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Removal of Nickel (II) by Finger Millet (Ragi) Husk as Adsorbent

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This experimental study was focused on finger millet husk as an alternative adsorbent for the removal of Ni(II) from wastewater. Batch experiments were conducted at room temperature 28°C to determine the various parameters such as contact time, adsorbent dosage, pH and initial concentration. The maximum removal efficiency of Ni(II) was 99.98% for 0.9g/50mL of ragi husk at pH 8.0. The experimental data was tested using Langmuir and Freundlich equations. The data fitted well to both Langmuir and Freundlich isotherms. The present study showed that ragi husk was capable of removing Ni(II) ions from aqueous solutions.

Key words: Ragi husk, Nickel(II)

Introduction

In India, there are more than 50,000 large, medium, and small scale electroplating units mostly scattered in urban areas1 and there are about 79 electroplating industries located in Karnataka state, out of which 71 industries are in and around Bangalore city only2. The water consumption is less in electroplating industries compared to other industries, and the effluent is more toxic than other wastes. These industries produce toxic hazardous waste containing heavy metals approximately 78,000kg/annum which adversely effect environment, especially humans, animals, plants, and aquatic life2. When wastewater containing heavy metals flows on the surface of the ground, it looses fertility and the wastewater containing nickel, originates primarily from metal industries, particularly during plating operations. Occurrence of dermatitis in some workers engaged in electroplating, polishing paints and pigments may be attributed to nickel poisoning. Heavy metals can pose health hazards, if their concentration exceeds allowable limits3. Therefore, before wastewater flows through waterbodies or land, it should be treated.

Effluents from industrial processes such as electroplating, mining, nuclear power operation, battery manufacturing, dye and pigment have been identified to contain high level of heavy metals, such as Cr(III), Cr(VI), Zn, Cd, Cu, Ni, Hg and Pb⁴. The methods

adopted are ion exchange, electrochemical reduction, evaporation, solvent extraction, reverse osmosis, chemical precipitation, membrane filtration, and adsorption⁵. Many researchers have identified the low cost adsorbents like saw dust⁶, rice husk⁷, coir pith⁸ coconut shell, waste tea powder, coconut husk⁹, sugarcane bagasse¹⁰ and others.

Even though the industries are not keen to adopt these adsorbents, all industries are adopting chemical processes only, due to difficulty in disposing of adsorbent materials after use.

Therefore, it is important to identify an adsorbent material like ragi husk for removal of nickel in electroplating industrial effluents which is having advantages of removal of pollutants from effluents effectively and do not have much adverse impact on environment when disposed of after treatment.

The main objective of study aims at providing economically viable treatment methodolgy of electroplating wastes using ragi husk as a locally available material.

Materials and methods

Finger millet (Ragi) husk

Ragi husk is a waste product derived at the time of harvesting and processing of ragi crop. It is a

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bio-degradable agricultural by-product. The main physico-chemical characteristics of the ragi husk are shown in the Table 1 and Table 2.

Table 1: Physical characteritics of Ragi husk

Density .	0.0729g/cm ³
рН	6.58

(Tested in B.I.T. laboratory)

Table 2: Chemical composition of Ragi husk

Parameter, mg/L, Max	%
Total Kjeldhal Nitrogen	28
Calcium as Ca	49
Phosphorous as P	14
Silicon di-oxide as SiO ₂	12.52
Total Aluminium dioxide(Al ₂ O ₃) + Iron oxide (Fe ₂ O ₃), percent by mass (minimum)	1.68
Magnesium oxide (MgO), percent by mass (maximum)	0.29
Loss on Ignition	80.6

(Tested in Civil Aid, Bangalore-2011)

Preparation of adsorbent

Ragi husk was obtained from Mandya district of Karnataka. Adsorbent was sieved with I.S.sieve (600-300µ). Sieved sample was washed with distilled water and dried at 28°C for 24 hours, and then sample was dried in hot air oven at a temperature 45°C for 8 hours and cooled in room temperature and preserved in air tight plastic container.

Instruments and reagents:

Chemito AA-203 Atomic Adsorption Spectrophotometer was used for the determination of Ni(II), with 250mL Erlenmeyer flasks and digital pH meter 2000 rpm centrifuge model of rotary shaker was used for agitating the mixture of effluent and adsorbent.

A stock solution containing 1000 mg/L of Ni (II) was prepared by dissolving the pure nickel metal in 1:1 hydrochloric acid solution and then diluting the same up to 1000mL in a volumetric flask with double distilled water.

Batch experiments

Batch equilibrium adsorption experiments were conducted by adding known quantity of ragi husk to

Erlenmeyer flasks containing 50mL of industrial effluent having Ni(II) concentration of 27.435mg/L. The pH of the solution was adjusted using dilute 0.1M HCl or 0.1M NaOH. The flasks were agitated 150 rpm in a rotary shaker. The experiments were conducted for contact time of one to five hours and pH ranging from 2 to 12. The adsorbent was separated from the solution by filtration. The removal efficiency of nickel using Chemito AA-203 Atomic Adsorption Spectrophotometer was depending upon the wavelength (357.48nm) and working standards. The percentage removal efficiency (η) and equilibrium concentration were determined.

Results and discussion

Effect of contact time on Ni(II) removal by Ragi husk

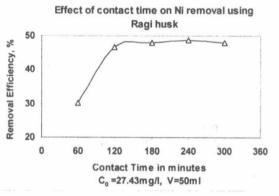


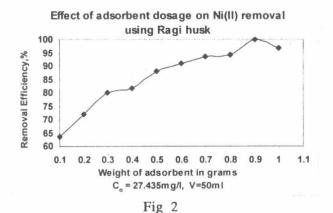
Fig 1.

The results for the effect of contact time on adsorption of Nickel (II) removal are shown in Fig 1. 0.1 to 1.0g of adsorbent was used for this experiment in contact time 60 minutes to 300 minutes of pH 2 to 12.

The percentage removal efficiency of nickel (II) ions increased with increase in contact time and reached equlibrium after 180 minutes Therefore 180 minutes was considered as optimum time. At the initial stage, the rate of removal of nickel (II) ions was higher due to availability of more than required number of active sites on the surface of ragi husk and became constant due to decreased or lesser number of active sites.

Fig 1 reveals that the curve is single, smooth and continuous, leading to saturation suggesting the possible mono layer coverage of nickel (II) ions on the surface of the adsorbent. Similar result has been reported in literature¹¹.

Effect of adsorbent dosage on Ni(II) removal using Ragi husk



The results for the weight of adsorbents on adsorption of Nickel (II) removal using Ragi husk are shown in Fig 2. The weight of ragi husk varying from 0.1g to 1.0g was used. The percentage removal enhanced as the adsorbent dosage was increased.

The effect of adsorbent dose on the percent removal of Ni(II) was 99.98% with the required optimum dosage of 0.9g/50mL of solution. Beyond the optimum dosage the removal efficiency did not change with the adsorbent dose. Since for a fixed initial adsorbate concentration increasing adsorbent dose provides greater surface area or more adsorption sites, for a given initial metal concentration the removal efficiency increased with increasing the adsorbent dose which was expected. Similar result has been reported in literature¹².

Effect on pH on Ni(II) removal using Ragi husk

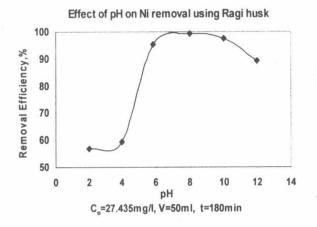


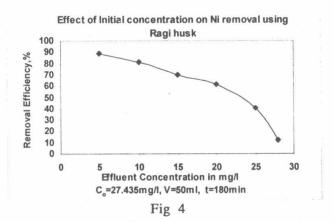
Fig 3.

The adsorption capacity of adsorbent as function of effluents pH was 2.42. The experiment was conducted over pH range of 2 to 12. pH is one of the most important parameters controlling the adsorption process. The effect of pH of the solution on the adsorption of nickel ion on ragi husk was determined. The pH of solution was controlled by the addition of 0.1M of HCL or 0.1M of NaOH.The uptake of the nickel ions at pH 6-8 was maximum and at pH 2 was minimum and slightly decreased at pH 10-12 as shown in Fig 3.

At low pH values, the adsorption percentage was low due to the positive charge density (protons) on the surface sites, resulting in the electrostatic repulsion between the Ni(II) ions and edges groups with positive charges (Si-OH²⁺ or Ca-OH²⁺) on the surface. Electrostatic repulsion decreased with increasing pH because of reduction of positive charges density on the sorption edges, thus resulting in an increase in Ni(II) ion adsorption on the surface.

In an alkaline medium, the surface of ragi husk becomes negatively charged. Referring to Fig 3, the maximum adsorption of Ni(II) ion occurred at pH 6-8. At pH values higher—than 8, Ni(II) precipitated as hydroxide which decreased the rate of adsorption and subsequently the percent removal of Ni(II) ions. Similar result has been reported in literature¹³.

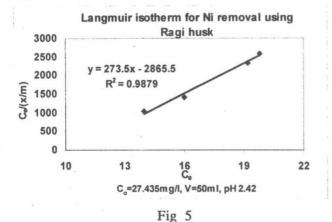
Effect on initial concentration on Ni(II) removal using Ragi husk



The experiment was carried out over initial concentrations 5mg/L to 27.435mg/L per 50mL of solution and at a contact time of 1-5 hours with 0.1 to 1.0g of ragi husk with a pH of 2.42. The maximum and minimum removal efficiencies of nickel were 90.086% and 12.36% respectively as shown in Fig 4. The experimental results of adsorptions of nickel ion

on the electroplating effluent at various concentrations (5, 10, 15, 20, 25, 27.435 mg/L) are shown in Fig 4. From Fig 4, it can be observed that the removal percentage increases when the initial concentration decreases. At low concentrations the ratio of surface active sites to the total Ni(II) in the solution was high and hence all Ni(II) may interact with the adsorbent and will be removed from the solution. Similar result has been reported in literature¹⁴.

Langmuir isotherm and Freundlich isotherm for Ragi husk



Freundlich isotherm for Ni removal using Ragi husk 3.45 3.35 3.25 3.15 3.05 D 2.95 y = 2.6628x - 0.0444 $R^2 = 0.9965$ 2 85 2.75 1.35 1.1 1.15 1.2 1.25 log C_e 1.3 V=50ml, C = 27.435mg/l, pH 2.42 Fig 6

Several equilibrium models have been developed to describe adsorption isotherm relationships. The adsorption of Ni(II) ions was carried out at different initial concentrations ranging from 5 to 27.435 mg/L with contact time of 3 hours. The data obtained was analyzed with the Langmuir and Freundlich isotherm equations as shown in Fig 5 and Fig. 6. The mean values of the regression co-efficient (R²) were found 0.9862 and 0.9965 in Langmuir and Freundlich isotherm equations respectively. The result shows that the experimental data best suits for both the Langmuir isotherm and Freundlich isotherm. Similar result has been reported in literature¹⁵.

Conclusions

The adsorption behaviour of nickel on Ragi husk was investigated in batch experiments. The adsorption was found to be drastically dependent on pH, adsorbent dosage, and contact time. The optimum pH for Ni(II) ion was found to be 8.0. The rate of Ni(II) adsorption was rapid. The Nickel-Ragi husk system attained equilibrium in 180 minutes.

Isotherm data analysis showed that the adsorption pattern of Ni(II) ions on ragi husk follows the Langmuir and Freundlich isotherm equations. The maximum adsorbent dosage was 0.9g/50mL used for treatment of electroplating effluent.

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Table 3: Adsorption isotherm for Nickel using Ragi husk

Weight of adsor bent in grams	Langmuir Isotherm		Freundlich Isotherm	
	Equation from Graph	R ² value	Equation from Graph	R ² value
0.1	y = 129.86x-2454.6	0.9833	y = 5.9079x - 5.3244	0.9959
0.5	y= 261.56 x- 3850.8	0.9875	y = 3.7508x - 1.7455	0.9971
1.0	y = 273.5 x -2865.5	0.9879	y = 2.6628x - 0.0444	0.9965

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