Activated Tree Bark as an Adsorbent for Heavy Metal Removal: Study Through Isotherm Analysis

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Abstract

Widespread industrial applications of nickel have lead to its presence in industrial effluents. High doses of nickel have various health hazards. Natural adsorbents are gaining importance due to their availability in abundance, low cost and environment friendly constitution. In this study, an attempt has been made to investigate the efficiency of guava bark as an adsorbent for removal of nickel. Batch adsorption experiments were carried out to study the various parameters such as effect of initial concentration, effect of adsorbent dose and contact time. The adsorption equilibrium data was analyzed by Freundlich and Langmuir isotherm models. Kinetics and thermodynamic study were very useful in understanding removal of nickel ions from aqueous solution.

Keywords: Adsorption, Isotherm, Heavy Metal

Introduction

Pollution load of the environment is increasing due to global rise in population and our quest to lead comforTable life is resulting in explosive growth of industrial and agricultural activities. Waste water commonly contains metal ions, Cu, Ni, Cd, Cr, Fe, Mn, Zn, Pb, Cs which are not biodegradable and hence are of vital concern[1].

Ni (II) is a naturally occurring, hard, silvery-white metal. Its widespread industrial applications such as nickel plating and making of steel, coins, jewellery, batteries and heat exchangers have resulted in its presence in many industrial effluents. Ni is an essential micronutrient, but with prolonged contact and at high doses it can cause skin allergic reactions, asthma, bronchitis, lung & heart disorders and adverse effects on stomach & blood. Some nickel compounds are carcinogens and metallic nickel may possibly be carcinogenic to humans. Hence it is necessary to reduce Ni from water / wastewater to accepTable level[2].

Among various types of methods for metal removal, adsorption has gained wide application. Agricultural adsorbents such as coffee husk[3], peanut shells[4], rice husk[5] and saw dust[6] are reported as efficient adsorbents. Researchers have conducted studies on removal of nickel by using agricultural waste products such as mangrove bark *Rhizophora apiculata*[7], rice husk[8], *Hevea brasiliensis*[9] etc. Guava (*Psidium guajava*) has been investigated for the adsorption of Hg(II)[10]. This work is aimed at studying the efficiency of guava bark as an adsorbent for the removal of nickel.

Material and methods

Guava bark was collected from biological sciences garden, Nagpur and locally available plants. All chemicals used were purchased from Merck India. Nickel concentrations were analyzed by Atomic absorption spectrophotometer (Model No.GBC 906AA)

Preparation of Adsorbent

The collected bark was washed with water several times to remove dirt particles and water soluble materials. The washing process was continued till the washed water contained no color. The washed material was then completely dried in an air oven at 105 ^{0}C to 110 ^{0}C for 24 hr. Bark was grinded into fine powder and stored in vacuum desiccators until required. The dried Guava bark powder (25 gm) was poured into 500 ml conical flask containing 250 ml of 0.2 N HCl. Acid activation was done to increase the surface area and to prevent the elution of tannin compounds. The mixture was shaken at 200 rpm for 4 hrs. The mixture was left overnight, was filtered to separate the sorbent which was washed several times with distilled water to provide neutral pH. The adsorbents were then oven dried at 85 ^{0}C for 2 hrs [11].

Batch experiment

Effect of heavy metal ion concentration, adsorbent dosage & contact time was studied. To study the effect of certain parameter, that parameter has been changed while keeping the other parameters constant. After adsorption experiment, contents of the flasks were filtered and filtrates were subjected to atomic absorption spectrophotometer. To study the effect of adsorbent dose, 0.1, 0.25 & 0.5 g of adsorbent was added to three conical flasks containing 50 ml Ni^{2+} (100 ppm) solution of pH 6.2. The flasks were agitated at 100 rpm for 5 hrs at temperature 30 ^{0}C.

To study the effect of initial ion concentration on the Ni(II) ions adsorption, 0.25 g of guava bark adsorbent was added to different concentration (100, 250, 500 mg/l) of Ni solutions (50 ml) at 30 ^{0}C. The mixtures were agitated at 100 rpm for 5 hr. To study the effect of contact time on adsorption, 50 ml of stock solutions of Nickel (100 ppm) was poured in a 250 ml conical flask containing 0.25 g of guava bark adsorbent. The mixtures were agitated at 100 rpm for different contact time. Effect of temperature was studied by performing experiments at different temperatures of 30 ^{0}C and 40 ^{0}C for the initial nickel concentrations of 100 ppm at constant adsorbent dose of 0.25 g/L. Equilibrium study was conducted as per literature[12,13].

Result and Discussion

Effect of adsorbent dose, initial concentration & contact time

From Figure 1, it is revealed that within a certain range of initial metal concentration, the percentage of metal adsorption on bark is determined by the sorption capacity of the bark. The maximum removal of nickel was obtained in the adsorbent dose of 0.25 g/L. As observed from the figure 2, the removal of Ni (II) ion is found to increase with increase in initial concentration Adsorption of nickel was measured at given contact time for 100 ppm solution of Ni. From Fig. 3, the plot reveals that the rate of percent nickel removal is higher at the beginning. This is probably due to larger surface area of the adsorbent being available at beginning for the adsorption of nickel ions. Maximum nickel removal was attained after about 150 min of shaking time after which it remained somewhat constant.

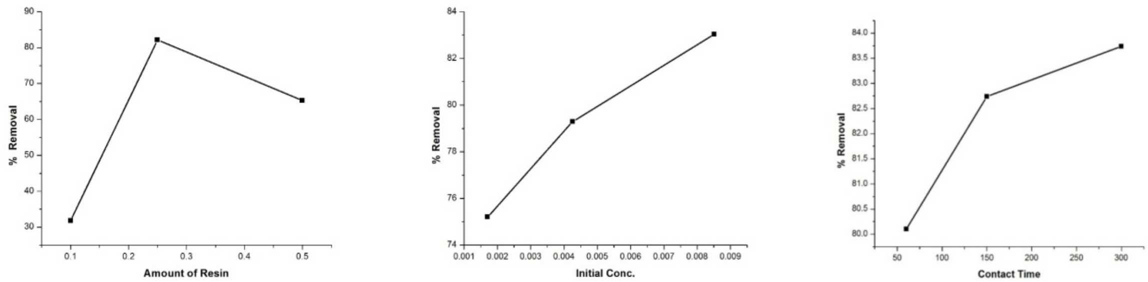
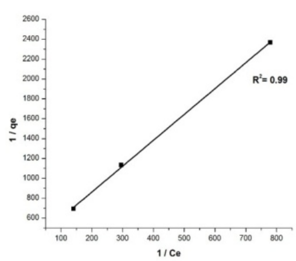


Fig 1, 2 & 3: Effect of adsorbent dose, Initial concentration and Contact time at 100 ppm.

The Langmuir & Freundlich isotherm:

The Langmuir adsorption equilibrium isotherm of nickel onto activated guava bark is presented in Fig. 4. Regression analysis reveals that the Langmuir model fits the Experimental data well with correlation factor higher than 0.99. A plot of $1/q_e$ versus $1/C_e$ was found to be a straight line with $1/q_m K_L$ as intercept and slope, and hence q_m and K_L can be calculated. Langmuir constants q_m and K_L, and the correlation coefficient R^2 are given in Table 1.



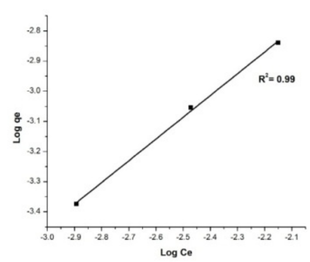


Fig 4: Langmuir adsorption isotherm for nickel. Fig 5: Freundlich isotherm adsorption isotherm

From Fig. 5, the Freundlich constants *Kf* and *n* were found to be - 1.2817 and - 0.884 respectively. The magnitudes of *Kf* and *n* show easy separation of nickel ions from the aqueous solution and indicate favourable adsorption. The intercept Kf value is an indication of the adsorption capacity of the adsorbent; the slope 1/*n* indicates the effect of concentration on the adsorption capacity and represents adsorption intensity. As seen from Table 1, *n* value was found high enough for separation.

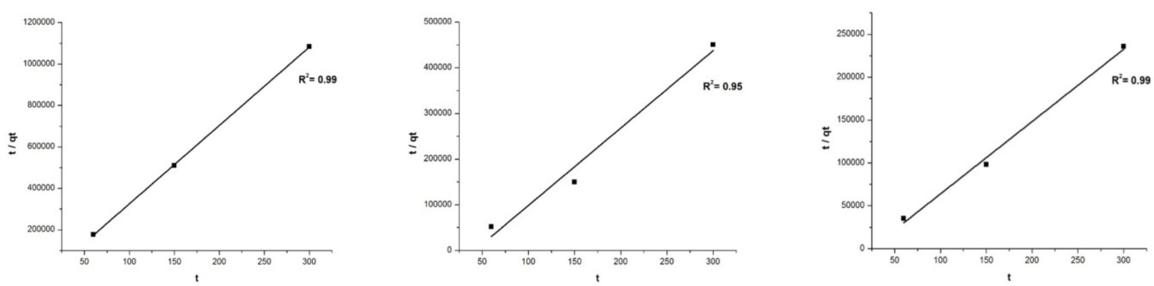
Table 1. Isotherm model constant and correlation coefficient for adsorption of nickel.

Langmuir Isotherm		Freundlich Isotherm	
K_L	R^2	K_f	R^2
340.913	0.99	-1.2817	0.99

Since the value of R^2 is nearer to 1 which indicates that the respective equation better fits the Experimental data. The observations confirm the capacity of guava bark to adsorb nickel.

Adsorption Kinetics

The kinetic studies were carried out using the pseudo-first order and pseudo-second-order models on Experimental data. The effect of initial nickel concentrations was investigated to find the best fit kinetic model. The kinetic constants and correlation coefficients of pseudo first-order kinetic model fail to give straight line. Therefore, Pseudo second-order kinetic model is preferred. The pseudo-second-order kinetic model was applied by plotting t/qt versus t, and this model gave high values of regression correlation coefficient as seen in Figure 6(A), 6(B), and 6(C). This implies that the mechanism of adsorption of Ni (II) ion on the activated guava bark follows the pseudo-second-order kinetics.



6(A) 6(B) 6(C)

Fig 6: Adsorption kinetics of Ni(II) by linear plots of Pseudo second rate equation 6(A) at 100 ppm, 6(B) at 250 ppm, and 6(C) at 500 ppm.

Thermodynamic

Thermodynamic parameters, ΔG^0 ΔH^0 and ΔS^0 were determined by plotting ln Kc versus 1/T. Positive ΔG^0 indicates that the adsorption process of nickel ions by activated guava bark is enhanced at elevated temperatures. The negative values of change in enthalpy (ΔH^0) suggest the exothermic nature of adsorption and the negative values of change in entropy (ΔS^0) can be used to describe the randomness at the solid solution interface during the adsorption of Ni (II) ion on guava bark (Table 2).

Table 2: Thermodynamic parameters calculated for the adsorption of NI(II) ions onto activated Guava Bark.

Graph No.	Initial Ni(II) conc.(mg/L)	ΔG(kJ/mol)	ΔH(kJ/mol)	ΔS(kJ/mol)
7	0.00851788	2.955	-1.427	-0.014

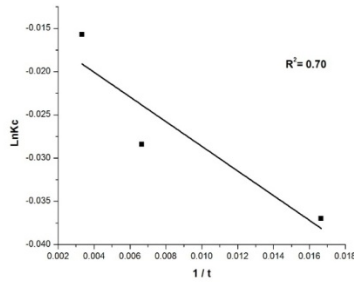


Fig 7: Plot of ln Kc vs 1/T for the estimation of thermodynamic parameter for adsorption of Ni(II) on to Guava bark.

Conclusion

Guava bark was found to be an effective adsorbent for removal of nickel from aqueous solutions. The results obtained from the present study revealed that the sorption efficiency was dependent on operating conditions such as adsorbent dose, contact time & initial metal ion concentration. Adsorption followed Langmuir and Freundlich isotherm models. From the Langmuir isotherm, the maximum adsorption capacity was calculated to be 0.99 mg g^{-1} of adsorbent. The R^2 values showed that the adsorption is favorable. The kinetic data was well described by the pseudo- second order kinetic model. Thermodynamic parameters indicated that the adsorption process was thermodynamically exothermic in nature.The findings of the study revealed that guava bark is a promising low cost adsorbent for the removal of nickel from contaminated waste water.

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