Removal of Heavy Metals from Waste Water Using Low Cost Adsorbent

T. Brahmaiah[1], L. Spurthi[2], K. Chandrika[2], L. Kausalya Chandra L[2], S. Yashas[2], S.Ramanaiah[1] and K. S. Sai Prasad[1]
[1]Department of Geology, S.V.University, Tirupati, Andhra Pradesh, India
[2]Sri Jayachamarajendra College of Engineering, Mysore, Karnataka, India

Abstract: Heavy metal toxicity due to industrial wastewater has been a threat to the environment for the past many decades, especially in the developing countries such as India, China and Thailand, where cost effectiveness of the removal process is a major factor. In this work, adsorption experiments were carried out using rice straw as an agricultural residue was assessed for heavy metals (Cr & Ni) adsorption from aqueous solutions. The effects of pH, contact time, and adsorbent dosage were studied in batch process. Rice straw was treated in order to increase their metal-binding capacity. The adsorption data has been correlated and found that date is well fitted with the Langmuir, Freundlich and Temkin isotherms. Results indicated that rice straw appeared to be the most practical use for adsorption of Cr & Ni from waste water. The modified rice straws could adsorb faster than unmodified one.

Keywords: *Rice Straw (RS), Adsorption, Sodium Hydroxide, Isotherms.*

I. INTRODUCTION

Environmental pollution is currently one of the most important issues facing humanity. It was increased exponentially in the past few years and reached alarming levels in terms of its effects on living creatures. Toxic heavy metals are considered one of the pollutants that have direct effect on man and animals. Rapid growth in human population is one of the major causes of environmental pollution. Increased industrialization and urbanization throughout the world results in consistent release of toxic effluents, several industrial processes generate metal containing wastes. One of these pollutants is heavy metals. They are introduced into the biological cycle through drinking water, food and air. Heavy metals are dangerous as they bioaccumulation.

Heavy metals are released from industries such as metal plating, mining, batteries, PCB manufacturing etc. Nickel is a non-biodegradable toxic heavy metal ion present in wastewater. Acute nickel toxicity effects are gastrointestinal symptoms like nausea, vomiting, abdominal discomfort and diarrhea. Nickel also affects the blood, liver kidney and immune system. Metallic nickel is teratogenic and carcinogenic to mammals.

The commonly used procedures for removing heavy metals from aqueous streams include chemical precipitation, coagulation, ion exchange, reverse osmosis etc [1&2]. The disadvantages like incomplete removal, high reagent cost and energy requirements, generation of toxic sludge that require careful disposal have made it imperative for a cost effective treatment method capable of removing heavy metals from aqueous effluents[3&10]. Adsorption is one in which certain adsorptive are selectively transferred from the fluid phase to the surface of particles suspended[14]. Adsorption has advantages over other methods because of simple design with sludge free environment and can involve low investment in terms of both initial cost and land required(4&9).

Rice straw is one of the abundant lignocellulosic naturally available materials in the world. In terms of total production, rice is the third most important grain crop in the world. Some of the advantages of using agricultural residues[17&19] such as rice straw include simple technique[7,15&20], little processing requirement, good adsorption capacity, low cost and easy regeneration[12]. The rice straw contains cellulose, hemicellulose and lignin. Rice straw has several characteristics that make it a potential adsorbent with binding sites capable of removing metals from aqueous solution [5&11].

The aim of this study is to find out the effectiveness of rice straw to be used as an adsorbent for the removal of chromium. In this work, the adsorption behavior was studied by a set of experiments at various conditions including pH, contact time and various adsorbent amounts.

II. MATERIALS AND METHODS

A. Analytical Method

The concentration of chromium was determined from a wastewater using Inductively Coupled Plasma Spectrophotometer (ICP).

B. Preparation of Synthetic Waste Water

Standard Nickel solution was prepared by adding 1g of nickel metal in 20ml of nitric acid and was allowed to dissolve completely and was diluted to 1 liter. The initial nickel concentration (85 mg/l) was prepared by dilution.

C. Materials

Rice straw which is an agricultural by producthas been used as low cost adsorbent. Untreated rice straw was prepared by cutting the straw into small pieces, washed with distilled water, dried in an oven over a period of 24 hrs and then grind into fine powder. Treated rice straw was prepared by using sodium hydroxide solution. 16 g of powdered rice straw was treated with 240 mL of sodium hydroxide solution and dried in oven at 100°C over a period of 24 hrs [8].

D. Experimental Procedure

Adsorption experiments were conducted in batch process, that is, the solution was kept in separate beakers and was stirred continuously for a particular time and finally samples were analyzed in batches for residual chromium concentration[16].

E. Batch Adsorption

The influence of rice straw on metal ions removal was investigated under the following experimental conditions. Batch experiments were conducted for varied pH, adsorbent dose, initial chromium concentration and contact time. At desired intervals, effluent samples were collected, filtered using whattman filter paper and analyzed for concentration of chromium. The amount of metal ion adsorbed was calculated as:

$$\% \text{ Adsorption} = (C_i - C_f)/ C_i X\ 100 \qquad (1)$$

Where C_i and C_f are the initial and final concentrations of the metal ions in the solution (ppm).

III. RESULTS AND DISCUSSIONS

Adsorption studies have been conducted for the removal of chromium and nickel from synthetic wastewater. In order to design any adsorption system, optimization of various operating parameters such as adsorbent dose, pH and contact time are of vital importance. To ascertain the above parameters batch adsorption studies were conducted. Based on the objectives of the present study, laboratory adsorption tests were conducted and the results have been discussed in the following sections.

Batch adsorption technique is widely used for water and wastewater treatments. In batch adsorption process the various operating parameters such as adsorbent dose, pH and contact time have been investigated. The batch adsorption data has been used in the adsorption isotherm models such as Freundlich, Langmuir and Tempkin equations.

A. Effect of pH:

The pH of the aqueous solution plays a vital role in controlling the adsorption process. The pH of aqueous solution governs the adsorption of metal ions. The effect of pH on the adsorption capacity of raw and modified rice straw may be attributed to the combined effect of the nature of the surface and the amount of adsorbed species. The minimal adsorption at very low pH may be due to the higher concentration and high mobility of H^+, which are preferentially adsorbed rather than metal ions. The effect of pH on chromium and nickel removal using both treated and untreated rice straw has been studied. At very low pH, the percentage adsorption decreased due to the involvement of less number of anions on the positive surface. At higher pH due to more OH^- ions adsorbent surface carrying net negative charges, which tend to repulse the metal anions[4]. Therefore, maximum removal from aqueous solution was achieved at higher pH. From the Fig.1, it is seen that adsorption rate for chromium increases with increase in pH for both treated and untreated rice straw from pH 2 to pH 6 and pH 2 to pH 4 respectively and there onwards chromium removal was found to be gradual.

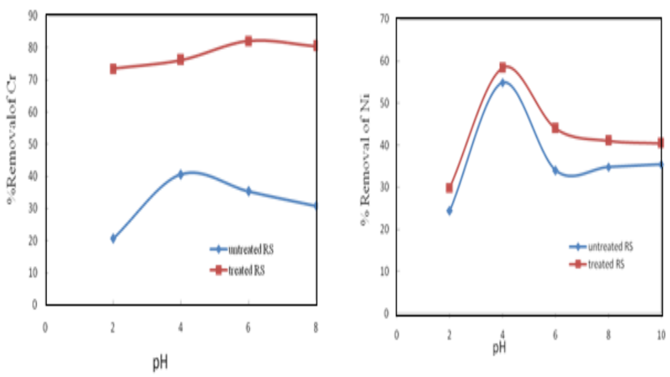

Figure 1: Effect of pH on the Removal of Chromium and Nickel

B. Effect of Adsorbent Dosage

The adsorbent dosage is an important parameter in adsorption studies because it determines the capacity of adsorbent for a given initial concentration of metal ion solution. To study the effect of adsorbent dose on adsorption of chromium, a plot is drawn for percent removal versus adsorbent dosage for fixed initial concentrations of 20mg/l for chromium for both untreated and treated adsorbent shown in Fig-2. From these figure, it is evident that the percent removal of chromium for both treated and untreated adsorbent increases with increase in adsorbent dosage. This may be due to some of the adsorption sites remaining unsaturated during the adsorption process. In the present study adsorbent dosage was varied and equilibrated at an initial chromium ion concentration of 20 mg/l. The removal efficiency decreased with increase in adsorbent dosage for a given initial metal concentration. The percent removal of chromium concentration for both treated and untreated adsorbent increased with increase in adsorbent dosage. The increase in the adsorbent dosage leads to a greater availability of the exchangeable sites or surface area of the adsorbent. For chromium, the optimum dosage for untreated and treated rice straw was found to be 8g/100ml.

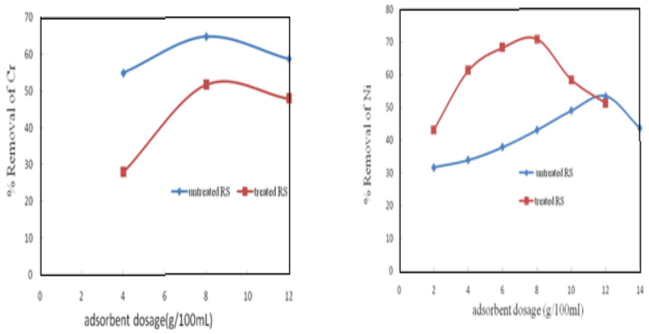

Figure 2: Effect of Adsorbent Dosage on the Removal of Chromium and Nickel

C. Effect of Contact Time:

Equilibrium time is a crucial parameter for an optimal removal of metal ions in the wastewater. From the Fig 4.5, it is observed that at 40 min the chromium removal was found to be maximum of 65% at 50 min, it was found to be 91% for untreated and treated rice straw (Fig.3).

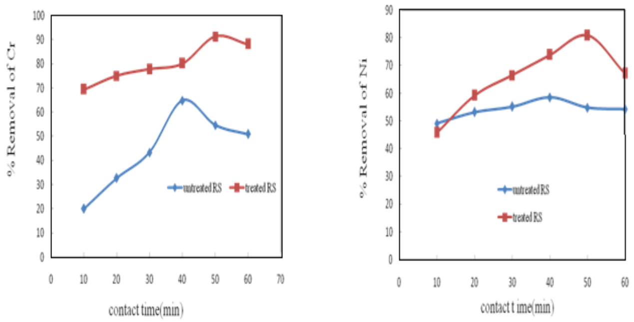

Figure 3: Effect of Contact Time on the Removal of Chromium and Nickel

D. Adsorption Isotherms

Adsorption isotherm is a quantitative relationship describing the equilibrium between the concentration of adsorbate in solution and its adsorbed concentration. In the present study adsorption isotherms have been used to describe adsorption behavior and to estimate the adsorption capacity of rice straw on the removal of heavy metals from wastewaters. In this, adsorption equilibrium data has been fitted with Langmuir, Freundlich, and Temkin adsorption isotherm equations.

E. Freundlich Isotherm:

Freundlich adsorption isotherm is obeyed by the adsorptions where the adsorbate forms a monomolecular layer on the surface of the adsorbent.

$$x/m = kp^{1/n} \quad \textbf{(Freundlich adsorption isotherm)} \qquad (2)$$

The linear form of Freundlich isotherm can be represented as:

$$\log x/m = \log k + 1/n \log C_e \qquad (3)$$

where **x** is the weight of the adsorbate adsorbed by **m** gm of the adsorbent, thus **x/m** represents the amount of adsorbate adsorbed by the adsorbents per gm (unit mass), **k** and **n** are constants at a particular temperature and for a particular adsorbent and adsorbate. The magnitude of the exponent, **1/n**, gives an indication of the favorability of adsorption. Values of **n > 1** represent favorable adsorption condition.

$$x/m = q_e \qquad (4)$$

In the present study the values of Freundlich constants 'k_f 'and '1/n' for chromium were determined from linear plots of log q_e against log C_e as depicted in Fig 4. The values of 'k_f' and '1/n' were found to be 8.317 and 0.830 for untreated rice straw, 2.606 and 0.208 for treated rice straw respectively (Table-1). The values of k_f and 1/n for nickel was found to be 93.325 and 0.871 for untreated rice straw and 40.36 and 0.534 for treated rice straw as shown in Fig 5.

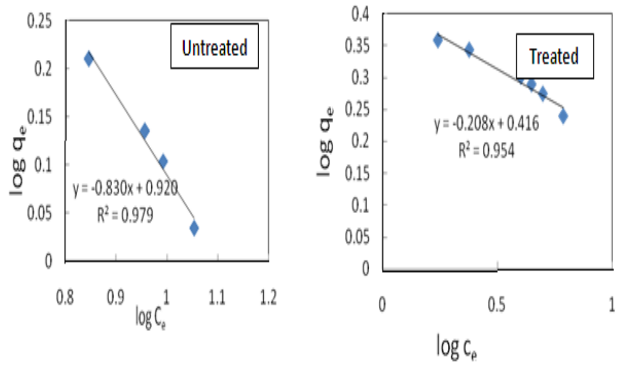

Figure 4: Freundlich Isotherm for Chromium Removal Using Rice Straw

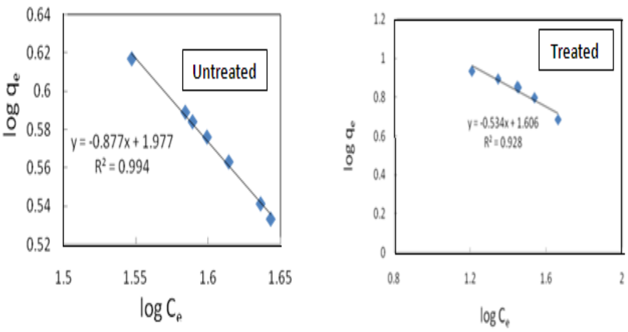

Figure 5: Freundlich Isotherm for Nickel Removal Using Rice Straw

Table 1: Freundlich Isotherm Constants for Chromium and Nickel

Parameters	Freundlich constants		
	K_f	1/n	R^2
Chromium			
Untreated rice straw	8.317	0.83	0.979
Treated rice straw	2.606	0.208	0.954
Nickel			
Untreated rice straw	93.325	0.871	0.994
Treated rice straw	40.36	0.534	0.928

Langmuir adsorption isotherm

The Langmuir[8] adsorption model is valid for single layer adsorption. The Langmuir isotherm is represented by Eqn. (5):

$$q_e = \frac{q_{mb} C_e}{(1+bC_e)} \qquad (5)$$

Where q_e = amount adsorbed per unit weight of adsorbent, b = Langmuir's constant related to the enthalpy of the process, q_m = adsorption capacity to form the single layer, C_e = equilibrium concentration of adsorbate in solution after adsorption in mg/L.

The linear form of Langmuir isotherm can be represented in Eqn. (6) as:

$$\left(\frac{C_e}{q_e}\right) = \left(\frac{1}{q_m\ b}\right) + \left(\frac{1}{q_m}\right) C_e \qquad (6)$$

In the present study, removal of chromium using untreated and treated rice straw as adsorbent has been attempted and the Langmuir constant q_m and b are determined from the linear plot of C_e/q_e versus C_e. The plots of C_e/q_e versus C_e for the untreated and treated rice straw have been made, is presented in Fig 6. From the Fig 7, the values of adsorption intensity 'q_m' and adsorption capacity 'b' were found to be 1.984 and 0.153; and 3.921 and 0.089 for untreated and treated rice straw, respectively.

The essential feature of the Langmuir isotherm can be expressed in terms of Separation factor (R_L) which is a dimensionless constant also referred to equilibrium parameter. R_L can be calculated by using Eqn. (7).

$$R_L = \frac{1}{(1+bC_o)} \qquad (7)$$

where, C_o is the initial adsorbate concentration (mg/L), **b** can be obtained from Langmuir plot of C_e/q_e versus C_e. The separation factor R_L indicates the isotherm shape as:

$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

In the present study the value of R_L was found to be 0.5252 for untreated rice straw and 0.0331 for the treated rice straw for chromium and 0.285 and 0.152 for nickel respectively (Table-2). From the result, it is evident that the values of R_L obtained for the removal of chromium and nickel using untreated and treated rice straw as adsorbents are between 0 and 1, the adsorption process was found to be favorable and best fitted to Langmuir isotherm.

Similar study was conducted by Khaldoun Al-Sou'od, [6], for the adsorption of chromium by Jordanian pottery material and it was found that Langmuir was the best with average R^2 value of 0.998 and the maximum value of monolayer adsorption capacity was found. Another study by Nameni et al.[13], showed that the Langmuir adsorption isotherm was the best model for the chromium removal on wheat bran with a correlation coefficient (R^2) of 0.997.

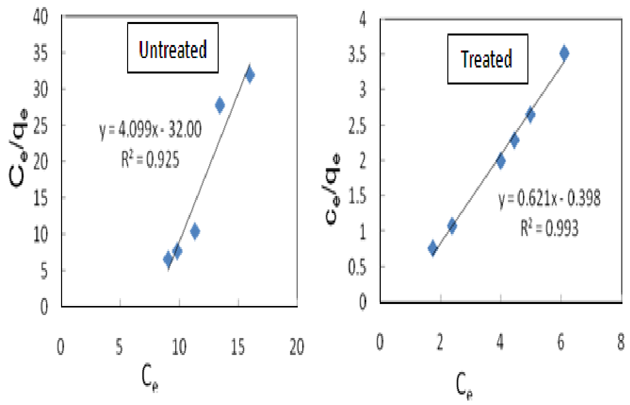

Figure 6: Langmuir Isotherm for Chromium Removal Using Rice Straw

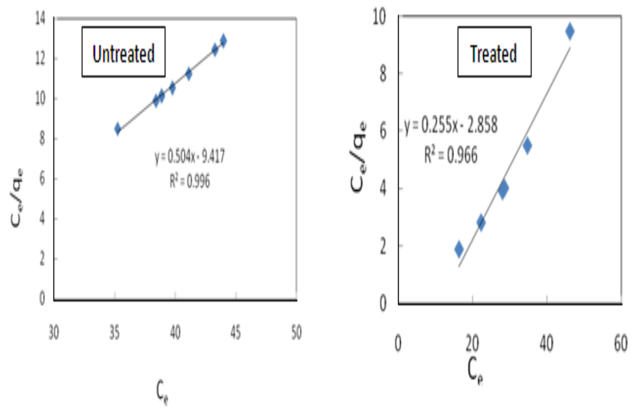

Figure 7: Langmuir Isotherm for Nickel Removal Using Rice Straw

Table 2: Langmuir Isotherm Constants for Chromium and Nickel

Parameter	Langmuir constants		R_L	R^2
	q_m	b		
Chromium				
Untreated rice straw	0.2852	0.1452	0.5252	0.898
Treated rice straw	1.6103	1.603	0.0331	0.993
Nickel				
Untreated rice straw	1.984	0.153	0.285	0.996
Treated rice straw	3.921	0.089	0.152	0.966

Temkin adsorption isotherm:

Temkin[18] adsorption isotherm equation assumes that heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interaction, and adsorption is characterized by a uniform distribution of the binding energies, up to certain maximum binding energy. Temkin isotherm can be expressed using the Eqn. (8)

$$\theta = \left(\frac{RT}{\Delta Q}\right) \log k_o C_e \qquad (8)$$

where, θ = (q_e/q_m) = Fractional coverage, **R** = Universal gas constant (KJ/mol/K), **T** = Temperature (K), **ΔQ** = Variation of adsorption energy (KJ/mol), k_o = Temkin equilibrium constants (L/mg)

The linear form of Temkin adsorption isotherm can be represented by Eqn. (9).

$$\theta = \left(\frac{RT}{\Delta Q}\right) \log k_o + \left(\frac{RT}{\Delta Q}\right) \log C_e \qquad (9)$$

The variation of adsorption energy (ΔQ) is positive for all the phenolic compounds studied, which indicates that the adsorption reaction is exothermic. However, in the present study the value of Temkin constants 'ΔQ' and 'k_o' were determined from linear plots of θ versus log C_e as shown in figs. 8 & 9 for chromium and nickel respectively. It is observed that the variation of adsorption energy (ΔQ) values for chromium is -16.172KJ/mol and -58.158KJ/mol for untreated and treated rice straw respectively. Similarly, the values for nickel are -13.465KJ/mol and -25.850KJ/mol for untreated and treated rice straw respectively (Table-3). The values are negative for untreated and treated rice straw for both chromium and nickel, which indicates that adsorption reactions are endothermic.

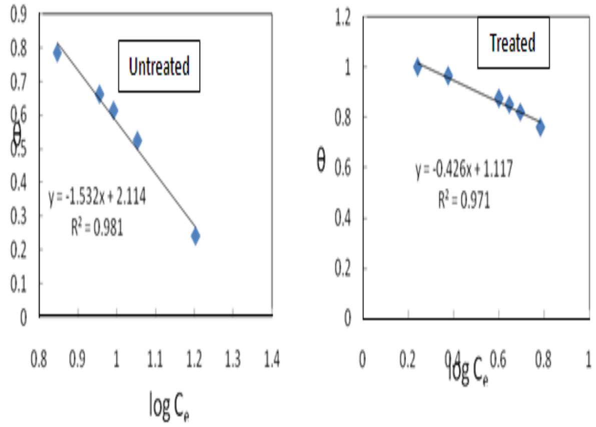

Figure 8: Tempkin Isotherm for Chromium Removal Using Rice Straw

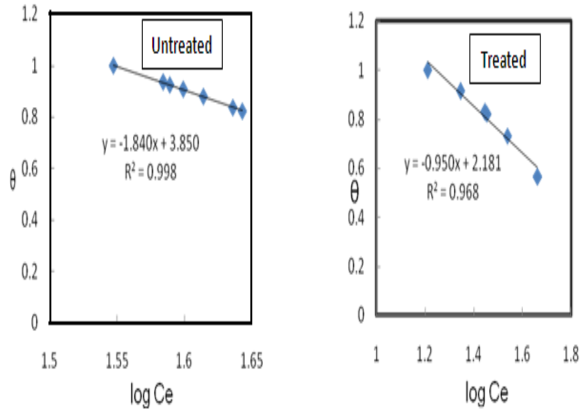

Figure 9: Tempkin Isotherm for Nickel Removal Using Rice Straw

Table 3: Tempkin Isotherm Constants For Chromium and Nickel

Parameter	Tempkinisotherm		R2
	Ko	ΔQ	
Chromium			
Untreated rice straw	0.968	-16.172	0.981
Treated rice straw	0.941	-58.158	0.972
Nickel			
Untreated rice straw	0.952	-13.465	0.998
Treated rice straw	0.948	-25.85	0.948

CONCLUSIONS

Batch adsorption tests were conducted on the removal of Nickel present in the wastewaters. Effects of adsorbent dosage depend upon initial solute concentrations. It is seen from the results that at 8 g/100mL and 8 g/100mL of untreated and treated rice straw could remove about 65 % at 40 min contact time and 80% at 50 min contact time of nickel respectively.

The optimum pH for untreated rice straw was 4 and for treated rice straw it was found to be 4. From the Temkin adsorption isotherm studies, the value of variation of adsorption energy (ΔQ) was found to be -13.465KJ/mol and -25.850KJ/mol for untreated and treated rice straw, respectively. The value of variation of adsorption energy (ΔQ) is negative for untreated and treated rice straw, which indicates, the adsorption reaction is endothermic. Among the various adsorption isotherms studied, the adsorption process fits well with the Langmuir isotherm.

References

[1] Achanai Buasri, Nattawut Chaiyut, Kessarin Tapang, Supparoek Jaroensin and Sutheera Panphrom, (2012), "Removal of Cu^{2+} from Aqueous Solution by Biosorption on Rice Straw - an Agricultural Waste Biomass", International Journal of Environmental Science and Development, Vol. 3, No. 1, pp: 10-14.

[2] Argun, M. E.; Dursun, S.; Ozdemir, C.; Karatas, M., (2006). Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics., J. Hazard. Mater., 141 (1),77-85.

[3] Baral, S. S.; Dasa, S. N.; Rath, P., (2006). Hexavalent chromium removal from aqueous solution by adsorption on treated sawdust,Biochem. Eng. J., 31 (3), 216–22.

[4] Gao, H.; Liu, Y.; Zeng, G.; Xu, W.; Li, T.; Xia, W., (2007).Characterization of Cr(VI) removal from aqueous solutions by a surplus agricultural waste-Rice straw., J. Hazard. Mater.,150 (2), 446-452.

[5] Hafiza Naila Khalid, Mukhtar-ul-Hassan, Nadia Jamil, Dania Ahmad, Hafza Bushra Fatima and Sara Khatoon, (2012), "Biosorption of Aqueous Lead (II) on Rice Straws (oryza sativa) by flash column process", Journal of Scientific Research, Vol. 9, No.11, pp: 1-8.

[6] Khaldoun Al-Sou'od, (2012), "Adsorption Isotherm Studies of Chromium (VI) from Aqueous Solutions using Jordanian Pottery Materials", APCBEE Procedia , Vol. 1, No. 3, pp: 116 – 125.

[7] Khaled Mohamed Mostafa, Abdul Rahim Samarkandy and Azza Awad El-Sanabary, (2012), "Harnessing of Chemically Modified Rice Straw Plant Waste as unique Adsorbent for Reducing organic and inorganic Pollutants", International Journal of Organic Chemistry, Vol. 2, pp: 143-151.

[8] Langmuir (1918), "The adsorption of gases on plane surfaces of glass, mica and platinum‘‘. –J. Am. Chem. oc. Vol.40, pp.1362 -1403.

[9] Mansour Alhawas, Mohamed Alwabel, Adel Ghoneim, Abdullah Alfarraj and Abdelazeem Sallam, (2013), "Removal of nickel from aqueous solution by low-cost clay adsorbents", Proceedings of the International Academy of Ecology and Environmental Sciences, Vol. 3, No. 1, pp: 160-169.

[10] Morshedzadeh, K.; Soheilizadeh, H. R.; Zangoie, S.; Aliabadi,M., (2007). Removal of chromium from aqueous solutions by lignocellulosic solid wastes., 1st. Environment conference, Tehran University, Department of Environment Engineering.

[11] Mousa W M, Soliman S I, El-Bialy A B and Hanaa A Shier, (2013), "Removal of some Heavy Metals from Aqueous Solution using Rice Straw", Journal of Applied Sciences Research, Vol. 9, No. 3, pp: 1696-170.

[12] Murali Naik. M, and Kalyan Kumar.M,(2015). Comparative studies of removal of Hexavalent chromium Cr(VI) from wastewater using Natural Adsorbent prepared from Neem Leaves and Sawdust. International Journal Of Engineering And Technical Research,Vol.4, Issue 9, pp.874-879.

[13] Nameni M, Alavi Moghadam M R and Arami M, (2008), "Adsorption of hexavalent chromium from aqueous solutions by wheat bran", International Journal of Environmental Science and Technology, Vol. 5, No. 2, pp: 161-168.

[14] Pushpendra Kumar Sharma, Sohail Ayub and Chandra Nath Tripathi, (2013), "Agro and Horticultural Wastes as Low Cost Adsorbents for Removal of Heavy Metals from Wastewater: A Review", International Refereed Journal of Engineering and Science, Vol. 2, No. 8, pp: 18-27.

[15] Pandharipande S L and Rohit P Kalnake P, (2013), "Tamarind fruit shell adsorbent synthesis, characterization and adsorption studies for removal of Cr(VI) & Ni(II) ions from aqueous solution", International Journal of Engineering Sciences & Emerging Technologies, Vol. 4, No. 2, pp: 83-89.

[16] Standard methods for examination of water and wastewater.(1992). 18th. Ed., Published by American Public Health Association, Washington DC, USA. Archive of SID.

[17] Suleman Qaiser, Anwar Saleemi R and Muhammad Mahmood Ahmad, (2007), "Heavy metal uptake by agro based waste materials", Electronic Journal of Biotechnology, Vol. 10, No 3.

[18] M.I. Tempkin. M.I, and Pyzhev. V ,(1940), Kinetics of ammonia synthesis on promoted iron catalyst, Acta Phys. Chim. USSR 12, pp.327 –356.

[19] Verma, A.; Chakraborty, S.; Basu, J. K., (2006). Adsorptionstudy of hexavalent chromium using tamarind hull-basedadsorbents. Separ. Purif. Tech., 50 (3), 336–341.

[20] Upendra Kumar, (2013), "Agricultural products and by-products as a low cost adsorbent for heavy metal removal from water and wastewater: A review", Scientific Research and Creativity, Vol. 1, No. 1, pp: 1-5.