed first-order adsorption rate expression and obeyed Langmuir and Freundlich models of adsorption. Effects of variations in parameters such as pH, contact time, adsorbent dose, initial Ni(II) concentration and particle size were also studied.

Key words: *Powder Activated Charcoal (PAC), Powder Babhul Bark(PBB), adsorption, mass transfer coefficient, Langmuir and Freundlich isotherm.*

Introduction

Heavy metals generally occur in water in low concentrations as a result of metal industries and partly through geological processes. But these cause direct toxicity, both to human and other living beings due to their presence beyond the specified limits. Nickel is comparatively a rare metal in nature, but its widespread use in many industrial applications leads to relatively high concentrations in aquatic environment[1]. Ni(II) is present in small quantities (0.1- 0.6 ppm) in plants, animals and occurs in trace amounts in sea water. The major sources of nickel into water bodies are electroplating industries, nickel mining and processing, etc. Some of the other industrial processes that contribute to the presence of nickel are bakery (0.43 mg/L), soft drinks and flavoring (0.22 mg/L), ice cream (0.11 mg/L), textile dyeing (0.25 mg/L), laundry (0.1 mg/L), car wash (0.19 mg/L) and miscellaneous foods (0.11 mg/L)[2].

The exposure to nickel is known to cause asthma and is related to hard metal related respiratory diseases. Excess risk of lungs and nasal cancers are associated with sulphide and oxide forms of nickel[3], Due to this, World Health Organization (W.H.O) has prescribed standards for desirable nickel concentration in drinking water as 0.1 mg/L and industrial effluents as 3.0 mg/L[4]. Therefore, it is necessary to bring the nickel concentration below the prescribed limits.

Various technologies employed to remove toxic metals include ion exchange, reverse osmosis, chemical precipitation, electro floatation and adsorption[5] These methods are costly and are not affordable in the developing countries like India. In wastewater treatment, the process of adsorption has an edge over other methods, due to its simplicity (since it operates without power) and sludge free clear operation[6]. Activated carbon is commonly used as an adsorbent. However, it is much expensive and suffers losses during regeneration. Therefore, low cost and non-conventional adsorbent materials are tried by various researchers in the recent time. In this paper, one such attempt has been made to remove toxic nickel metal ions by adsorption using powder activated charcoal (PAC) and non-conventional adsorbent modified Indian powder babhul bark (PBB).

Materials and methods

All the reagents used were of AR grade. Stock solution of the metal ions was prepared by dissolving $NiSO_4$ in distilled water as per the standard methods (1992)[7].

Concentration of nickel ions was measured by spectrophotometer (model - Systronics India Ltd.) and pH was measured by pH meter (Elico Pvt. Ltd, Hyderabad). Electrical shaker (Remi model No. RS-24, Remi Instruments Ltd, Mumbai) was used for agitating the samples. The method adopted to remove Ni(II) by adsorption using PAC and bio-adsorbent bark, *Acacia arabica* (babhul) is given in the following section. All experiments were conducted using double distilled water and analytical grade chemicals. Adsorption studies were performed by batch adsorption process at room temperature (30° ± 1°C). 200 mL of the solution, each containing the required amount of Ni(II) ions, was transferred into 250 mL glass stopper reagent bottle to carry out the experimental work. To these reagent bottles, suitable doses of adsorbents were added and shaken thoroughly on an electrical shaker for the required period. The suspension was then filtered through Whatman filter No. 41 and the filtrate was analysed using spectrophotometer

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for the estimation of residual nickel ion concentration. The effect of pH, contact time, adsorbent dose, initial nickel concentration and particle size was studied. Initial pH of samples were adjusted by adding 0.1 N HCL or 0.1N NaOH. Buffer solution was added to maintain the pH throughout the experiment.

Bio-adsorbent material development

The bio-adsorbent bark was collected from locally available *Acacia arabica* (babhul) tree. It was first washed with distilled water to remove dust. The bark was then soaked overnight in 0.1N NaOH solution to remove the lignin content. Excess alkalinity was then neutralised with 0.1 N HCl solution. The bark was washed with distilled water several times till the wash water became colourless. Bark was then dried in an oven, ground, again dried and then cooled to room temperature in a desiccator. It was sieved through a sieve size of 149 µm (sieve No. 100) and retained on a sieve size of 74 µm (sieve No. 200) to obtain bark in powder form. The powder activated charcoal (PAC) supplied by M/s. E. Merck India, was used after washing in distilled water and dried in oven.

Results and discussion

Effect of initial Ni (II) concentration

As mentioned in earlier literature, with increase in metal ion concentration, there was considerable decrease in the percentage reduction and the adsorption capacity (q_e) of the adsorbent remains constant independent of the concentration of adsorbate[2]. The present study also reports the same. 98% and 83.4% reduction was obtained by PAC and PBB respectively for initial nickel concentration of 10 mg/L and as it is increased to 50 mg/L, only 51% and 44% reduction was observed as shown in **Fig. 1**. Villaescusa *et al.*, (2000) also observed the same trend for adsorption of Ni(II) by yohimbe bark[12]. He indicated that uptake of Ni(II) increases with the initial sorbate concentration.

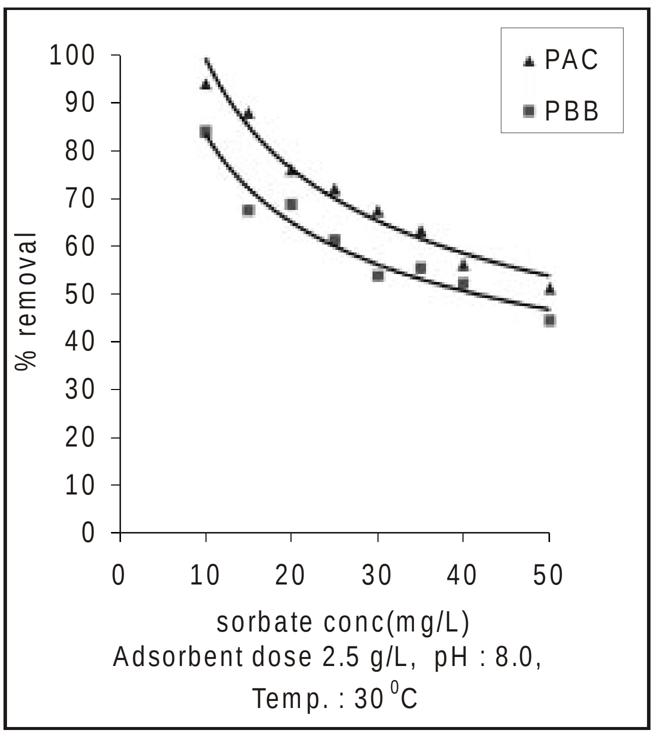

Fig 1 : Effect of initial sorbate concentration

Effect of contact time

The observed effect of contact time upto 3.0 hours on the adsorption of Ni(II) on PAC and babhul tree bark is shown in **Fig. 2**. It is seen from the figure that uptake of Ni(II) increases with time and attains saturation in 120 min by PAC and PBB. It is noted that the rate of adsorption is fast in the initial stages of contact time and gradually decreases with time until saturation.

Surface area and porosity in case of PAC is more than powder babhul bark (PBB), providing more active sites for adsorption, hence adsorption in case of PAC is observed to be more as compared to PBB.

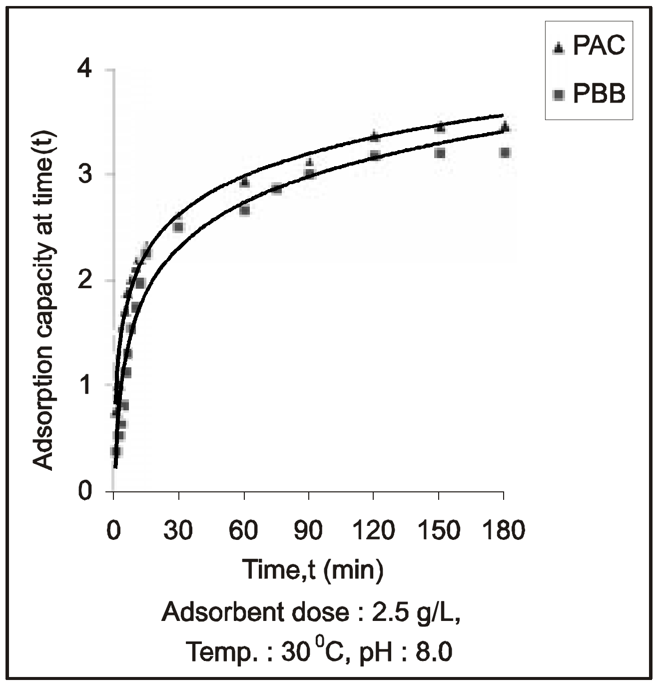

Fig 2 : Effect of contact time

Effect of pH

The effect of pH on the adsorption process is shown in **Fig. 3**. These runs were undertaken at initial nickel concentration of 10 mg/L with adsorbent dose of 2.5 g/L, and temperature 30°C. There was continuous increase in percentage reduction with increase in pH, indicating that the pH of the aqueous solution is an important controlling parameter in the adsorption process. A maximum reduction of 98% and 84%

was obtained by PAC and PBB respectively at pH 8.0 at optimum contact time.

The increase in percentage reduction may be attributed to higher degree of ionization of metal ion at higher pH and the reduced competition of H+ ions with the metal ions for adsorption sites. The physicochemical characteristics of the adsorbent may also play an important role. It was reported that free metal ions are adsorbed better than hydroxides of the metal ions[1].

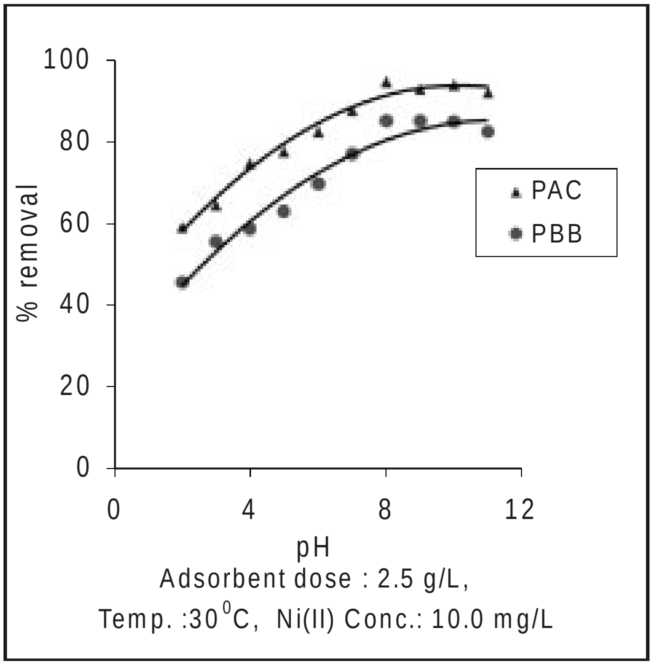

Fig 3 : Effect of pH

Effect of adsorbent dose

The effect of adsorbent dose on the removal of Ni(II) ions is depicted in **Fig. 4**. It is observed that the removal of Ni(II) ions increases with an increase in the adsorbent dose in all the experimental runs. Ni(II) ion concentration was fixed at 10 m/L. The adsorbent dose was varied from 0.5 g/L to 5.0 g/L in aqueous solutions at their optimum pH value.

The percent removal of Ni(II) ions was higher in case of PAC followed by PBB. The removal of Ni(II) ions by PAC and PBB found to increase from 51% to 98.2% and 40.6 to 84% respectively, with an adsorbent dose varying from 0.5 g/L to 5.0 g/L. However, with the further increase in adsorbent dose, there was no appreciable increase in nickel removal.

Effect of particle size

Experiments were conducted to evaluate the influence of adsorbent particle size for a constant weight on the removal of Ni(II) ions. Seive analysis was carried out on babhul bark for determination of particle size.

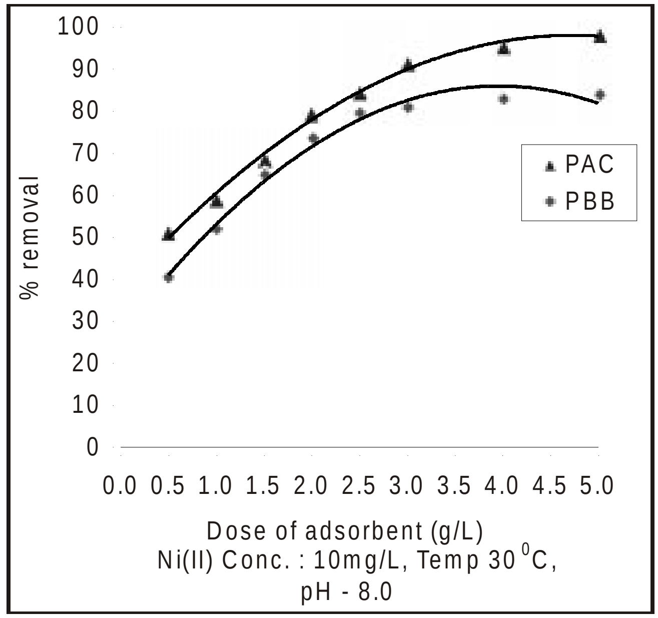

Fig 4 : Effect of adsorbent dose

Adsorbent particle size has significant influence on the kinetics of adsorption due to change in number of adsorption sites. Bark ranges in size from 74 to 349 micron. The removal of Ni(II) by different particle sizes showed that the uptake of Ni(II) ions increases with decrease in particle diameter as shown in **Fig. 5**. The presence of large number of smaller particles provides the sorption system with a greater surface area available for Ni(II) removal and it also reduces the external mass transfer resistance[2].

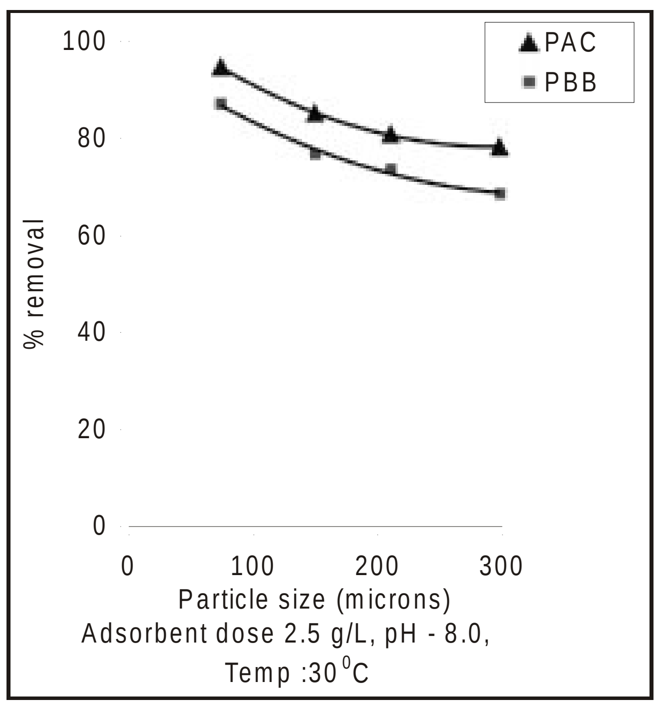

Fig 5 : Effect of particle size

Adsorption isotherm

Equilibrium adsorption isotherm, i.e. adsorption capacity, q_e versus concentration of nickel at equilibrium, Ce is plotted for babhul bark as shown in **Fig. 6**. The surface concentration or adsorption capacity q_e in mg/g was calculated from the following equation

$$qe = (Co - Ce) \times \frac{V}{M} \qquad ----1$$

where C_o is initial concentration of nickel in mg/L, C_e is the concentration of nickel at equilibrium in mg/L, V is the volume of solution in litre and M is the mass of adsorbent in gms.

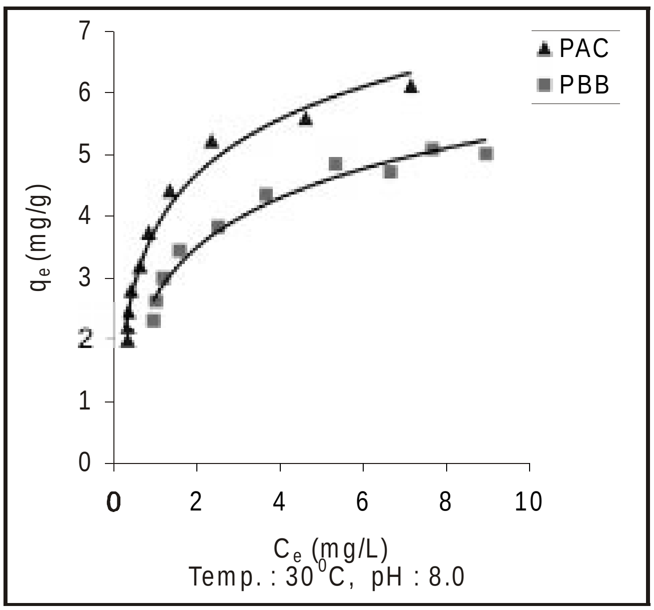

Fig. 6 : Adsorption Isotherm

To quantify the adsorption capacity for the removal of nickel from water, Langmuir and Freundlich adsorption equations were used.

Langmuir equation was applied in the form:

$$1/q_e = 1/(Q°bC_e) + 1/Q° \qquad ----2$$

where Q°(mg/g) and b (l/mg) are Langmuir constants, indicating the adsorption capacity and energy of adsorption respectively.

The linear plot between $1/C_e$ and $1/q_e$ for PAC and babhul bark as shown in **Fig. 7** indicates the validity of Langmuir adsorption isotherm, consequently suggesting the formation of monolayer coverage of the adsorbate on the surface of the adsorbent in the concentration range studied. The values of Q° and b were determined from the slopes and intercepts of the plots and are reported in **Table 1.**

The dimensionless equilibrium parameter, R is defined by

$$R = 1/(1+b\,Co),$$

where b is Langmuir constant (l/mg) and Co is the initial concentration (mg/L). R values observed as shown in **Table 1** are between 0 and 0.2 indicating favorable adsorption[8].

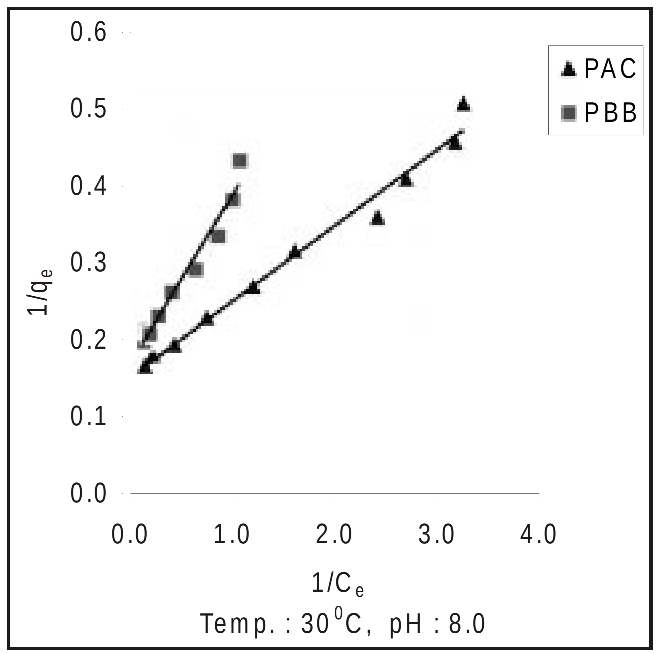

Fig. 7 : Langmuir adsorption isotherm

Table-1: Isotherm Constants

	Langmuir Constants				Freundlich Constants		
	Q0	b	R	r2	Kf	1/n	r2
Powder activated charcoal	6.662	1.512	0.061	0.9827	3.526	0.3441	0.9299
Powder babhul bark	5.942	0.759	0.115	0.9658	2.709	0.3177	0.9302

Freundlich equation is applied in the form:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad \text{----3}$$

Where K_f and 1/n are Freundlich constants, indicating the adsorption capacity and adsorption intensity respectively. The Freundlich model as observed in **Fig. 8** was also found to be linear. The coefficient of correlation value (r^2) was also high. Values of Freundlich constants are depicted in **Table 1**. Since the value of 1/n is less than 1, it indicates favorable adsorption. A smaller value of 1/n indicates better adsorption mechanism and formation of relatively stronger bond between adsorbate and adsorbent[9].

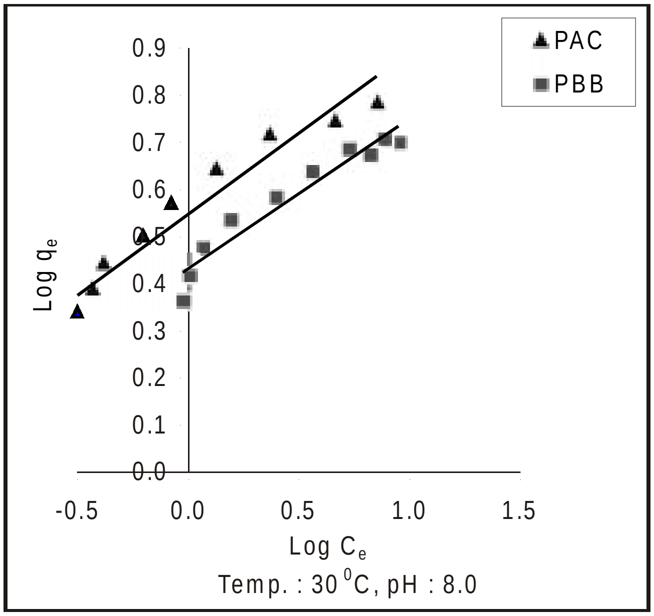

Fig. 8 : Freundlich adsorption isotherm

Adsorption dynamics

Kinetics of adsorption, describing the solute uptake rate, which in turn governs the contact time of adsorption process, is one of the important characteristics defining the efficiency of adsorption. Kinetics of nickel removal was therefore carried out to understand the behavior of barks.

The rate constant of adsorption k_{ad}, was determined using the following first order rate expression given by Lagergren (1898)[10].

$$\log(q_e-q_t) = \log q_e - (k_{ad}/2.303) \times t \quad \text{---- 4}$$

here q_t and q_e (both in mg/g) are the amounts of nickel adsorbed at time t (min) and at equilibrium respectively. A straight line plot of log (q_e-q_t) against time (min) as shown in **Fig.9** indicates the applicability of the above equation. The values of k_{ad} are reported in **Table 2.**

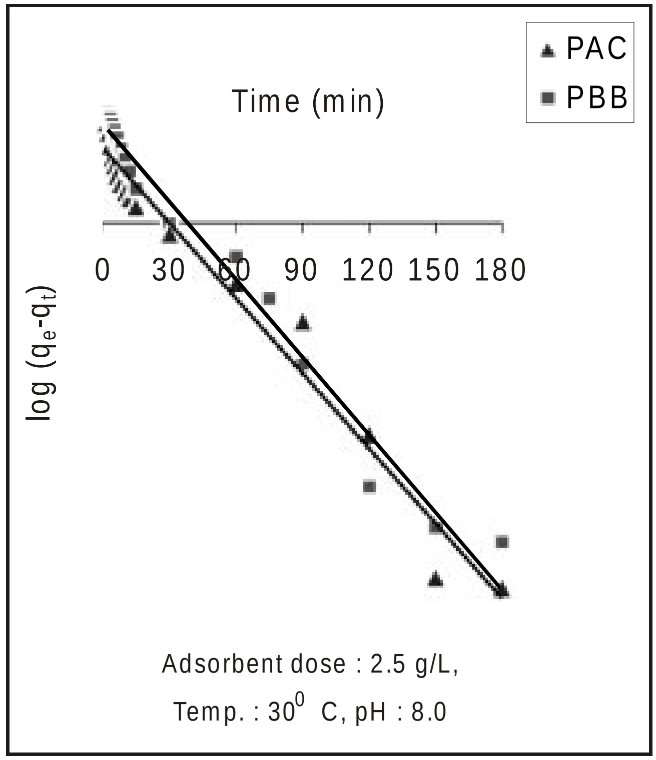

Fig. 9 : Lagergren plots

Mass transfer coefficients were determined by the expression[11],

$$\ln((C_t/C_o)-(1/(1+mK_L))) = \ln(mK_L/(1+mK_L)) - ((1+mK_L)/mK_L)\, b_L \times S_s \times t \quad \text{--------------- 5}$$

where C_o is the initial adsorbate concentration (mg/L), C_t is the adsorbate concentration (mg/L) at time t, m is the mass of adsorbent per unit volume of particle free adsorbate solution (g/L), b_L the mass transfer coefficient (cm/s), K_L the constant (obtained by multiplying Q^0 and b) and S_s is the outer surface of adsorbent per unit volume of particle free slurry (/cm).

$$m = W/V, \quad \text{-------------- 6}$$

$$S_s = 6\, m/d_p \times r_p \times (1- e_p) \quad \text{------------- 7}$$

where W is weight of adsorbent (g) taken, V is the volume of solution in which W (g) of adsorbent was taken, d_p the diameter of adsorbent (cm), r_p the density (kg/m^3) and e_p is the porosity of the adsorbent.

The straight line plots of $\ln((C_t/C_o)-(1/(1+mK_L))$ against time t as shown in **Fig.10** at various concentrations, suggest the validity of McKay equation for the present system. The values of mass transfer coefficient, b_L were calculated from the slopes and intercepts of the plots and are indicated in **Table 2.**

Table 2 : Rate Constants and Mass Transfer Coefficients

	Adsorption rate constant k_{ad} (min^{-1})	**Mass transfer coefficient b_L (cm/s) × 10^{-6}**
Powder Activated Charcoal	0.046	0.108
Powder Babhul Bark	0.031	0.087

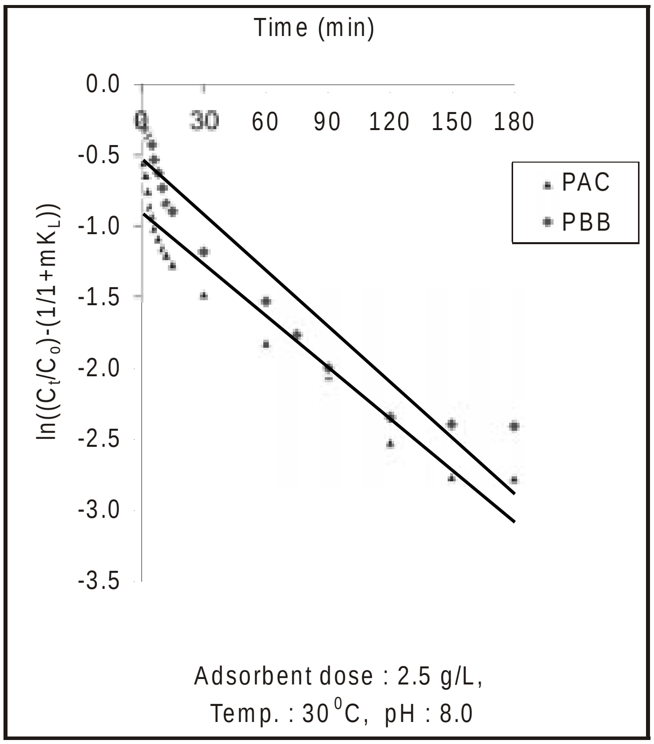

Fig. 10 : McKay plots

Conclusion

Conventional powder activated charcoal (PAC) has showed more sorption capacity for the removal of nickel than powder babhul bark. PAC and PBB are effective at pH 8.0, hence can be efficiently used at pH 7.0 - 8.0, which is more preferable.

With the application of very small dose of PBB, it is possible to reduce Ni(II) ion concentration more than 80%, and gives the nickel concentration in the effluent within limits of effluent standards for safe disposal. Recovery and regeneration of PAC is difficult, however PBB can be disposed of safely. Adsorption with low cost adsorbent is not only cheaper but require less maintenance and supervision. Regeneration is also not required because it can be used once and burnt after drying.

It is suggested that the use of powder babhul bark (PBB) for removal of nickel from industrial wastewater is an effective and low cost process.

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