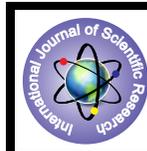


Borassus Flebellifer Ferra Drupe Prepared From Biomass as an Bio Sorbent for the Removal of Ni(II) From Aqueous Solutions



Environmental Science

KEYWORDS : *Borassus flebellifer ferra drupe* (BFFD), metal ion, Adsorption, Kinetics, Isotherms, pH, Desorption.

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ABSTRACT

Borassus flebellifer ferra drupe (BFFD) dust was used to remove Ni(II) from aqueous solutions and industrial wastes by the adsorption. Batch mode adsorption experiments are carried out to assess kinetic and equilibrium parameters. They allow initial adsorption coefficient, adsorption rate constant and maximum adsorption capacities are to be computed. Removal of mg/g increases with increase of metal concentration and contact time. The adsorption data have been analyzed and fitted to both Langmuir and Freundlich classical adsorption isotherm models. The adsorption capacity (Q_0) calculated from Langmuir isotherm was 2.05 mg Ni(II)/g of BFFD at initial pH of 5.0 at 27±20C for particle size 0.430mm. Increase in pH from 2-10 increased percent removal of metal upto 5 latter on wards removal of metal is negligible, coupled with regeneration study of Ni(II) by HCl, allowed us to propose an adsorption mechanism by ion-exchange between metal ion and H⁺ ions on the BFFD surface quantitative recovery of Ni(II) is possible by HCl.

INTRODUCTION

Ni(II) is a well known toxic heavy metal, which pose serious threat to the fauna and flora of receiving water bodies when discharged from industrial wastewaters. Ni(II) presents in the effluents of silver refineries, electroplating, zinc base casting and storage battery industries. Kadirvelu et al., (2000a). As it resists corrosion even at high temperature, it can also be used in gas turbines, rocket engines and distillation plants. It is also used in coinage and costume jewelry. Skin contact with nickel causes a painful disease called 'nickel itch' which leads to death (Abbasi and Soni, 1990). The acceptable limit of nickel in drinking water in india is 0.01 mg/L and for discharge of industrial wastewater is 2.0 mg/L (Kadirvelu, 1998). At higher concentrations, Ni(II) causes cancer to the lungs, nose and bones. Dermatitis (nickel itch) is the most frequent effect of exposure to nickel, such as coins and costume jewelry. Nickel carbonyl [Ni(Co)4] has been estimated as lethal in humans at atmospheric exposures of 30 ppm for 30 min (Namasivayam and Ranganathan, 1994). Acute poisoning of ni(II) causes headache, dizziness, nausea, tightness of the chest, chest pain, and shortness of breath, dry cough, cyanosis and extreme weakness (Parker, 1980). The toxic nature of Ni(II) on fish, crops and algae was also reported (David, 1977). Perennial toxicity associated with nickel chloride exposure on female rats was also reported (Kate Smith et al., 1993).

Conventional methods used for the removal of Ni(II) include chemical precipitation, ion-exchange, filtration, chemical reduction, electro-deposition and adsorption on activated carbon (La Grega et al., 1994). It is quite well known that granular activated carbon (GAC) is used and as a matter of fact, is recommended by the US, EPA as the best available technology to remove contaminants, in particular organics from water and air by adsorption with great efficiency. However, GAC technology is relatively expensive for developing countries like India. For this reason, in recent years, much attention has been focused on the removal of heavy metals using industrial wastes and agricultural wastes. Many authors have used natural adsorbents including activated clay (Hawash et al., 1994b), peanut hull (Periasamy et al., 1995). Flyash (Viswakarma et al., 1989). Blast furnace slag (Dimitrova 1996), Coir pith carbon (Kadirvelu et al., 2001). Rice bran, soya bean and cotton seed hulls (Marshall and Johns, 1996). Activated carbon from soya bean, peanut, pecan and walnut shells (Marshall and Champagne, 1995 and Johns et al., 1998). Peat (Viraraghavan and Drohamraju 1993) and sorghum peat moss (Lo

Y S et al., 1995) for the removal of Ni(II) from wastewater. Pollard et al., (1992) have reviewed low-cost adsorbent for water and wastewater treatment, while Coconut shell was also used for the wastewater treatment (Arulanantham et al., 1989).

EXPERIMENTAL

Adsorbent : Borassus flabellifer ferra drupes

The Borassus flabellifer ferra drupes were collected near village of Visakhapatnam, Andhra Pradesh, cleaned thoroughly with water and soaked in distilled water for 24 hrs and again washed with distilled water and dried under sun light. The dried drupes were pulverized and the pulverized material was screened for various particle sizes like 0.430, 0.600 and 0.800 mm.

Adsorbate: Nickel Ammonium Sulphate solution

AR grade Nickel Ammonium sulphate was used to prepare Ni(II) solution. A stock solution of 1000 mg/L of Ni(II) was prepared by dissolving 6.7280g of Nickel Ammonium sulphate in 5 ml of 1% HNO₃ solution to prevent hydrolysis and diluted with double distilled water and made up to 1000 ml.

Batch mode adsorption studies:

Batch mode adsorption studies to determine the adsorption rates and maximum adsorption capacities. Batch mode adsorption studies were carried out at 27±20C using 50ml of metal ion solution containing the desired concentration and 75mg of adsorbent in 250ml conical flasks with lids stirring speed 160 rpm samples were separated and filtered. Ni(II) was analysed by spectrophotometer (Stewart 1974 & APHA 2005). All the experiments were carried out at initial pH of 5 where the adsorption is significant but pH is more than 5 metal hydroxide precipitation occurs. The metal concentration on the adsorbent phase (q_e , mg/g) was calculated by using the following equation

$$q_e = \frac{(C_0 - C_e)V}{m}$$

Where C_0 , C_e are the initial and equilibrium concentrations of metal ion in solution (ml) and m mass of adsorbent (mg). Adsorption isotherms were performed at 27±20C with an initial conc. Of Ni(II) ranging from 10-40 mg/L a solution of volume 50 ml and an adsorbent weight of 75 mg.

the stirring time was 80 min. the effect of pH on % removal was studied from initial pH 3-10 using 50 ml metal ion solution 10 mg/L with 75 mg adsorbent 0.1M HCl or 0.1 NaOH used to adjust the pH.

Batch mode desorption studies :

After adsorption experiments, the metal ion loaded BFFD were separated and slightly washed with distilled water to remove unadsorbed metal ions on the BFFD surface. They are stirred with 50ml of HCl of various concentrations ranging from 0.02 - 0.1M for 80 min, metal ion concentrations were analysed as all the chemicals are used of analysed reagent grade. All the experiments were carried out in duplicate and mean values are presented maximum deviation was $\pm 5.0\%$.

Results and discussion -Approach of the adsorption:

The effects of pH:

The effects of pH on the adsorption of Ni(II) ion was carried out using 75 mg of the *Borassus flabellifer ferra* drupe dust in 50 ml solution of 10 mg/L of Ni(II) concentration. The pH of the solutions was adjusted to different pH values ranging from 3.0 to 10.0 and was equilibrated for 80 min. The equilibrated solutions were tested for Ni(II) conc. spectrophotometrically (Stewart 1974 & APHA 2005). The percentage of adsorption increased with increase in pH, reached a maximum of 91.85 % at pH 5.0 and remained almost constant in the pH range 6.0-10.0. The adsorption of metal cations depends on the nature of metal ions, adsorbent surface and the species of the metals. The percentage of adsorption was low when pH was low. This may be due to the reason that protons competed with metal ions for adsorption sites, thus decreasing the uptake of metal ions. As the pH of the solution increased, the percent removal also increased due to decrease in the amount of competing protons. Similar results were reported for the adsorption of Ni(II) as reported by Navaneet Joshi et al., (2003) and Pranas Baltrenas et al., (2006). At pH more than 6.0, precipitation started and hence pH of 5.0 was selected for this study. It was observed that at pH more than 6.0, the percent removal of Ni(II) by adsorption was greater than that by precipitation. Removal of nickel by adsorption using Peat was found to be high in the pH range 4.5 to 5.0 (Viraraghavan et al., 1993).

Figure 1: Effect of pH on Ni(II)removal

Kinetic study

The kinetic study of the adsorption of Ni(II) was conducted at optimum pH where only adsorption takes place. The effect of contact time and initial metal ion concentration on Ni(II) adsorption on to BFFD. The adsorption equilibrium was reached at 6.19, 11.57, 15.07 and 17.20 mg/g adsorbed for 10, 20, 30 and 40 mg/L respectively. The contact time required for all the concentrations of Ni(II) removal is very short. This result is interesting because equilibrium time in one of the parameters for economical wastewater treatment plant applications. According to these results, the stirring time was 80 min for the further experiments to make sure to reach adsorption equilibrium. The adsorption rate constants were calculated by using the following equation given by Lagergren (Lagergren 1898)

$$\text{Log}(q_e - q) = \text{log } q_e - \frac{\text{Kad } t}{2.303}$$

Where q and q_e are the adsorption capacities at time (t) and equilibrium time, respectively. Kad is adsorption rate

constant. The Kad values were calculated from slope the respective linear plots of $\text{log}(q_e - q)$ vs 't' The results show that the removal of Ni(II) follows first order reaction. Kad values were comparable with previous reports for adsorption Ni(II) on to various adsorbents Kalyani et al., 2004.

Table 1

Ni(II)(mg/L)	$K_a \times 10^{-2}$	Q (mg/g)
10	6.78	0.114
20	5.68	0.195
30	6.02	0.493
40	5.89	0.825

Adsorption isotherms

Adsorption isotherms of Ni(II) onto BFFD are explained with help of two models Langmuir and freundlich equations to determine adsorption of Ni(II) on to BFFD. Langmuir isotherm was tested to determine maximum adsorption capacities and energy of adsorption using following equation given by Langmuir (Lodha 1997).

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

Where C_e is equilibrium concentration (mg/L), q_e is amount adsorbed at equilibrium (mg/L) and Q_0 (mg/g) and 'b' (L/mg) is Langmuir constants related to adsorption capacity and energy of adsorption, respectively. The linear plot of C_e/q_e vs C_e shows that adsorption of Ni(II) on BFFD obeys Langmuir isotherm model. Q_0 and 'b' were determined from the slope and intercept of the plot and found to be 2.05 mg/g and 0.14 L/mg respectively, Kadirvelu et al., (2003). The adsorption capacity of other adsorbents for Ni(II) are summarized in table-2 for comparison. Freundlich isotherms is also used to explain observed phenomenon with following equation

Table-2

Adsorbent	Q_0 , mg/g	Reference
Rice hull	0 5 . 5 8	Suemitsu et al., 1986
Natural clay	1 2 . 5 0	Hawash et al., 1994
Pea moss	09.18	Lo et al., 1995
Soya bean hull	89.52	Marshall and Champagne 1995

Given by Freundlich (Freundlich 1906).

$$q_e = K_f C_e^{1/n}$$

Where C_e is equilibrium concentration (mg/L), q_e is amount adsorbed (mg/g) and K_f [(mg/g)(L/mg)^{1/n}] and 'n' are constants incorporating all factors affecting the adsorption process, such as capacity and intensity $\text{log } q_e$ vs $\text{log } C_e$ shows that the adsorption follows Freundlich isotherms model. K_f and 'n' values were calculated from the intercept and slope of the plot and were found to be 0.78 and 3.64 respectively Kadirvelu et al., (2003).

Effect of BFFD concentration

The removal of Ni(II) as a function of BFFD concentration. Increasing BFFD concentration increased the percent removal. This is due to availability of more functional surface area, functional groups. For quantitative removal of Ni(II) from 50 ml of 10 mg/L a maximum concentration of 150g is required. Similar results reported in literature Kannan et al., 2003, Prabhavati Nagarajan et al., (2006).

Desorption Studies:

Desorption studies help to elucidate the adsorption mecha-

nism and also aids the recovery of the adsorbent. Desorption of Ni(II) was tried with various HCl concentrations. The percentage of desorption increased with increase in concentration of HCl. A maximum of 78.0 percent of Ni(II) was desorbed with HCl concentration of 0.10M at agitation time of 80min. This may be due to the fact that in acidic conditions, H⁺ ions replace the metal ions from the adsorbent surface leading to desorption of the positively charged metal ion species. Kadirvelu et al., (2003) and Shanmugavalli et al., (2006) reported the desorption of Ni(II) from the adsorbents in acidic medium.

Desorption studies were carried out to confirm the adsorption mechanism proposed above and to recovery the metal from the adsorbent. The quantitative recovery of metal ion indicates that regeneration of adsorbent was possible. This further suggests that ion-exchange may also be involved in the adsorption mechanism (Lin et al., 1992).

Removal of Ni (II) from nickel plating wastewater:

The characteristics of the wastewater collected from the Nickel plating industry, adsorption of Ni(II) was carried out at pH 5. Figure-1 shows the effects of adsorbent dosage on the removal of Ni(II) from the wastewater. The percentage of adsorption increased with increase in adsorbent dosage and quantitative removal was possible with a dosage of 600 mg. A maximum of 85.20 percent of Ni(II) ions, at agitation time 80min, were removed from the wastewater containing Ni(II) concentration of 18.50 mg/L, the *Borassus flabellifer ferra drupe* indicating the adsorbate can be effectively used for the treatment of industrial wastewater containing Ni(II) ions Manonmani, (2002), Selvaraj et al., (1998).

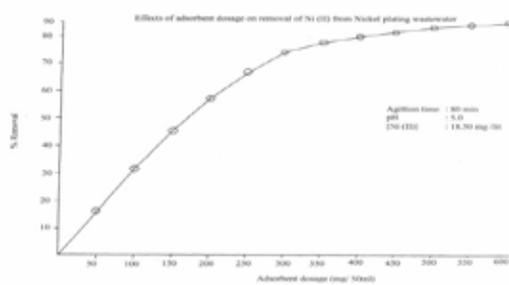


Figure 1 Effect of absorbent dosage on removal of Ni(II) from Nickel Plating waste water

CONCLUSION :

Experimental conditions such as pH, BFFD concentration and reaction time have been optimized to utilize BFFD as adsorbent for the removal of Ni(II) from aqueous solution. Adsorption capacity increases with decrease of metal ion concentration and increase with pH. The pH effect and desorption studies were studied to understand adsorption mechanism. Adsorption followed both Langmuir and Freundlich adsorption isotherms. The adsorption capacity (Q_0) was 2.05mg Ni(II)/g of BFFD at the initial pH of 5.0 for the particle size of 0.430mm. The kinetic studies show that the removal of Ni(II) follow first order rate reaction given by Lagergren. Experimental results allow us to conclude an adsorption mechanism by ion-exchange between metal ion and H⁺ ions on the BFFD surface. These reactions induce a release of H⁺ ions in solution and thus decrease of final pH. Recovery of metal ions from BFFD and regeneration BFFD are possible. Since raw material is waste and available in plenty, resulting BFFD is expected to economical for waste waters containing Ni(II).

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