Biosorption of Ni(II) from aqueous solution by chemically modified rice husk and wheat bran

Dr.R.Asha

Assistant Professor, Department of Chemistry, Infant Jesus College of Arts and Science for Women, Mulagumoodu, Kanyakumari, Manonmaniam Sundaranar University, Abishekapatti, Tirunelveli – 627 012, Tamilnadu, India

***Abstract*: Heavy metal pollution of water is becoming a major issue of public health and environment as these are non-biodegradable, toxic and carcinogenic. Biosorption is affordable adsorbents for the removal of heavy metals from aqueous solutions. In the present work chemically modified adsorbents such as rice husk and wheat bran are used as adsorbents to remove Ni(II) ions from aqueous solutions. The effect of pH, adsorbent dosage and initial metal ion concentration were investigated. The results are compared for both the adsorbents. Experimental results were analyzed using Langmuir and Freundlich isotherms. Thermodynamic parameters including changes of free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) during the biosorption were determined.**

Key words—Biosorption, Ni(II), Rice husk, Wheat bran, Isotherms, Thermodynamic parameters.

I. INTRODUCTION:

Industries discharge waste water directly into aquatic stream which contains lot of chemicals, both organic and inorganic, colored substances, heavy metals and many more. Direct discharge of heavy metals into aquatic ecosystem poses a great risk to aquatic organisms even at very low concentration. These metals are non-biodegradable in nature and affect living organisms, causes various disease and disorders. Removal of toxic metals is necessary when the heavy metals level exceeds the permissible discharge level in industrial effluent. Ni is a heavy metal used in a large number of industries like electroplating, Ni-Cd batteries manufacturing, mining, coal and oil-burning power plants, etc [1]. In drinking water, maximum contamination limit set up by United States Environmental Protection Agency is 0.1 mg/L. As per the recommendations of WHO maximum admissible concentration of Ni (ii) ions in aqueous solution is 0.02 mg/L. But metal ions are discharged into water bodies at much high concentration than the permissible limit by industrial activities[2]. High concentration of Ni causes lungs and bone cancer. Exposure to Ni results in skin irritation, damage to nervous system and mucous membrane[3]. Various techniques which have been used for the removal of heavy metal ions from industrial effluents include ion exchange, chemical precipitation, electrode dialysis, membrane filtration, reverse osmosis, ultra-filtration, coagulation and adsorption[4,5,6]. From the above mentioned techniques adsorption method is widely used because of its cost effective nature. In recent years, the searches for low cost agricultural by-products have been widely studied for metal ion removal from water and wastewater. These include watermelon shell[7], papaya peel[8], natural leaves[9], maize stalks[10], coconut husk[11] and apple wastes[12]. This paper presents the study of biosorption characteristics of chemically modified rice husk and wheat bran for the removal of Ni(II) ions from aqueous solutions.

II. MATERIALS AND METHODS:

Preparation of adsorbent:

The rice husk and wheat bran were collected from a local rice mill. The adsorbents were ground using a mechanical grinder, and the resultant powder was sieved in a 150 mm particle sized mesh. They were thoroughly washed with distilled water to remove dust, mud and other impurities and they were placed separately in a hot air oven dried at at 80ºC for 2 hours. About25gofoven-driedadsorbentswere pouredinto500mlflaskcontaining250mlof0.1M NaOH solution, and then were shaken at 200rpmfor4hatroomtemperature.Themixture was left overnight, and then was filtered to remove the sorbent, which was washed several timeswithdistilledwatertoprovideneutralpH. Theadsorbentwasthenovendriedat85ºCfor2hours. The chemically modified rice husk and wheat bran were labelled as RH and WB and these adsorbents used for further adsorption studies.

Preparation of stock solution:

Stock solution of nickel was prepared by dissolving nickel sulphate in deionized water. All working solutions of varying concentrations were obtained by diluting the stock solution with deionized water. The pH of the effluent was adjusted by using 0.2M acetic acid and 0.2M sodium acetate solutions. The concentration of metal ions in effluent was analyzed by atomic absorption spectrophotometer (AAS).

Biosorption experiments:

Biosorption experiments were carried out by shaking a stopper flask containing 25 ml of 100 mg/L metal ion solution and 0.2 g of adsorbent at 200 rpm for 60 min. The sample was allowed to settle and then it was filtered through a Whatmann filter paper. The filtrate of the sample was analyzed in an AAS for the final concentration of metal ions in aqueous solution. The amount of metal adsorbed per unit mass of the adsorbent was calculated using the following equation:

$$q = \frac{V(C_i - C_f)}{M} \qquad (1)$$

where, q is the metal uptake (mg/g), C_i and C_f are the initial and final or equilibrium metal concentration inthe solution (mg/L), V is the volume of the metal solution in the flask (L) and M is the dry mass of biosorbent (g). The percentage removal (%R) of metal ions was calculated from the following equation:

$$\%R = \frac{(C_i - C_f)}{C_i} \times 100 \qquad (2)$$

III. RESULTS AND DISCUSSION:

Effect of pH:

The percentage removal of Ni(II) ions was studied, using RH and WB as adsorbents in the pH range of 3 to 6. The experimental results are shown in Fig.1. The percentage removal of Ni(II) ions investigated was found to increase with an increase in the solution pH upto 5, and then it decreased with the increase in the solution pH. At a lower pH, the surface of the adsorbent was surrounded by H^+ ions. The adsorbent surface becomes more positively charged, so that the attraction between the adsorbent and metal ions get reduced. As the pH increases, the adsorbent surface becomes less positively charged and this facilitates higher metal ion removal. The maximum percentage removal of Ni(II) was observed as 64% for RH and WB at pH 5.

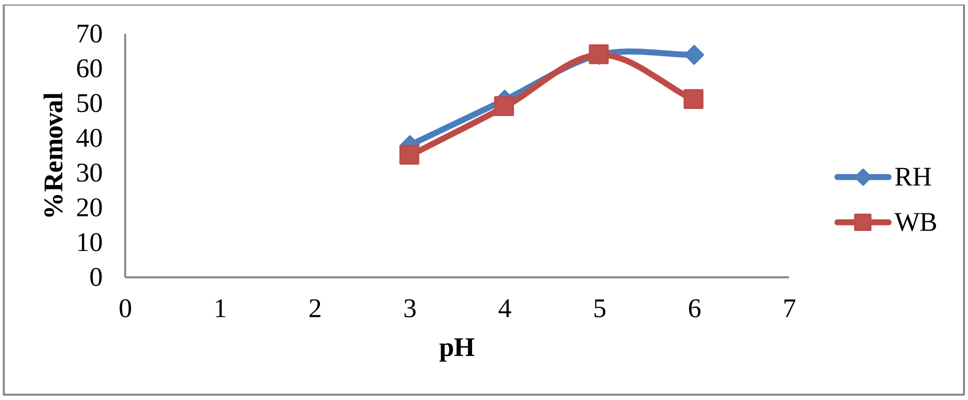

Figure 1: Effect of pH on the biosorption of Ni(II) by RH and WB

Effect of adsorbent dosage:

The percentage removal of Ni(II) ions was studied, using RH and WB as adsorbents in the adsorbent dosage range of 0.1 to 0.5 g. The experimental results are shown in Fig.2. It is evident from the plot that the percentage removal of metal ions from the aqueous solution increases with the increase in the adsorbent dosage. Such behavior is obvious because the number of active sites available for metal ion removal would be more as the amount of the adsorbent increases. The maximum percentage removal of Ni(II) was observed as 78% for RH and 64% for WB at 0.5 g of adsorbent dosage.

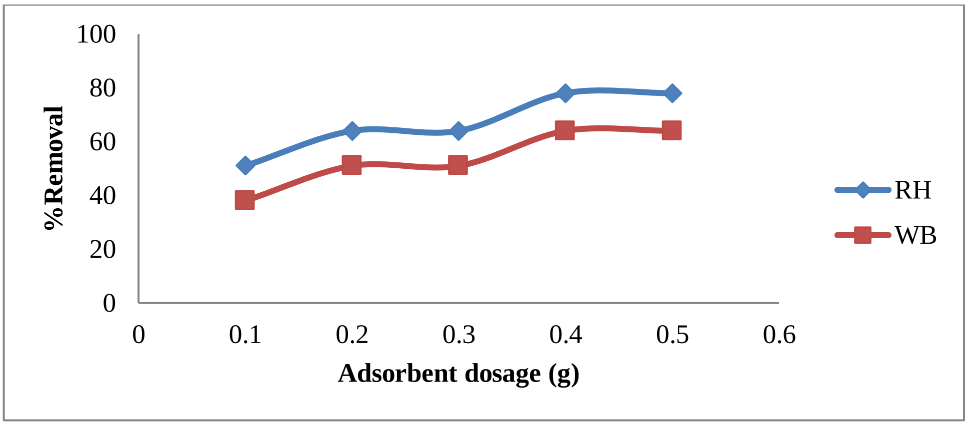

Figure 2: Effect of adsorbent dosage on the biosorption of Ni(II) by RH and WB

Effect of initial metal ion concentration:

The effect of initial metal ion concentration on the biosorption of Ni(II) ions by RH and WB were investigated. The experimental results are shown in Fig.3. The biosorption of metal ions decreases gradually with increase in the metal ion concentration. At low concentrations, metals are adsorbed by specific sites, while with increasing metal concentrations the specific sites are saturated and exchange sites are filled. The percentage removal of Ni(II) by RH decreased from 64% to 43.33% when the initial concentration of the solution was increased from 100 to 300 mg/L. Similarly the percentage removal of Ni(II) by WB decreased from about 50% to 38.67% when the concentration of the solution was increased from 100 to 300 mg/L.

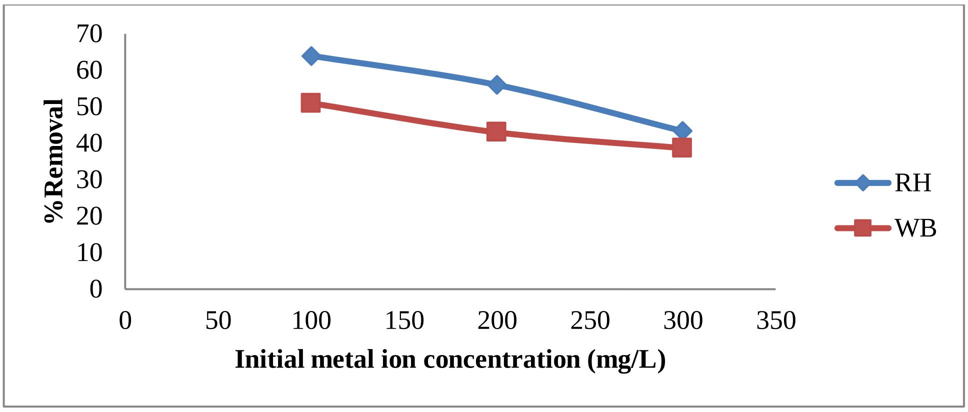

Figure 3: Effect of initial metal ion concentration on the biosorption of Ni(II) by RH and WB

Isotherm studies:

Adsorption isotherm studies were conducted to determine the nature of the adsorption isotherm and the adsorption capacity of the adsorbent for the removal of metal ions. For the isotherm studies the initial metal concentrations were varied from 100 to 300 mg/L. The experimental data were applied to the two parameter isotherm models: Langmuir and Freundlich.

Langmuir isotherm:

The Langmuir isotherm assumes that the uptake of metal ions on a homogeneous surface by monolayer adsorption without any interaction between adsorbed ions[13]. The Langmuir isotherm can be expressed as

$$q = \frac{q_{max} b C_f}{1 + b C_f} \qquad (3)$$

where, q is the metal uptake (mg of metal ion/g of adsorbent), q_{max} is the maximum metal uptake per unit mass of adsorbent (mg/g), b is Langmuir constant (L/mg) related to energy of sorption which reflects quantitatively the affinity between the adsorbent and metal ions. The linearised Langmuir isotherm allows the calculation of adsorption capacities and the Langmuir constants and is calculated by the following equation.

$$\frac{C_f}{q} = \frac{1}{q_{max} b} + \frac{C_f}{q_{max}} \qquad (4)$$

The values of q_{max} and b were calculated from slope and intercept of the linear plot of C_f /q versus C_f.

Freundlich Isotherm:

The Freundlich isotherm is an empirical equation based on adsorption on a heterogeneous species[14]. The equation is commonly represented as:

$$q = K C_f^{1/n} \qquad (5)$$

where, K and n are Freundlich constants related to adsorption capacity and intensity of adsorption respectively. The above equation is rearranged in linear form to give:

$$\log q = \log K + \frac{1}{n} \log C_f \qquad (6)$$

K and n are, respectively, determined from the intercept and slope of plotting in q versus in C_f. The linearised Langmuir and Freundlich isotherms of Ni(II) are shown in Fig.4 and Fig.5. The Langmuir and Freundlich parameters and correlation coefficients (R^2) for the adsorption of Ni(II) by RH and WB are shown in Table1. From the R^2 values the adsorption of Ni(II) ions onto the RH and WB is well represented by the Langmuir model, than the Freundlich isotherm model, which is based on monolayer adsorption of metal ions by the adsorbents.

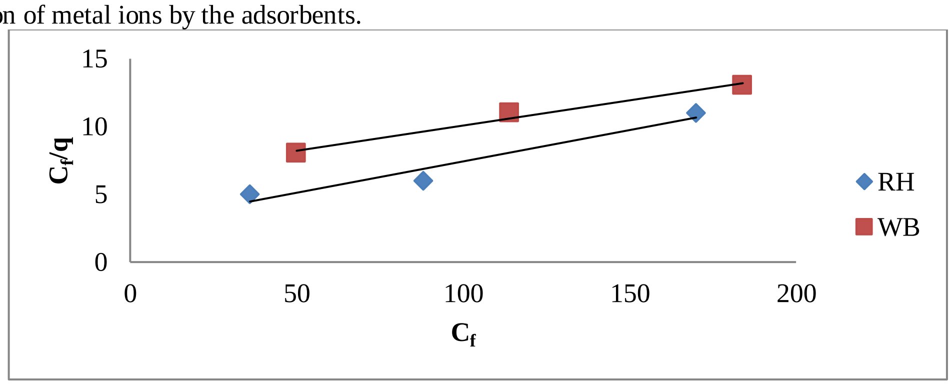

Figure 4: Langmuir isotherm plots for the biosorption of Ni(II) by RH and WB

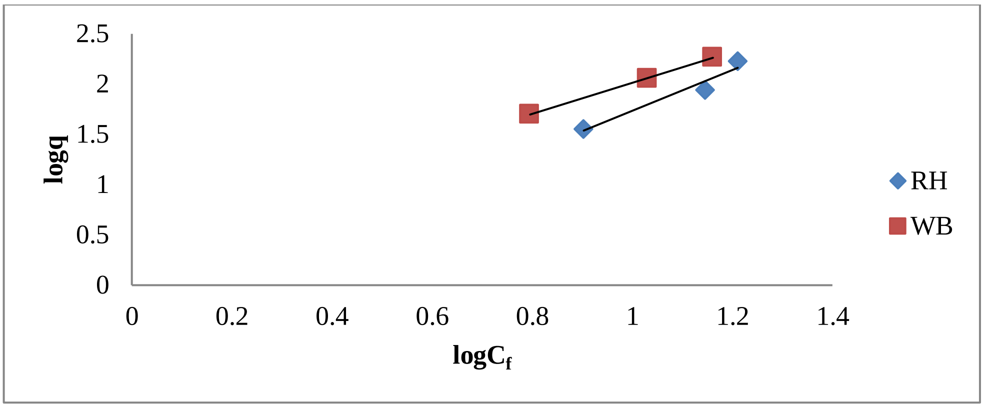

Figure 5: Freundlich isotherm plots for the biosorption of Ni(II) by RH and WB

Table 1: Langmuir and Freundlich isotherm constants for biosorption of Ni(II) by RH and WB

Adsorbent	Langmuir isotherm			Freundlich isotherm		
	q_{max} (mg/g)	b (L/mg)	R^2	n	K	R^2
RH	22.2222	0.0168	0.990	2.1459	1.5667	0.945
WB	29.4117	0.0053	0.992	1.5455	0.4988	0.999

Thermodynamic studies:

Biosorption experiments were conducted at different temperatures (313 K, 323 K and 333 K) to find the thermodynamic parameters including the changes in free energy ΔG (KJ/mol), enthalpy ΔH (KJ/mol) and entropy ΔS (KJ/mol/K), in order to illustrate the thermodynamic behavior of adsorption process. Thermodynamic parameters of adsorption can be evaluated from the following equations [15]

$$K_c = \frac{q_e}{C_e} \qquad (7)$$

$$\Delta G = -RT\ln Kc \qquad (8)$$

$$\Delta G = \Delta H - T\Delta S \qquad (9)$$

where Kc is the equilibrium constant, Ce is the equilibrium concentration in solution (mg/L) and q_e is the amount of metal ions adsorbed per unit mass of the adsorbent (mg/g), R is the gas constant (8.314 J/mol K) and T is the temperature (K). The values of ΔH and ΔS were determined from the slope and the intercept from the plot of ΔG versus T (Fig.6). The thermodynamic parameters are listed in Table 2. The ΔG values are found to be negative which indicate that the adsorption process is spontaneous. The positive values of ΔH showed the endothermic nature of adsorption and it governs the possibility of physical adsorption.

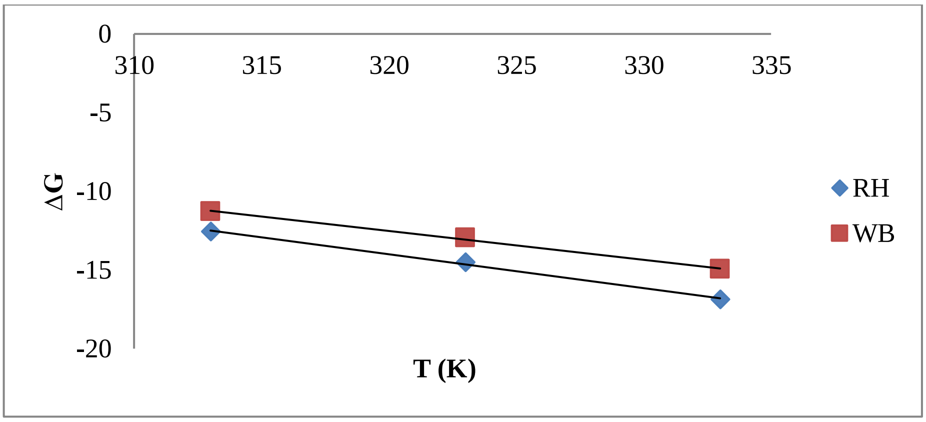

Figure 6: Thermodynamic plot for the biosorption of Ni(II) by RH and WB

Table 2: Thermodynamic parameters of Ni(II) biosorption by RH and WB

Adsorbent	-ΔG (KJ/mol)			ΔH (KJ/mol/K)	ΔS (KJ/mol/K)	R^2
	313 K	323 K	333 K			
RH	12.5646	14.5112	16.8716	54.90	0.215	0.996
WB	11.2907	12.9661	14.9604	46.19	0.183	0.997

IV. CONCLUSION:

The experimental investigation concluded that RH and WB could be used as potential biosorbents for removal of Ni(II) ions from aqueous solution. The percentage removal of Ni(II) ions in aqueous solution increased with increase in the pH and adsorbent dosage and decreased with increase in initial metal ion concentration. The Langmuir isotherm model showed the best fit for the experimental data. Thermodynamic parameters ΔG, ΔH and ΔS showed that the process of biosorption Ni(II) is spontaneous and endothermic process and rise in temperature favors the adsorption.

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