

Adsorption of Nickel (II) by Silica from Rice Husk

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Abstract: The removal of nickel ions from aqueous solution by adsorption on hybrid precursor was investigated. The Rice husk were obtained from Rice mills Shahdol. A Silica adsorbent derived from rice husk by nitric acid treatment was used for the removal of Ni(II) from aqueous solution. The solution of nickel was prepared of 1000 ppm & analyzed by AAS. Sorption of metal ion has been studied as a function of contact time, temperature, pH of the solution and metal ion concentration. These factors have remarkable positive effect on sorption process. The adsorption data of RHHP at different initial concentration was fitted to Freundlich & Langmuir adsorption isotherms and monolayer sorption capacity determined was 83.56 (pH 6.0 temperature 40^oc). Thermodynamic Parameter indicated that the sorption is exothermic, spontaneous with a greater affinity of metal species for the adsorbent.

Keywords: Sorption, RHHP, Adsorption, Hybrid precursor, Activated carbon, AAS

1. Introduction

Most of the reported work on the use of agricultural by-products for removal of heavy metals has to do with the capability of such materials in adsorbing heavy metals¹. The principle behind exploring agricultural by-products in this work is the fact that most agricultural by-products are composed of cellulose in the plant cell walls. A number of methods are available for the removal of metal ions from aqueous solutions. Processes including chemical precipitation, Coagulation, Solvent extraction, electrolysis, membrane separation, ion exchange and adsorption are commonly used to solve pollution problems caused by heavy metals. For this purpose, activated carbon adsorption is well known method for removal of heavy metals^{2,3,4} but the high cost of activated carbon restricts its large-scale use for the abatement of heavy metal pollution in developing countries. Therefore the application of these processes is sometimes restricted, due to technical and economic restrictions⁵.

Activated carbon is manufactured from variety of sources primarily coal, wood, lignite and coconut shell etc. While agricultural by-products as precursors for the preparation of activated carbon have minimum cost, the benefits of the preparation of activated carbon from agricultural by-products wood also include removal of polluting waste product and economic gains for products manufactured from abundant sources. It has been reported that activated carbons have been prepared from the following precursors: coconut shells and wood⁶ almond shells, plum stones, cane baggage and banana pitch and rice husks.

Activated carbons are unique and versatile adsorbent because of their large surface area, micropore structure, varied adsorption effect and high adsorption capacity. Commercially available activated carbons are expensive & their use requires elaborate regeneration and reactivation procedure. The gradual loss of activated carbon during regeneration can materially affect the economic viability of the process.

2. Experimental

The Rice husk hybrid precursor is prepared by Standard Novel method. For our analytical purpose we made a stock solution of Nickel of 1000 ppm from Nickel anhydrous sulphate. 0.4782 gm of NiCl₂ · 6 H₂O dissolved in 100 ml of water. All reagents are AR or GR Grade. 100 ml of metal solution is taken with 2.5 gm of hybrid precursor in a shaker (100 rpm). After about 45 minutes samples were withdrawn from the shaker, centrifuged and the supernatant solution was analyzed for residual metals by AAS.

3. Results and Discussion

Studies of various factors such as contact time, p^H adsorbent dose, metal ion concentration & temperature on the adsorption can be given in following way. The results obtained from AAS Study is shown in table 1 and. It is evident that the adsorption of Ni(II) is maximum at this concentration and at pH 6.0. The Contact time was 45 minutes.

Table 1: Removal of Ni(II) by RHHP HNO₃-A
Temp.- 293K, pH = 6.0

S.No.	Weight of Adsorbent (gm)	Time (Min.)	Amount Adsorbed ppm	% Removal of metal ion
1	2.5	15	350.6	35.06
2	2.5	30	400.4	40.04
3	2.5	45	778.0	77.80
4	2.5	60	820.6	82.06
5	2.5	75	840.3	84.03
6	2.5	90	800.4	80.04
7	2.5	105	730.06	73.06

RHHP = Rice Husk Hybrid Precursor

The dependence of sorption of Ni (II) on contact time was determined by batch technique at different time intervals of 15 mints, 30 mints, 45 mints, 60 mints, 75 mints, 90 mints and 105 mints at 293 K. Maximum adsorption was achieved at 75 mts 84.03 percent.

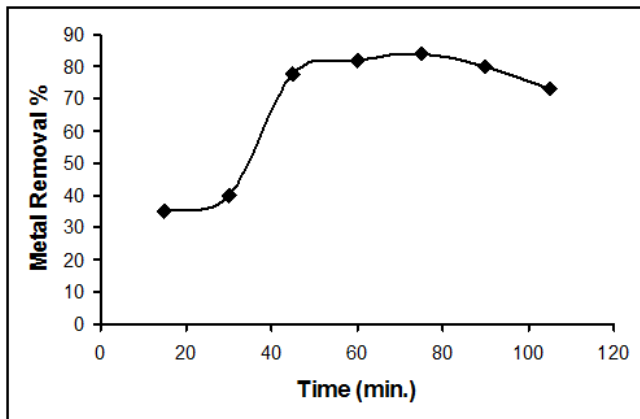


Figure 1: Effect of Contact time on adsorption of Ni (II) at 293K on RHHP

The removal of metal ions from aqueous solution by adsorption is highly dependent on the pH of the solution which affects the surface charge of the adsorbent the degree of Ionization and speciation of the adsorbate.

The Table 2 & Figure 2 illustrates the influence of pH on adsorption and indicates the pH of the solution plays a vital role in any adsorption process. The removal of these metals increased with increase in pH and reached a shoulder – like maximum a followed by a sharp increase in removal reaching close to 90% over the pH range of 8.0 to 10.0.

The observed increase in Ni (II) from 46 to 85% can be explained as, according to stability constant calculations, in the presence of Cl⁻ the predominant species at pH < 4.0 is NiCl₂. The formation of these has been found to decrease the Ni adsorption. Another plausible explanation can be, at low pH value excess H⁺ ions present in solution competes with metal ions for active sites leading to less metal removal.

However when the pH was increased the concentration of H⁺ ion decreases, but the concentration of metal ions remains the same leading to increased uptake by adsorbent.

The sharp increase in metals removal beyond pH 6.0 is due to the precipitation of metals which leads to an active removal close to 90% over the pH range 8.0 to 10.0 .

Table 2: Effect of pH on Adsorption of Ni(II) by RHHP
 Temp.- 293K, Adsorbent weight- 2.5 gm, Contact Time- 60 Min

S. No.	pH	Removed Amount of Ni(II) in ppm	Removed % Ni(II)
1	2	460	46.00
2	4	560	56.00
3	6	640.2	64.02
4	8	780.0	78.00
5	10	850.0	85.00

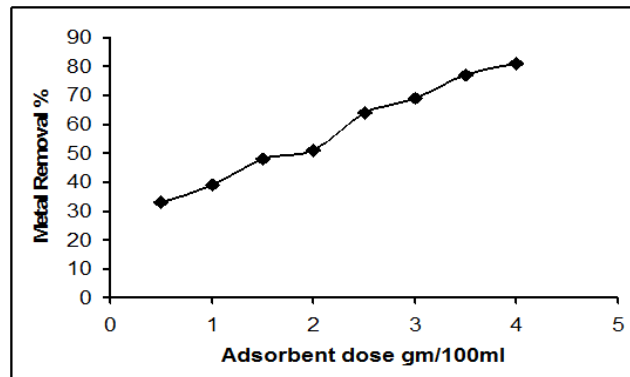


Figure 2: Effect of pH on adsorption of Ni (II) at 293K on RHHP

The effect of adsorbent dose was studied by varying the amount of adsorbent dose (0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0 gm) and performing the studies at pH 6.0. The data obtained are depicted in table 3 and figure 3.

The data obtained in the study indicate that the amount of Ni (II) adsorbed on RHPP significantly increased with increase in the adsorbent dose.

Similarly removal percentage of Ni (II) with the increasing adsorbent dose rise form 33% to 81%. So, like the other factors of adsorption dose of adsorbent also plays a vital role in the removal of metal ion from the salvation.

The higher dose of adsorbent, due to an increased surface area would have cause, the availability of more number of adsorption sites resulting in higher metal removal. At the adsorbent dose 4.0gm maximum uptake (81) of metal was obtained.

Table 3: Effect of adsorbent dose on Adsorption of Ni (II) by RHHP

Temp.- 293K, pH - 6.0, Contact Time- 60 Min			
S. No.	Adsorbent dose gm/100ml	Removed Amount of Ni(II) in ppm	Removed % Ni(II)
1	0.5	330.0	33.00
2	1.0	390	39.00
3	1.5	480	48.0
4	2.0	510	51.00
5	2.5	640.2	64.02
6	3.0	690	69.00
7	3.5	770.0	77.00
8	4.0	810.0	81.00

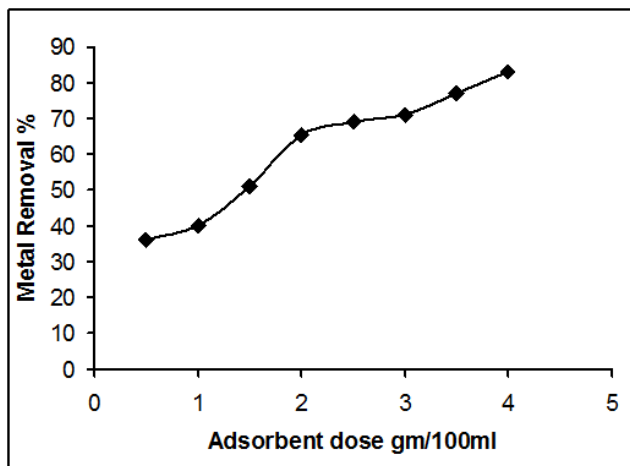


Figure 3: Effect of Adsorbent dose on adsorption of Ni (II) at 293K on RHHP

The effect of initial concentration of metal ions on the sorption potential of adsorbent RHHP at the temperature 293 K was investigated at pH 6.0 and the adsorbent dose 2.5gm. The contact time was 60 minutes. The adsorption data of adsorbent at different initial concentration of Ni (II) is shown in table 4. The results so obtained were fitted to linearised Freundlich and Langmuir adsorption isotherm.

The adsorption increases with the metal ion concentration increase as shown in table.4

Table 4: Adsorption of Ni(II) On RHHP With Varying Metal Concentration
 Temp.- 293K, Adsorbent weight- 2.5 gm, pH - 6.0, Contact Time- 60 Min

Initial Con. mg/L	Ce	X	X/m	Log Ce	Log X/m	1/Ce	1/X/m
50	2.53	47.47	0.018988	0.40	-1.72170	0.3952	52.66
100	9.60	90.4	0.03616	0.81	-1.44170	0.1041	24.65
150	24.6	125.4	0.05016	1.39	-1.24964	0.406	19.93
200	37.2	162.8	0.06512	1.57	-1.1862	0.2688	15.35
250	40.8	209.2	0.08368	1.61	-1.0773	0.2450	11.95

The Freundlich & Langmuir model has been applied to the experimental data & result shows that both models are fit to the study. The linear plots of 1/X/m versus 1/Ce clearly indicate monolayer coverage of adsorbate at the outer surface of the sorbent.

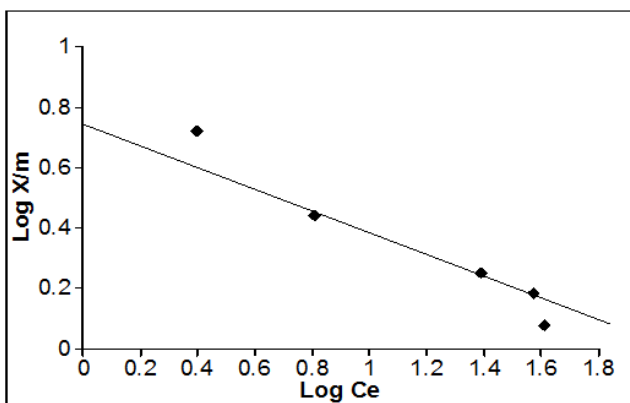


Figure 4: Freundlich adsorption Isotherm of Ni (II) at 293 K on RHHP

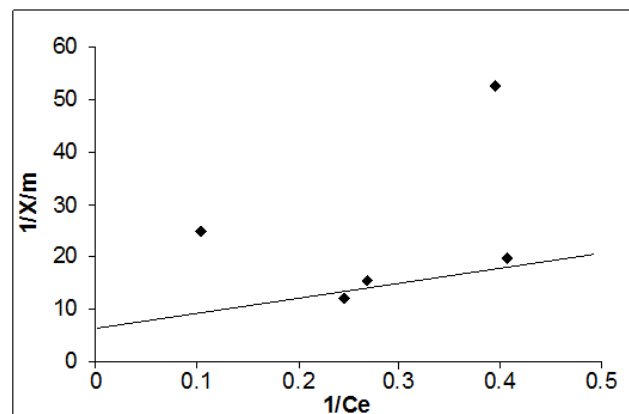


Figure 5: Langmuir adsorption Isotherm of Ni (II) at 293K on RHHP

The adsorption data obtained with the adsorbent correlate well with the Freundlich and Langmuir adsorption models. Freundlich constant from adsorption data are given in the Table 5. The Value of K increased as temperature increased indicating that adsorption increases as temperature increases. The Value of r comes between 1 to 10 represents beneficial adsorption.

Table 5: Values of Freundlich constants for Ni(II)

Metal Ion	log k		1/n		r (corr. coefficient)	
	293 K	313 K	293K	313 K	293K	313 K
Ni(II)	0.72	0.90	0.30	0.75	0.9752	0.9702

Values of Freundlich & Langmuir constants, RL values & thermodynamic parameters are calculated and shown in the table 6 and 7. From the data shown in table –6 it is evident that the endothermic nature of the adsorption is indicated by a increase in q_0 with rise in temperature. The results shown in table 6 also indicate that ΔG^0 values are negative which means that the reactions are spontaneous. The values of ΔG^0 decreases with rise in temperature pointing towards gradual spontaneity of the reaction and gradual change in affinity of metal ions by RHHP. The value of enthalpy of an adsorption process may be used to distinguish between chemical and physical adsorption. For chemical adsorption the enthalpy values range from 83 to 830 kJ mol⁻¹ while for physical sorption the range from 8 to 25kJ mol⁻¹. On the basis of above distinction, metal ion adsorption by RHHP could be a chemical process. Positive values of ΔH^0 for Ni suggest that the process is endothermic, So a increase of temperature encourages metal ion sorption. As indicated in table ΔS^0 values for the adsorption process are positive. A positive entropy of adsorption also reflects the affinity of adsorbent material for Ni (II). The positive value of entropy also suggests a high degree of disorder ness at the solid – solution interface during the adsorption of metal ions on to Rice husk hybrid Precursor (RHHP).

The value of R_L indicates the shape of the isotherm to be either unfavorable ($R_L > 1$), Linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

This study shows that shape of the isotherm is favorable i.e. R_L value $0 < R_L < 1$.

Table 6: Values of Langmuir Constants and thermodynamic parameters at 293K

Metal ion	q ₀ Value related to the equilibrium constant (L mole ⁻¹)		b (Lmg ⁻¹)		ΔG ⁰ (kJ mole ⁻¹)		Mean ΔH ⁰ (kJ mole ⁻¹)	Mean ΔS ⁰ (Jk ⁻¹ mole ⁻¹)
	293 K	313 K	293 K	313 K	293 K	313 K		
Ni	6.5	16	0.030	0.009	-45.00	-71.21	314.30	1.225

Table 7: Equilibrium parameter, R_L calculated from Langmuir adsorption isotherm.

Metal ion concentration (mg/L)	Ni (II)	
	293 K	313 K
50	0.4000	0.6896
100	0.2500	0.5263
150	0.1818	0.4255
200	0.1428	0.3076
250	0.1176	0.3076

References

- [1] Quack S.Y., Wase D.A.J. and Foster C.F., The use of Sago waste for the sorption of lead and copper, *Water S. Afr.*, 24 (3),251-256 (1998).
- [2] Gupta V.K. Jain C.K., Ali I., Shama M., and Sani V.K., Removal of cadmium and Nickel from waste water using baggage fly ash: A sugar industry waste, *Wat. Res.*,37,4038-4044,2003
- [3] Lalvani S. B. Wiltosvaski T., HubnerA., Wetson A.,and Mandich N., Removal of hexavalent chromium and metal cations by a selective and novel carbon adsorbent ,*Carbon*, 36,1219-126,1998
- [4] Pollard S. J. T. ,Fowler G.D., Sollars C.J., and Perry R., Low cast adsorbent for waste and waste water treatment: A review ,*Sci. Total Envnickel.*,116,31-52,1992.
- [5] Martin Dupont F. Gloaguen V., Ganet R.,Guilloton M., Morvan H. and krausz P., Heavy metal adsorption by crude coniferous barks: A modeling study.*J.Envnickel. Science. Health*,A37(6),1063-1073,2002.
- [6] Bernardo E., Egashira R. and Kawasaki J., *Carbon*,35,1217-1221,1997.