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# Treatment of Nickel Plating Industrial Wastewater by Fungus Immobilized onto Rice Bran

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## Abstract

The removal of Ni (II) from industrial wastewater was examined by pure rice bran, free *Rhizopus arrhizus* and immobilized *R.arrhizus* onto rice bran, and results were compared with each other. Nickel plating industry was imitated in this study and, as a model, synthetic wastewater was used containing approximately 100 mg $Ni^{+2}$/L. When the pH value was adjusted to 7.0 in the treatment studies made by using free *Rhizopus arrhizus*, the value of $q_{eq}$ was found as 37.8 g/g. In the experiment conducted by pure rice bran, at a pH value of 5.0, the parameter $q_{eq}$ was determined as 3.18 mg/g. For enhancing the treatment efficiency and observing the immobilizing characteristics of this fungus, *Rhizopus arrhizus* was immobilized onto rice bran. The $q_{eq}$ values were obtained as 4.23 mg/g at a pH value of 5.0, and the removal was made a maximum at 90 minutes with a $q_{eq}$ value of 6.83 mg/g.

**Keywords:** Biosorption; *Rhizopus arrhizus*; Rice bran; Nickel removal; Immobilization; Nickel plating industry

## Introduction

As today's technology progresses, the natural environment suffers from the detrimental effects of pollution. The natural process of transportation of metal ions between soil and water consolidates metal contamination in high concentrations that affect the areas of natural ecosystems.

Heavy metal releases to the environment have been increasing continuously as a result of industrial activities and technological development, posing a significant threat to the environment and public health because of their toxicity, accumulation in the food chain and persistence in nature. It is therefore important to develop new methods for metal removal and recovery from dilute solutions (1–100 mg/L) and for the reduction of heavy metal ions to very low concentrations (Zafar et al., 2007).

Nickel ion is a common environmental pollutant which is considered as toxic (e.g. in concentrations of 15 mg/L), especially to activated sludge bacteria, and its presence is detrimental to the operation of anaerobic digesters used in waste water treatment plants. Nickel (II) ions exist frequently encountered in industrial waste waters (e.g. from mine drainage, plating plants, paint and ink formulation, porcelain enamelling). In mine drainage, nickel concentrations can approach 0.19-0.51 mg/L, 0.46-3.4 mg/L (acidic), and 0.01-0.18 mg/L (alkaline). Nickel plating industry has an important place among the industries releasing nickel ion to the aqueous medium. The nickel ion concentrations in different nickel plating industry wastewaters can vary (10-1000 mg $Ni^{2+}$/L) (Kadirvelu et al., 2001). According to the US Environmental Protection Agency, the permitted value for heavy metal ions is usually less than 1.0 mg/L (Sag and Kutsal, 1997).

Traditional technologies for the removal of heavy metals, such chemical reduction and precipitation, reverse osmosis, evaporative and ion exchange, are often ineffective and/or very expensive when used for the removal of heavy metal ions to very low concentrations. Moreover, these methods are specific to each metal ion (Zhao et al., 1999). New technologies are required that can reduce heavy metal concentrations to environmentally acceptable levels at affordable costs.

Biosorption, which is a property of certain types of inactive, dead microbial biomass to bind and concentrate heavy metals from even very dilute aqueous solutions, is one of the most promising technologies involved in the removal of toxic metals from industrial waste streams and natural waters, and offers a potential alternative to existing methods (Aksu et al., 2002). Biosorption can be considered as a collective term for a number of passive accumulation processes such as physical and chemical adsorption, ion exchange, coordination, complexation, chelation and micro-precipitation (Sag and Kutsal, 1997). Of the different techniques employed for metal removal from multi-elemental system, biosorption has been found to be highly selective depending on the typical binding profile of the biosorbents (Ansari and Malik, 2007).

The passive phenomenon of biosorption has several advantages over the active phenomenon of bioaccumulation. A major disadvantage of bioaccumulation is recovery of the accumulated metal by destructive means whereas in biosorption desorption is accomplished by simple physical methods without damaging the biosorbent's structural integrity (Kuyucak and Volesky, 1988).

Biosorption has been studied in various types of biomass such as marine algae, bacteria, fungi, rice bran and agricultural wastes (Vijayaraghavan et al., 2005; Guler et al., 2007; Büyükgüngör et al., 1996; Büyükgüngör, 2000). Rice bran contains different vitamins, carbohydrates, potassium, nitrogen and phosphorus compounds, which induce to water to contact with it. These compounds not only have no pollution effects but they are nutritious

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to the plants. Therefore, the use of bran to eliminate pollution from water reveals the significance of the bran or natural products (Zafar et al., 2007).

Bio removal of metal ions using microorganisms is affected by several factors. These factors include the specific surface properties of the microorganism and the physicochemical parameters of the solution such as temperature, pH, initial metal ion concentration and biomass concentration. In this work, effect of pH and contact time on the biosorption of nickel ions and the efficiency of rice bran, free *Rhizopus arrhizus* and *Rhizopus arrhizus* immobilized onto pure rice bran were studied.

## Materials and Methods

### Microorganism and growth conditions

*Rhizopus arrhizus,* a filamentous fungus, was obtained from the US Department of Agriculture Culture Collection (NRRL 2286). *R. arrhizus* was grown at room temperature in liquid media containing malt extract (Merck) (17.0 g/L) and soybean peptone (Acumedia) (5.4 g/L).

### Preparation of the microorganism for biosorption

After the growth period (5–6 days), *R. arrhizus* was washed twice with distilled water, inactivated using 1% formaldehyde (Merck) and then dried in an oven at 70°C for 24 h. Dried *R. arrhizus* was homogenized in a mixer (Severin) to destroy cell aggregates and sieved at Fritsch (Alnalysette 3, model SPARTAN) sieve. Biomass particles had a size range of 0.063–0.090 mm were used for this metal biosorption study. Finally, for adsorption studies, a weighed amount of dried cells (10 g) were suspended in 1 L of distilled water (Bahadir et al., 2007).

The biosorbent rice bran was collected from Samsun, Turkey. Rice bran biomass was dried at 70°C for 1 week after it was washed with deionized water.

### Immobilization of *Rhizopus arrhizus* onto rice bran

Some of rice bran was added into the liquid media prepared for *Rhizopus arrhizus* and shaken in the shaker for a week at the room temperature. After the incubation period (a week), *R. arrhizus* immobilized on pure rice bran was washed twice with distilled water, inactivated using 1% formaldehyde (Merck) and then dried in an oven at 70°C for 24 hours.

### Preparation of biosorption media containing nickel ions

The experiments were conducted using solutions of nickel in the form of $NiNO_3 \cdot 6H_2O$. These synthetic solutions had an initial metal concentration of approximately 100 mg/L. Known amounts of biomass were contacted with these solutions. Before mixing with the fungal suspension, the pH values of these metal solutions were adjusted by using $H_2SO_4$ and NaOH.

### Biosorption studies

The treatment conditions and biomass characteristics are listed in Table 1. Biosorption studies were conducted in three steps mentioned below.

### Biosorption studies with *Rhizopus arrhizus*

The fungal suspension (5 mL) was mixed with 45 mL of the nickel (II) solution in an Erlenmeyer flask. The flasks were placed on a rotary shaker set (Edmund Bühler SM-30) at a constant shaking rate of 150 rpm (Sag and Kutsal, 1997) at 29±1°C for 24 h, which was more than the sufficient time for adsorption equilibrium. Nickel adsorption to the flask walls and filter paper were negligible. After the samples were filtered by Whatman (pore size 45μm) the concentration of unadsorbed nickel (II) ion in the supernatants were measured by using spectrophotometer (T 70 UV/VIS Spectrometer) with 1.14785.0001 Nickel-test kit (Merck) in accordance with Standard Methods (Clescerl et al., 1999). Biosorption experiments were carried out in duplicate.

| Parameter | Value |
|---|---|
| Biosorption temperature (°C) | 29 |
| Shaking speed (rpm) | 150 |
| Treatment period (hour) | 24 |
| Concentration of *R.arrhizus* (g/L) | 1.0 |
| Concentration of *Rice bran* (g/L) | 5.5 |
| Concentration of Immobilized *R.arrhizus* (g/L) | 5.5 |
| The size range of *R.arrhizus* (mm) | 0.063-0.090 |
| pH range studied | 3.0-9.0 |
| Nickel (II) ion concentration (mg/L) | 87-105 |

**Table 1:** Treatment conditions and characteristics of biomasses.

### Biosorption studies with rice bran

In the case of rice bran, 0.25 g of rice bran was used instead of 5 ml of fungal suspension. Both pure rice bran particles (not sieved) and rice bran particles with a size of 0.5-0.25 mm were used for this metal biosorption study. The size of particles was selected as referred by Zafar et al. (2007). Also the present biosorption study was conducted as mentioned in Section (Biosorption studies with *Rhizopus arrhizus*).

### Biosorption studies with immobilization of *Rhizopus arrhizus*

*Rhizopus arrhizus* immobilized onto pure rice bran (0.25 g) was mixed with 45 mL of the nickel (II) solution in an Erlenmeyer flask. The other all operations were made as explained above (section Biosorption studies with *Rhizopus arrhizus*).

## Results and Discussion

In this study to observe the removal efficiency of *Rhizopus arrhizus* immobilized onto rice bran, firstly the fungus and the rice bran were studied separately. Then this fungus was immobilized on the rice bran as mentioned in section 2 (Materials and Methods) and the studies were conducted with this new biomass, immobilized fungus.

### Biosorption by *Rhizopus arrhizus*

In the experiments conducted by *Rhizopus arrhizus*, the effect of the pH value on the removal efficiency of nickel from the synthetic water was studied. The $q_{eq}$ value was estimated by the following equation;

$$q_{eq} = \frac{V(C - C_{eq})}{M} \quad (1)$$

where $q_{eq}$ (metal uptake, mg/g) is the amount of metal ions adsorbed on the biosorbent, V(L) the volume of metal containing solution in contact with the biosorbent, C(mg/L) is the initial concentration of metal ions in the solution, $C_{eq}$ (mg/L) is the final concentration of metal ions in the solution after biosorption study and M (g) is the dry weight of biomass (*R.arrhizus* or rice bran or immobilized fungus and rice bran) (Bahadir et al., 2007).

At the end of the removal studies, the change of $q_{eq}$ value with the pH range of 3 to 9 is illustrated in Figure 1.

The pH value is an important parameter in the biosorption studies. The initial pH of adsorption medium is related to the adsorption mechanisms onto the adsorbent surface from water and reflects the nature of the physicochemical interaction of the species in solution and the adsorptive sites of adsorbent. It was clearly seen from Figure 1 that the removal of nickel (II) ions increased with increasing pH values. The optimum pH for the adsorption of nickel from the synthetic solution was seemed to be 7.0 with a $q_{eq}$ value of approximately 38 mg/g. This value is almost consistent with Sag and Kutsal (1997).

At the pH values above 7, poorly soluble hydroxyl species was formed and precipitation of nickel would occur (Schecher and McAvoy, 1992). Because of chemical precipitation, the initial nickel concentration was determined as approximately 34 mg/L for pH 9 and the $q_{eq}$ values were estimated with this initial concentration at this pH value.

**Adsorption by rice bran (0.5-0.25 mm)**

In the studies conducted by rice bran, particles of 0.5–0.25 mm range were used to see the adsorption performance of these materials. The effect of pH value on the removal of nickel was investigated. The results obtained are shown in Figure 2.

It was seen from Figure 2 that the removal was optimum with rice bran particles (0.5-0.25 mm) at a pH value of 7. Also the studies were conducted above this value but chemical precipitation was occurred at pH 9 and pH 11. So the studies were conducted under pH 9. Zafar et al. (2007) studied at a pH range of 1-7 by protonated rice bran and found that the optimum pH was 6. Also, it was told in the work of Zafar et al. (2007) that above the pH of 6 chemical precipitations could be occurred. However, in the present study made by rice bran without protonate, the pH range was 3-9. Chemical precipitation occurred at a pH of 9.0, while this precipitation was not observed at pH 7. The removal efficiency at pH 7 was found to be higher than that of pH 6 and below.

**Adsorption by pure rice bran**

At the treatment processes made by immobilized fungus, pure rice bran particles were used. So, to assess the removal efficiency of these particles when they used alone, another study was conducted. The $q_{eq}$ values varying to the pH values studied are shown in Figure 3.

When Figure 3 is examined, it is seen that the pH value of 5.0 gives the optimum results. At pH 3 and below this value, due to the cation competition effects with oxonium (hydronium) ion $H_3O^+$, the nickel uptake is taken place less than the other pH values studied. Also, the same situation because of chemical precipitation was occurred at higher pH.

**Biosorption by immobilized fungus onto pure rice bran**

To observe the effect of immobilization of fungus to the nickel uptake, *R.arrhizus* was immobilized onto pure rice bran and the treatment studies were conducted with this new biomass. The effect of the pH on nickel uptake of this immobilized fungus was investigated. Results obtained are shown in Figure 4.

It has been understood from Figure 4 that the optimum pH is

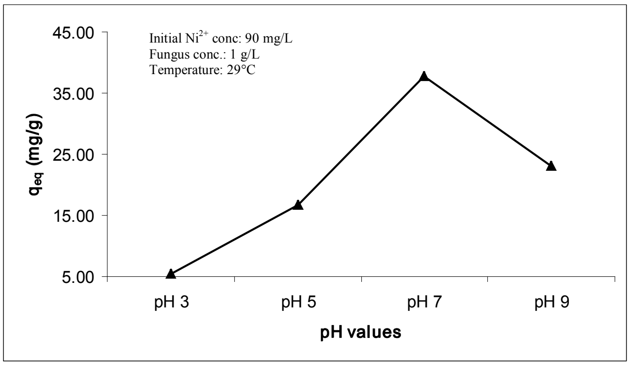


**Figure 1:** The effect of initial pH value on the equilibrium of nickel uptake by *R.arrhizus*.

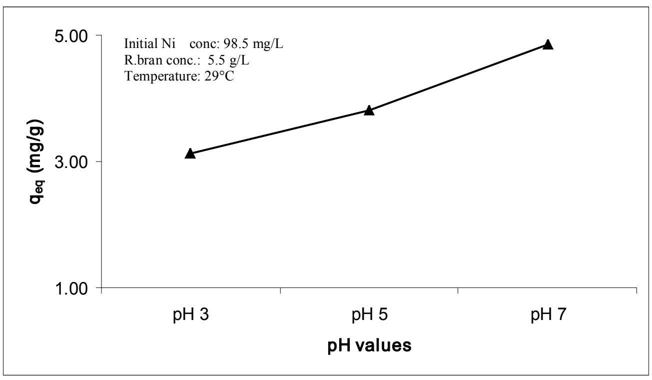


**Figure 2:** The effect of initial pH value on the equilibrium of nickel uptake by rice bran.

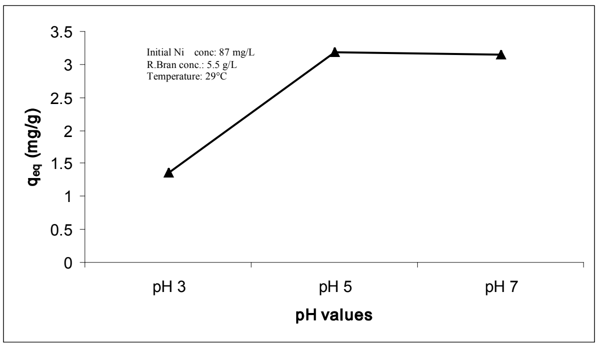


**Figure 3:** The effect of initial pH value on the equilibrium of nickel uptake by pure rice bran.

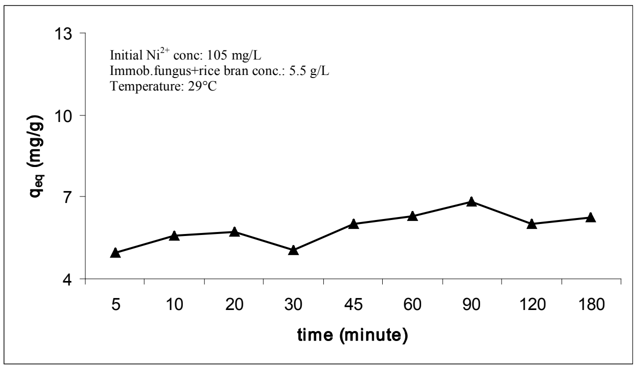


**Figure 4:** The effect of initial pH value on the equilibrium of nickel uptake by *R. arrhizus* immobilized onto pure rice bran.

5.0. At a pH of 3.0 the removal is greater than the value obtained in the study made only with pure rice bran. Also when the pH values 5.0 and 7.0 were assessed in point of removal efficiency, it was seen that better results were obtained compared with pure rice bran. But if these results were compared with the others obtained only with *R.arrhizus*, it could be told that *R.arrhizus* was seemed rather well than the immobilized form of this fungus. While the concentration of free *R.arrhizus* (1 g/L) used in the experiments is less than pure rice bran, the removal efficiency of this free fungus is very high. Also, in immobilization process, the concentration of immobilized fungus and rice bran is higher than the free form of *R.arrhizus*. But this immobilization process could not be realized successfully because of the undesirable characteristics of the fungus. So, only a little portion of *R.arrhizus* was attached on the rice bran. The uptake of nickel was enhanced from 3.2 to 4.2 mg/g by immobilized *R.arrhizus* when compared with pure rice bran.

Another study was performed to find the equilibrium time of nickel uptake by immobilized fungus onto rice bran. The $q_{eq}$ values are demonstrated in Figure 5 versus time. The pH of solution containing nickel was adjusted to 5.0 according to the optimum pH achieved in the previous study mentioned above.

In this study, at the first five minutes of the treatment process the nickel concentration was decreased approximately to 75 mg/L from an initial metal concentration of 105 mg/L. In advancing time period of the adsorption study as it was seen from Figure 5 that there was no significant increase in the uptake of nickel. Also at 90 minutes, a maximum $q_{eq}$ value of 6.83 mg/g was achieved. In the adsorption process it was clearly seen from Figure 5 that immobilized fungus onto rice bran was not stable in point of removal versus time, and it had been told that this material was released the nickel which adsorbed, in the advancing time periods of treatment process.

## Conclusions

A study was conducted for removal of nickel from aqueous solutions by using a filamentous fungus *R.arrhizus*, rice bran, and immobilized *R.arrhizus* onto rice bran. The effect of pH was studied for each material used for uptake of nickel. Also the variation of removal efficiency of nickel from aqueous solutions by immobilized fungus was investigated according to treatment time. It was concluded that the removal was enhanced a little bit by immobilized fungus when compared with pure rice bran. But this enhancement was rather low. Also $q_{eq}$ values of *R.arrhizus* used alone was much better than the immobilized form of this fungus. This could be explained by the immobilization process which was not occurred as desired. Fungus grew on the upper side of the liquid media which was contained rice bran particles. The liquid media was shaken for enhancement of fungus immobilization onto rice bran, but only a little portion of fungus was attached on rice bran. So it can be concluded that this microorganism is not suitable for immobilization onto rice bran particles due to these unfavorable characteristics. Also as another result, free *R.arrhizus* is much better than rice bran particles in point of nickel removal efficiencies.

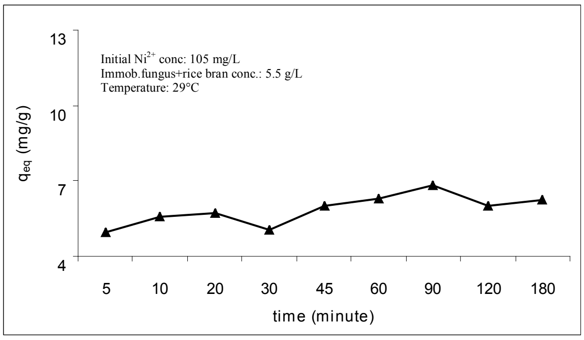


**Figure 5:** The variation of $q_{eq}$ value with time in nickel uptake by *R. arrhizus* immobilized onto pure rice bran.

### References


1. Aksu Z, Açýkel U, Kabasakal E, Tezer S (2002) Equilibrium modelling of individual and simultaneous biosorption of chromium (VI) and nickel (II) onto dried activated sludge. Water Res 36: 3063-3073. » CrossRef » PubMed » Google Scholar
2. Ansari MI, Malik A (2007) Biosorption of nickel and cadmium by metal resistant bacterial isolates from agricultural soil irrigated with industrial wastewater. Bioresour Technol 98: 3149-3153. » CrossRef » PubMed » Google Scholar
3. Bahadir T, Bakan G, Altas L, Buyukgungor H (2007) The investigation of lead removal by biosorption: An application at storage battery industry wastewaters. Enzyme Microb Tech 41: 98-102. » CrossRef » PubMed » Google Scholar
4. Büyükgüngör H, Wilk M, Schubert H (1996) Biosorption of lead by C. Freundii immobilized on hazelnut shells. In: Procedding of V. AIChE. World Conference 2: 437-42. » CrossRef » PubMed » Google Scholar
5. Büyükgüngör H (2000) Biosorption of heavy metals by immobilized microorganism on agricultural wastes, ABSTR PAP AM CHEM. ENVR Part 1: 200-20. » CrossRef » PubMed » Google Scholar
6. Clescerl LS, Greenberg AE, Eaton AD (1999) Standard methods for the examination of water and wastewater. 20th ed. APHA, AWWA, WEF 1325. » CrossRef » PubMed » Google Scholar
7. Guler I, Gurel L, Bahadir T, Buyukgungor H (2007) Biosorption of nickel(II) ions from aqueous solutions by rhizopus arrhizus attached on rice bran. J Biotechnol 131: S79. » CrossRef » PubMed » Google Scholar
8. Kadirvelu K, Thamaraiselvi K, Namasivayam C (2001) Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste. Bioresour Technol 76: 63-65. » CrossRef » PubMed » Google Scholar
9. Kuyucak N, Volesky B (1988) Biosorbents for recovery of metals from industrial solutions. Biotechnol Lett 10: 137-142. » CrossRef » PubMed » Google Scholar
10. Sag Y, Kutsal T(1997) The simultaneous biosorption process of lead (II) and nickel (II) on *Rhizopus arrhizus*. Process Biochem 32: 591-597. » CrossRef » PubMed » Google Scholar
11. Schecher WD, McAvoy DC (1992) MINEQL+: A software environment for chemical equilibrium modeling. Comp Environ Urb Sys 16: 65-76. » CrossRef » PubMed » Google Scholar
12. Vijayaraghavan K, Jegan J, Palanivelu K, Velan M (2005) Biosorption of copper, cobalt and nickel by marine green alga Ulva reticulata in a packed column. Chemosphere 60: 419-426. » CrossRef » PubMed » Google Scholar
13. Zafar MN, Nadeem R, Hanif MA (2007) Biosorption of nickel from protonated rice bran. J Hazard Mater 143: 478-485. » CrossRef » PubMed » Google Scholar
14. Zhao M, Duncan JR, Van Hille RP (1999) Removal and recovery of zinc from solution and electroplating effluent using *Azolla filiculoides*. Water Res 33: 1516-1522. » CrossRef » PubMed » Google Scholar