Removal of Ni(II) from Aqueous Medium Using Low Cost Adsorbent

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The adsorption technique using coconut husk was applied for the removal of Ni^{2+} ions from aqueous samples. The dried and powdered husk was contacted with acidified formaldehyde and the product so obtained is highly efficient in adsorbing Ni^{2+} ions from the solutions. The extent of removal/adsorption was dependent upon the pH, amount of adsorbent used and the time of contact. The sorbent is effective for quantitative removal of Ni^{2+} ions in alkaline conditions and equilibrium has been achieved in 1 h. This method is quite feasible, economic, time saving and low cost.

Key Words: Adsorbent, Coconut husk, Ni(II).

INTRODUCTION

Nickel is one of the ubiquitous elements and ranks twenty third in order of abundances; its average concentration in earth's crust being 75 mg/kg.[1] Ni is used most extensively in nickel plating and alloy manufacturing. High alloys are used in chemical, marine, electrical, nuclear and aerospace applications. Nickel is also used as a catalyst in oil refining and other industrial processes. The current users of nickel include nuclear power plants, gas turbine, cryogenic engines, container and pollution abatement equipment[2,3].

Wastewater containing nickel originates from metal processing industries, steel foundries, motor vehicle, aircraft industries, printing and in some cases the chemical industry. In the presence of complexing agent such as cyanide, nickel may exist in a soluble complex form. The presence of nickel cyanide complexes interferes with both cyanide and nickel treatment. Nickel forms insoluble nickel hydroxide upon the addition of lime, resulting in a minimum solublity of 0.12 mg/L at 10–11 pH. Nickel can also be precipitated, may be expected to yield residual nickel concentrations in the order of 0.15 mg/L after sedimentation and filtration. Recovery of nickel can be accomplished by ion-exchange or evaporation, provided the nickel concentrations in the wastewater are at sufficiently high level.

The Sadbury deposits in Canada are associated with basic igneous rocks like gabbros and norites and the average content is about 1.26% of Ni and 0.94% of Cu. In New Caledonea, the nickel deposits are found associated with serpentines. The ore mineral, garnierite, occurs both in veins and in concretionary masses. In

India, there is no significant production of nickel. However, nickeliferrous pyrites had been recorded from many parts of India.

First time, Hasrolhoff[4] demonstrated that high concentration of nickel has shown toxic effects on corn and other plants by using solutions culture. In oats, Vergnano and Hunter[5] observed that nickel toxicity closely resembled iron deficiencty. In plants the uptake and translocation of several essential nutrients are reduced by high nickel concentration present in the nutrient medium[6] and thus damage the metabolism of plants[7]. Nickel appears to be relatively non-toxic to mammals and exhibits only low toxicity because of reduction in fecundity and survival by 50% at 1.6 mg/L[8]. Ni is present in smaller quantities in plants, animals while in sea water, petroleum and coal it is present in traces[9].

Sources of Ni^{2+} ions and its concentration in industrial wastewater from some non-metallic industrial processes are meat processing (0.07 mg/L), fat rendering (0.28 mg/L), fish processing (0.14 mg/L), bakery (0.43 mg/L), miscellaneous foods (0.11 mg/L), brewery (0.4 mg/L), soft drinks and flavouring (0.22 mg/L), ice cream (0.11 mg/L), textile dyeing (0.25 mg/L), fur dressing and dyeing (0.74 mg/L), miscellaneous chemicals (0.10 mg/L), laundry (0.1 mg/L) and car wash (0.19 mg/L)[10].

In recent years considerable attention has been devoted to the study of different types of low cost materials such as peanut skin, tree bark, waste rubber, onion skin and saw dust for the adsorption. Here adsorbent material prepared from coconut husk has been employed for the removal of Ni from aqueous solutions. Coconut husk is a commonly available and inexpensive byproduct of coir industry.

EXPERIMENTAL

Preparation of sorbent: Coconut husk was used for the preparation of adsorbent and was collected from a local coir source, washed with distilled water and dried. To prevent colour leaching and to improve physical characteristics of sorbent, two parts of coconut husk were treated with twenty parts of 0.2 N H_2SO_4 and five parts of 39 per cent of HCHO.[11] It was kept in an air oven at 60°C for about 6 h with occasional stirring. The product formaldehyde polymerized coconut husk (FPCH) was washed several times with distilled water, dried at 60°C and then powdered.

The IR spectrum of FPCH shows absorption band at 3345 cm^{-1} which is attributed to —O—H or —N—H,[12] 1614 cm^{-1} to aromatic —C=C—, 1069 cm^{-1} to primary alcohol C—O, 723 cm^{-1} to monosubstituted benzene (—C—H bending).

Adsorption: Adsorption studies were carried out by batch adsorption process at room temperature. Nickel salt ($NiSO_4$) was dissolved in double distilled water to get synthetic wastewater. Few sets of 50 mL of the solution containing the desired amount of Ni(II) ions were taken in 100 mL conical flasks for the purpose of the experimental work. To these conical flasks suitable doses of adsorbents were added and shaken thoroughly on an electric shaker for the required period. The suspension was then filtered through Whatman 41 filter paper and the filtrate was analysed using UV-Vis spectrophotometer for the estimation of Ni(II) ion concentration. The effects of pH, contact time, adsorbent dose and initial Ni(II)
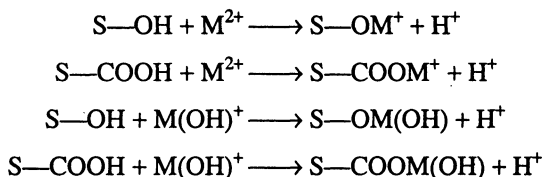
concentration were studied. Initial pH of samples was adjusted by adding 0.1 N HCl or 0.1 N NaOH. All the experiments were conducted at room temperature.

RESULTS AND DISCUSSION

Effect of pH: The results of effect of pH on adsorption are shown in Fig. 1. The removal of Ni(II) increases from 5.0 to 18% when pH is increased from 3.5 to 5.0. At pH 6, it is 25%. When pH increases from 7 to 10 removal increases from 54–86%. In alkaline pH, as the concentration of H^+ ions is lowered, the FPCH surface becomes available for accumulation of nickel; therefore the adsorption increases. At low pH range, concentration of H^+ ions is quite high and may affect the solubility of metals. At higher pH, these may be in precipitated form due to presence of base[13].
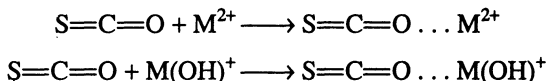
$$Ni^{2+} + Na_2CO_3 \longrightarrow NiCO_3 + 2Na^+$$

The presence of groups like —OH and —COOH adsorbs the metal ion as follows[14]:

$$S—OH + M^{2+} \longrightarrow S—OM^+ + H^+$$

$$S—COOH + M^{2+} \longrightarrow S—COOM^+ + H^+$$

$$S—OH + M(OH)^+ \longrightarrow S—OM(OH) + H^+$$

$$S—COOH + M(OH)^+ \longrightarrow S—COOM(OH) + H^+$$

where S = sorbent and M = metal.

There may be interaction between keto groups[15] and M^{2+} or $M(OH)^+$.

$$S\!=\!C\!=\!O + M^{2+} \longrightarrow S\!=\!C\!=\!O \ldots M^{2+}$$

$$S\!=\!C\!=\!O + M(OH)^+ \longrightarrow S\!=\!C\!=\!O \ldots M(OH)^+$$

Acidic mineral oxides mainly silica and alumina may also act as sorbent for different Cu(II) species. The metal oxides present in the sorbent develop positive or negative charge surface[16].

basic dissociation   acidic dissociation
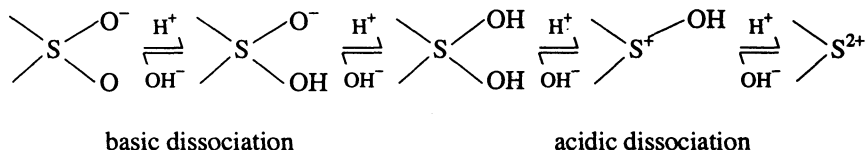
where S = metal—Si or Al.

Thus in acidic medium positive charge developed on sorbent surface does not favour the association of cationic sorbate species. In alkaline medium negatively charged surfaces favour association of cationic sorbate species.

Results indicate that adsorbent is efficient in the pH range 8–10. At pH 10, Ni(II) removal was mostly due to precipitation and not by sorption. Hence pH 8 was considered as optimum pH for further studies.

Effect of time of contact: The sorption kinetics of FPCH at pH 8.0 for the effect of contact time have been presented in Fig. 2. pH was kept at 8.00, initial

concentration of Ni was 3.0 mg/L, amount of adsorbent 0.5 g. The time of contact was varied from 15 to 90 min. The system achieved equilibrium in 60 min; thereafter there was no further appreciable change in the amount of Ni(II) adsorbed. Therefore 60 min has been kept as an optimum time of contact for further adsorption studies.
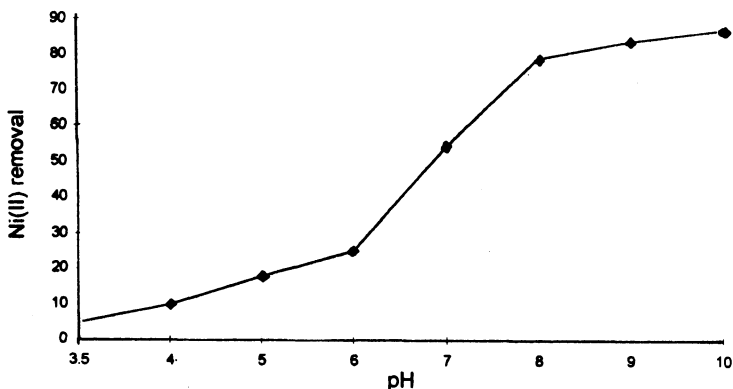

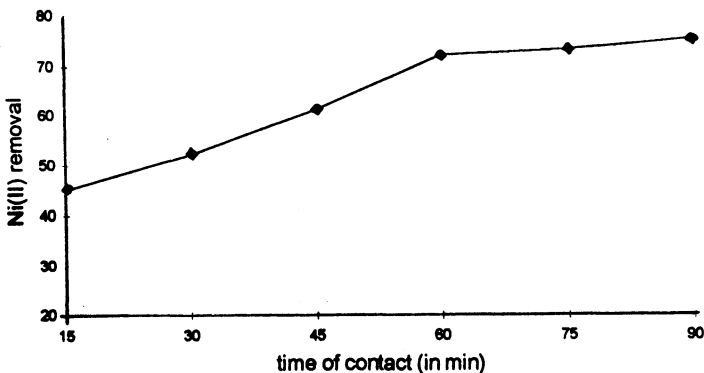Fig. 1. Removal of Ni(II) by FPCH at different pH

Fig. 2. Removal of Ni(II) by FPCH at time of contact

Effect of initial concentration: During adsorption, initial concentration of pollutants plays an important role because the resistance to the uptake of solute from the solution decreases with the increase in initial concentration. Effect of initial Ni(II) concentration on the extent of removal has been plotted in Fig. 3. For this set the constant parameters were : amount of adsorbent = 0.5 g, time of contact = 60 min, pH = 8.0. It was observed that the percentage removal of Ni(II) decreases with increase in initial concentration of Ni(II). Per cent removal decreases from 80.00 to 59.00 with increase in initial concentration from 1.0 to 6.0 mg/L of Ni(II).

Effect of amount of adsorbent: Amount of FPCH used for treatment has varied and data collected is plotted in Fig. 4. The other parameters were pH = 8.0, time of contact = 60 min, initial Ni concentration = 5.0 mg/L. As the amount of
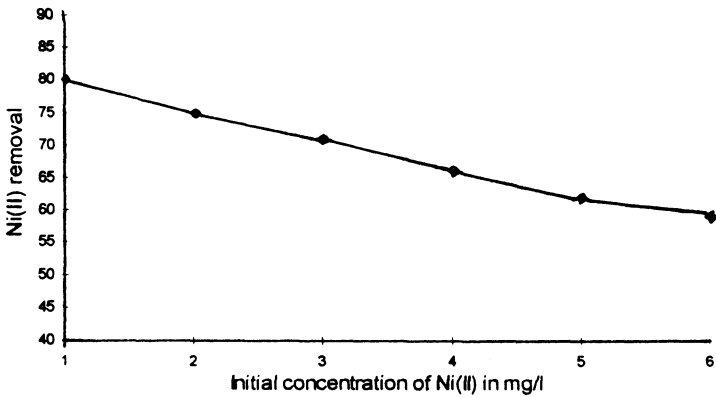
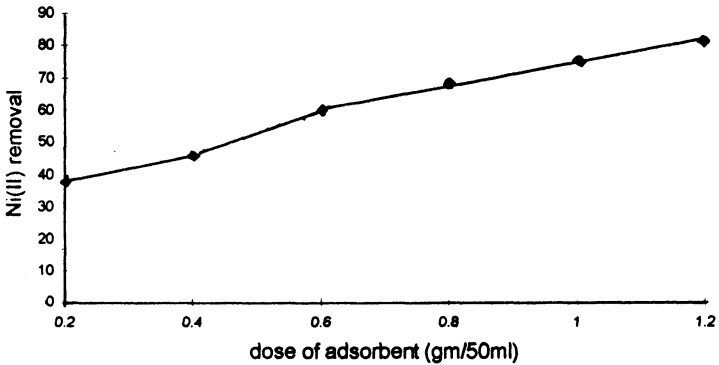Fig. 3. Removal of Ni(II) by FPCH at different initial concentrations

Fig. 4. Removal of Ni(II) by FPCH at different doses of FPCH

adsorbent increases the number of active sites present on the adsorbent simultaneously increases, resulting in the enhancement of removal of Ni(II). As the amount of adsorbent increases from 0.2 to 1.2 (g/50 mL) the per cent removal increases from 38.00 to 81.00.

Langmuir isotherm:

$$C_e/(X/m) = 1/(bV_m) + C_e/V_m$$

where X is the amount of adsorbate adsorbed, m is the amount of adsorbent, C_e is the equilibrium concentration of the adsorbate in the solution, b is a constant that represents adsorption bond energy and V_m is the maximum adsorption density corresponding to a monolayer covering the surface of the adsorbent. If the adsorption data follow Langmuir pattern, a plot of $C_e/(X/m)$ with C_e should yield a straight line. Constants b and V_m may be calculated from the slope and intercept.

Freundlich isotherm:

$$X/m = k_f C_e^{1/n}$$

where C_e, X and m have the same meaning as described in Langmuir isotherm,

k_f is the measure of sorption capacity, $1/n$ is sorption intensity. Taking log on both sides,

$$\log (X/m) = \log k_f + 1/n \log C_e$$

If the adsorption data follow Freundlich pattern, the plot of $\log (X/m)$ with log C_e, should yield a straight line and n and k_f may be calculated from the slope and intercept, respectively.

Attempts were made to fit the adsorption data for Ni(II) in Freundlich (2) and Langmuir (1) isotherms separately up to the 6.0 mg/L initial concentration.

Langmuir equation:

$$C_e/(X/m) = 2.2 + 1.875 \times C_e \qquad \qquad \dots (1)$$

Freundlich equation:

$$\log (X/m) = 0.623 \times \log C_e - 0.66 \qquad \dots (2)$$

Freundlich and Langmuir constants (k_f, n, b, V_m) calculated from these equations are given in Table-1. Langmuir isotherm plot is shown in Fig. 5.

TABLE-1
FREUNDLICH AND LANGMUIR CONSTANTS FOR Ni(II) ADSORPTION

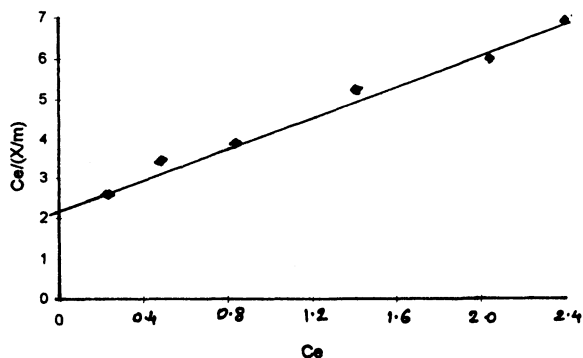| K_f	n	r^2	V_m	b	r^2
0.2187	1.6	0.7253	0.533	0.8528	0.9880

Fig. 5.   Langmuir isotherm plot for adsorption of Ni(II).

As the value of r^2 is higher for Langmuir equation than for Freundlich equation, the fit is better in Langmuir form. Lower value of bond energy constant (b = 0.8528) points towards the possible multilayer adsorption.

The comparative study of the results clearly shows that the use of coconut polymer husk for the removal of Ni(II) from aquous solutions is quite satisfactory. This is because of the fair adsorption property of FPCH. The efficiency of Ni(II) removal process can be enhanced by keeping optimum conditions.

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