Development of bio-sorbent for the Elimination of Heavy metal from industrial wastewater - Batch mode

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Abstract:

Date nuts dust was used to remove Ni(II) from aqueous solutions and industrial wastewaters 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 increase with increase of metal concentration and contact time. The adsorption data that have been analyzed and fitted to both Langumuir and Freundlich classical adsorption isotherm models. The adsorption capacity (Q_o) calculated from Langumuir isotherm was 1.71mg Ni(II)/g of Begasse at initial pH of 5.0 at 27+2^{o}C for particle size 0.430 mm. Increase in pH from 2-10 increased percent removal of metal upto 5.0 later onwords 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 was on the *Date nuts dust* surface quantitative recovery of Ni(II) is possible by HCl.

Introduction

Nickel is used in electroplating industry, in the making of coins, chemical reagents, alloys preparation, nickel compounds, house wear utensils, machine parts, preparation of stainless steel, spare parts in automobiles, leather and textile industries.

Nickel and its compounds are naturally present in the earth's crust and releases to the atmosphere occur from natural discharges such as windblown dust and volcanic eruptions, as well as from anthropogenic activities. It is estimated that 8.5 million kg of nickel are emitted into the atmosphere from natural sources such as windblown dust, volcanoes and vegetation each year. Five times that quantity is estimated to come from anthropogenic sources.

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).

Key words: pH, adsorption, kinetics, pollution, isotherm and *Date nuts dust*.

Adsorbent:

The *Date nuts* were collected in bulk, vendors shop at Visakhapatnam, Andhra Pradesh and made into small pieces, cleaned well and soaked in distilled water for 24 hrs and washed with distilled water and dried under sun light and the material was pulverized and sieved to different particle sizes. Adsorbent of particle sizes 0.430 mm, 0.600 mm and 0.800 mm were used for characterization.

Adsorbate: Nickel Ammonium Sulphate solution

Analytical reagent 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 6.7280 g of Nickel Ammonium sulphate in 5 ml of 1% HNO_3 solution to prevent hydrolysis and diluted with doubled distilled water and made up to 1000 ml.

Results and discussion- approach of the adsorption

Effects of pH on the Ni(II) Adsorption

The effects of pH on the adsorption of Ni(II), experiments were carried out using 100 mg of the adsorbent (*Date nuts dust*) dust in 50 ml solution of 10 mg/l of Ni(II) concentration, adjusted to different pH values ranging from 3.0 to 10.0 using 0.1N HCl and 0.1N NaOH solutions. The solution after equilibrium for a period of 90 min. The equilibrated solutions were analyzed for Ni(II) concentration spectrophotemetrically (Stewart 1975 & APHA 2005). The percentage of adsorption increased with increase in pH, reached a maximum of 97.45 percentages at pH 5.0 and remained almost constant thereafter in the pH range 6.0 - 10.0. This may be due to the reason that protons might have competed with metal ions for adsorption sites, thus decreasing the uptake of metal-ion. As pH of the solution increased, the percentage removal also increased due to decrease in the amount of competing protons. Similar results were reported for the adsorption of Ni(II) in the literature (Sevgi Kocaoba, 2008, Pratik *et al*., 2007 and Meenakshi Goyal *et al*., 1999). At pH above 6.0 precipitations was noticed and hence pH 5.0 was selected for the study. It was observed that at pH more then 6.0, the percent removal of Ni(II) by adsorption was greater than that by precipitation. Removal of Ni(II) by adsorption using peat was found to be high in the pH range 4.5-5.0 (Viraraghavan and Drohamraju, 1993).

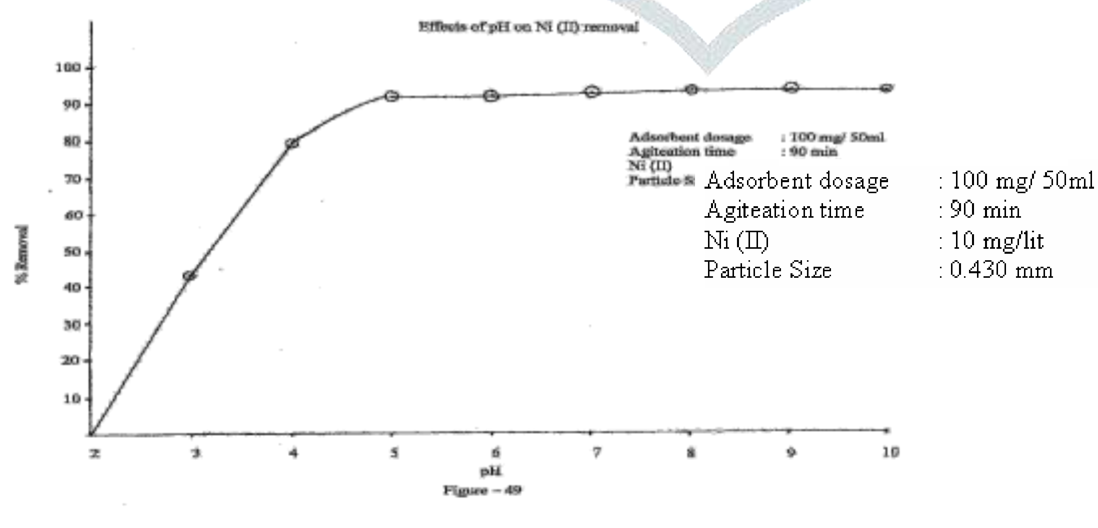

Fig – 1: The effects of pH on Ni(II) removal

Batch mode adsorption study

Batch mode adsorption studies to determine the adsorption rates and maximum adsorption capacities. Batch mode adsorption studies were carried out at 27+2°C using 50 ml of metal ion solution containing the desired concentration and 100 mg of adsorbent in 250 ml conical flasks with lids stirring speed 250 rpm samples were separated and filtered. Ni(II) was analyzed by spectrophotometer (Stewart 1975 & APHA 2005). All the experiments were carried out at initial pH of 5.0 where the adsorption is significant but pH is more than 5.0 metal hydroxide precipitations occurs. The metal concentration on the adsorbent phase (q_e, mg/g) was calculated by using the following equation.

$$Qe = \frac{(co - ce)V}{m}$$

Where C_o and 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+2°C with an initial concentration of Ni(II) ranging from 10-40 mg/L a solution of volume 50 ml and adsorbent weight of 100 mg the stirring time was 90 min. The effect of pH on percent removal was studied from initial pH 3-10 using 50 ml metal ion solution 10 mg/L with 100 mg adsorbent 0.1M HCl or 0.1M NaOH used to adjust the pH.

Batch mode desorption studies

After adsorption experiments, the metal ion loaded *Date nuts dust* were separated and slightly washed with distilled water to remove unadsorbed metal ions on the *Date nuts dust* surface. They are stirred with 50 ml of HCl of various concentrations ranging from 0.02 – 0.12M for 90 min, metal ion concentrations were analyzed as all the chemicals are used of analytical reagent grade. All the experiments were carried out in duplicate and mean values are presented maximum deviation was +5.0%.

Kinetic study

The kinetic study of the adsorption of Ni(II) was conducted at optimum pH, where only adsorption takes place. The effects of contact time and initial metal ion concentration of Ni(II) adsorption on to *Date nuts dust*. The adsorption equilibrium was reached at 4.63, 8.59, 11.23 and 13.78 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 Lagergern(Lagergern1898)

$$\log(qe - q) = \log qe - \frac{Kadt}{2.303}$$

Where q and q_e are the adsorption capacities at time (t) and equilibrium time, respectively. K_{ad} is adsorption rate constant. The K_{ad} values were calculated from slope the respective linear plots of log(q_e-q) vs 't' . The results show that the removal of Ni(II) follows first order reaction. K_{ad} 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_{ad} x 10^{-2}	Q(mg/g)
10	5.80	04.67
20	5.59	08.59
30	4.68	11.32
40	4.60	13.78

Adsorption isotherms

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

$$\frac{Ce}{qe} = \frac{1}{Qob} + \frac{Ce}{Qo}$$

Where C_e is equilibrium concentration (mg/L) , q_e is amount adsorbed at equilibrium (mg/L), Q_o (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 Begasse obeys Langmuir isotherm model. Q_o and 'b' were determined from the slope and intercept of the plot are found to the 1.71 mg/g and 0.13 L/mg respectively, Kadirvelu et al., (2003). The adsorption capacity of other adsorbents for Ni(II) are summarized in Table- 2 for comparison. Freundlich isotherm is also used to explain observed phenomenon with following equation

Table - 2

Adsorbent	Q_e mg/g	Reference
Rice hull	05.58	Suemitsu et al., (1986)
Natural clay	12.50	Hawash et al., (1994)
Pea mass	09.18	Lo et al., (1995)
Soya been hull	89.52	Marshal and Champage (1995)

Given by Freundlich (Freundlich 1906)

$$qe = KfCe^{1/n}$$

where C_e is equilibrium concentration (mg/L), q_e is amount adsorbed 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 log q_e vs 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 0.65 and 2.22 respectively Kadirvelu et al (2003).

Effects of *Date nuts dust* concentration

The removal of Ni(II) as a function of *Date nuts dust* concentration. Increasing *Date nuts dust* 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 180 mg 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 mechanism 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 81.33 percentage of Ni(II) was disrobed with HCl concentration of 0.12M at agitation time of 90 min. This may be due to the fact that in acidic pH, H^+ ions replace the metal ions from the adsorbent surface leading to desorption of the positively charged metal ion species. Comparable results on desorption of Ni(II) by using HCl solution were reported by Kadirvelu et al., (2003) and Shanmugavalli et al., (2006)

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 suggest that ion-exchange may also involve in the adsorption mechanism (Lin et al,.1992)

Removal of Ni(II) from Chromium plating wastewater

The characteristics of the wastewater collected from the chromium plating industry, collected solution pH = 6.40 and adjusted to pH = 5.0 using acidic solution, adsorption of Ni(II) was carried out at pH=5.0 Fig-3 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 800 mg. A maximum 87.50 percent of Ni(II) ions at agitation time was 100 min, were removed from the chromium plating wastewater containing Ni(II) concentration of 18.50 mg/L, suggesting that the Begasse indicating the adsorbate can be effectively used for the treatment of industrial wastewater containing Ni(II) ions Manonmani, (2002), Selvaraj et al., (1998).

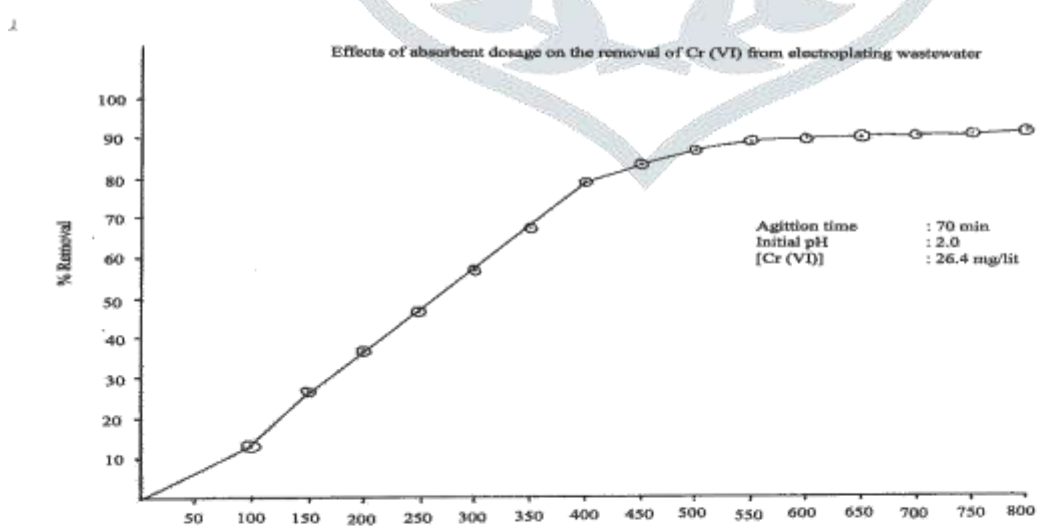

Figure – 10

Conclusion

Experimental conditions such as pH, *Date nuts dust* concentration and reaction time have been optimized to utilized *Date nuts dust* as adsorbent for the removal of Ni(II) from aqueous solution. Adsorption capacity increase with decrease of metal ion concentration and increase with pH, reached a maximum of 93.00% at pH 5.0. The pH effects and desorption studies were studied to understand adsorption mechanism. Adsorption followed both Langmuir and Freundlich adsorption isotherms. The adsorption capacity (Q_o) was 1.71 mg Ni(II)/g of *Date nuts dust* at the initial pH of 5.0 for the particle size of 0.430 mm. The kinetic studies show that the removal of Ni(II) followed 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 *Date nuts dust* surface. These reactions induce release of H^+ ions on the *Date nuts dust* surface.

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