

# BATCH ADSORPTION STUDIES OF TOXIC Ni(II) IONS FROM WATER BY ESTERIFIED RICE (*Oryza sativa*) HUSK

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## ABSTRACT

Heavy metals find their way into water bodies mainly from the refuge of electroplating, tannery, paint and power generation industries. These metals are toxic and non biodegradable and their accumulation in the living tissues can cause various diseases and disorders. Hence there is a need to remove these metal ions from the wastewaters from industries before discharging into the environment. The use of agricultural products and by-products as low-cost sorbents has been widely studied. In the present paper removal of Ni(II) by esterified rice (*Oryza sativa*) husk have been investigated. Batch studies suggest that removal is dependent upon contact time, metal ion concentration and pH. Maximum removal by chemically modified adsorbents at pH 5 in 2.5 hr have been achieved for the concentration range 30 to 300 mgL<sup>-1</sup>. The sorption data obtained at optimum conditions have been subjected to Freundlich, Langmuir Tempkin isotherm studies. Kinetic studies at optimum conditions have been studied using Lagergren pseudo first order and pseudo second order equations. The possibility of intraparticle diffusion has been studied by using the Morris–Weber equation.

**Keywords :** acid value, adsorption, esterified rice husk, saponification value

## 1. INTRODUCTION

Industrial activities leads to disposal of toxic metals into wastewaters are considered as the main cause and major source of worldwide concern in the last few decades. Nickel contamination is mainly due to industries related to electroplating, battery, mining and metallurgy of nickel, aircraft industries, pigments, and ceramic industries. The permissible level of nickel in drinking water is 0.5 mg/L [1].

Chemical modification of agricultural by-product could enhance their natural capacity for the uptake of metal ions [2]. Corn stalk treated with acrylonitrile [3], corncob treated with citric acid [4], rice husk treated with nitric acid and potassium carbonate [5], bagasse treated with sulfuric acid [6], polyacrylamide grafted rice (*Oryza sativa*) husk and (*Tectona grandis*) saw dust [7], thiolated cassava fiber, cassava bark waste and rice husk [8-10], esterified coir pith, rice husk, lemon and saw dust [11-14], have been used.

Batch adsorption tests provide information on adsorption equilibrium characteristics and adsorption kinetics. However, batch operations are not economical in practice and data on continuous flow fixed bed column operations are essential for industrial adsorber design. The objective of the present study is to study the

adsorption potential of esterification of rice husk with succinic anhydride followed by activation with sodium bicarbonate has been investigated for Ni(II) ions in batch studies.

## **II. EXPERIMENTAL**

### **2.1 Preparation of adsorbents**

The rice (*Oryza sativa*) husk (variety PR 106) was procured from the agricultural land of Sangrur, Punjab, India. These were crushed, sieved, washed with distilled water and dried at  $\sim 80^{\circ}\text{C}$ . The particles retained on 212, 425 and 600 micron mesh size were used for the experiment

### **2.2 Preparation of Esterified rice husk**

Esterification [11] was carried out by stirring 7.5 g of rice husk with 7.5 g of succinic anhydride in 100 ml of *N,N*-dimethyl formamide (DMF) at  $80^{\circ}\text{C}$  for two hours in the presence of catalyst, triethylamine (0.1 eq.). Esterified rice husk was treated with 1N NaHCO<sub>3</sub> solution (50 ml, 1h,  $20^{\circ}\text{C}$ ), washed with distilled water (50 ml) and dried for 12 h at  $105^{\circ}\text{C}$ .

### **2.3 Preparation of metal ion solution**

Stock solution of the metal ions was obtained by dissolving the required amount of metal sulphate (Merck, A.R.grade) in distilled water to get solution having concentration 300 mg/L of Ni<sup>+2</sup> ions. Different concentrations were prepared by making suitable dilutions.

### **2.4 Characterization of adsorbent**

#### **(a) FTIR analysis**

The samples were prepared by mixing 1mg of each material with 100mg of spectroscopy grade KBr. The FTIR spectra were recorded using Nicolet Impact 410 equipment with detector at 4cm<sup>-1</sup> resolution from 500 to 4000cm<sup>-1</sup> and 32 scans per sample.

#### **(c) Acid value**

Esterified rice husk (150 mg) was mixed with 5 ml of 0.1 N H<sub>2</sub>SO<sub>4</sub> in 50 ml of distilled water and titrated [14] using 0.1 N NaOH with phenolphthalein as indicator. Acid value for esterified rice husk was found to be 2.33 meq/g.

#### **(d) Saponification value**

Esterified rice husk (300mg) was put into a 100 ml flask equipped with a reflux condenser in 20 ml of 0.5 N KOH in methyl alcohol. The flask was heated at  $65^{\circ}\text{C}$  for 1 hr and then 25 ml of 0.5 N H<sub>2</sub>SO<sub>4</sub> was added, followed after 1hr by 50 ml of distilled water. Titration was carried out with 0.1 N KOH using phenolphthalein as indicator [14]. Saponification value for esterified rice husk was found to be 9.5meq/g.

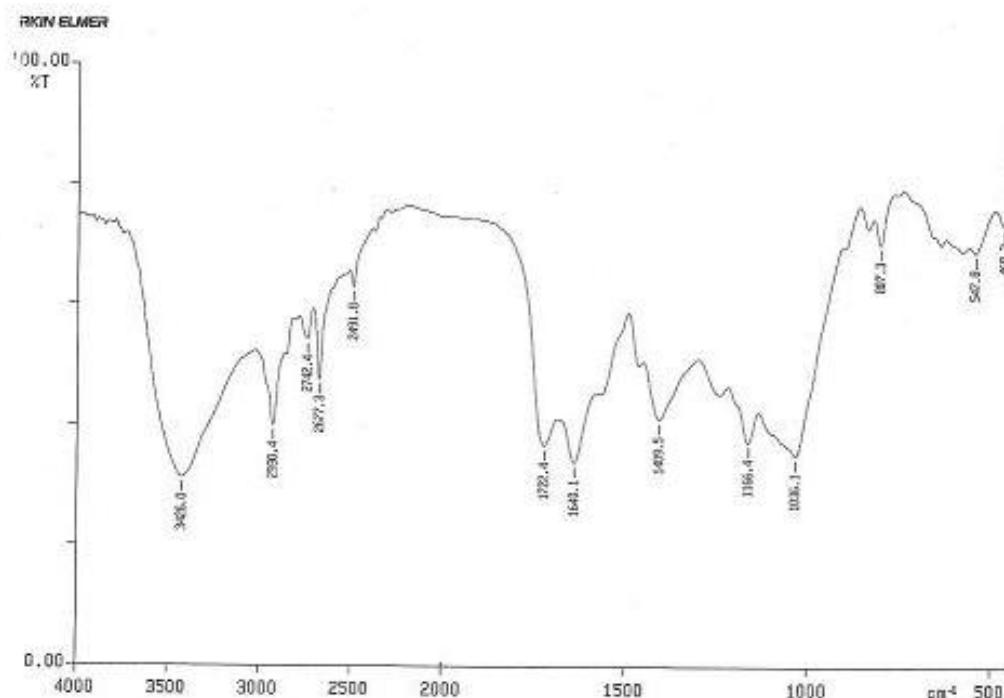
## 2.5 Batch adsorption studies

Batch experiments were carried out by agitating 0.5g esterified rice husk with 100 ml of metal ion solutions of different concentrations. The suspension was continuously stirred in a shaker, the effect of pH and initial metal ion concentration have been studied for pH range 2-8 and for initial metal ion concentrations ranging from 30-300 mg/L of Ni(II), which corresponds to the concentration of the metal ion found in effluents from related industries [13]. The pH of the solution was adjusted by the addition of ammonium hydroxide in the presence of ammonium chloride, to prevent the precipitation of lead at higher pH, or HNO<sub>3</sub> solutions. The contact time was varied from 0.5 to 3.0 hrs and the amount of Pb<sup>2+</sup> ion concentration was determined titrimetrically by the standard method using EDTA solution [15]. Each set of experiments was carried out in duplicate in order to check the reproducibility of the results and values were found to differ by  $\pm 2\%$ , which is well within the experimental error.

## III. RESULT AND DISCUSSION

### 3.1 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

In FTIR spectrum of esterified rice husk most changes occurring on the adsorbent after adsorption of nickel are reflected in the bands 3386.7 cm<sup>-1</sup> which may be assigned to complexation of nickel ions with the ionized O-H group of “free” hydroxyl groups and bonded O-H bands of carboxylic acids. The changes in peaks observed between 1728.9 cm<sup>-1</sup>, are indicative of stretching vibration of C-O bonds due to non-ionic carboxyl groups (-COOH, -COOCH<sub>3</sub>) and may be assigned to hydrogen bonding between carboxylic acids or their esters and nickel [16] which confer their ability to exchange ions.



**Fig. 1. FTIR Spectrum of esterified rice husk**

### 3.2 Effect of pH

Effect of pH on the adsorption characteristics of esterified rice husk was determined in the pH range 2-8. As is apparent from Fig.2, that the system is pH dependent and esterified rice husk shows maximum adsorption at at pH 5, due to introduction of carboxylic acid groups to the surface via esterification with cyclic anhydrides such as succinic anhydride. The hydroxyl groups of adsorbents react with succinic anhydride by the ring opening of anhydride and generate esterified rice husk bearing carboxylic acid groups [11]. Thus surface modification of the adsorbent increases the total number of carboxylic acid groups which leads to the increase in the number of adsorption sites on the surface of rice husk for adsorption of Ni(II) ion. The sorption rate is lower in acidic ranges, because at low pH due to high positive charge density on the adsorbent surface, there is electrostatic repulsion resulting in lower rate of adsorption [13]. With increasing pH, electrostatic repulsions decrease due to reduction of positive charge density on the sorption sites resulting in an increase in adsorption.

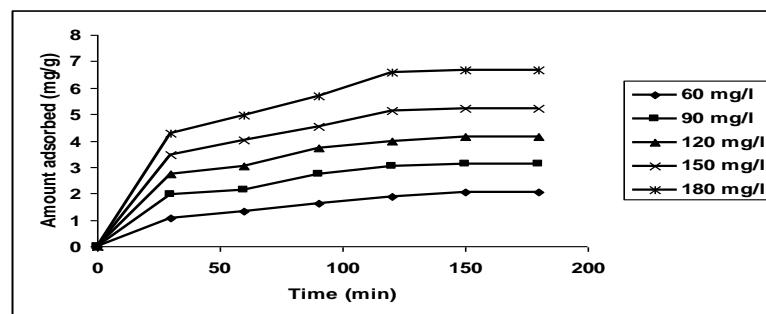
**Fig. 2. Amount of Ni(II) adsorbed on esterified rice husk vs time at 298 K, metal ion concentration 300mg/l on particle size 212 micron at different pH**

### 3.3 Effect of contact time

The nickel percent adsorption increases with contact time until the equilibrium was attained as shown in Fig.2. Studies conducted on the adsorption kinetics of Ni(II) removal revealed that the majority of metals ions were removed within the initial half hour contact with the adsorbents and increases very slowly later, this may be attributed to the availability of a larger number of adsorption sites in the beginning, similar results have been reported earlier [17] researchers. Maximum removal is attained at 2.5 hours. After it reached the equilibrium, there was no a significance changes in nickel concentration in the solution. The data obtained from effect of contact time were further used to determine the kinetics of Ni(II) adsorption.

### 3.4 Effect of metal concentration

The amount of metal ion adsorbed increases with concentration, in the concentration range studied as shown in Fig 3. However, percentage removal increases with decrease in the concentration of Ni(II) ions. The increase in percentage adsorption with dilution is explained [17] on the basis of availability of larger number of surface sites of the adsorbent for a relatively small number of adsorbing species at high dilution.



**Fig. 3. Amount of Ni(II) adsorbed on esterified rice husk at different contact time, 298 K and pH 5 on particle size 212 micron at various metal ion concentration**

### 3.5 Effect of particle size

Adsorption of Ni(II) has been studied on different adsorbents particles of varying sizes those retained on 212, 425 and 600 micron mesh size respectively. The experimental data shows that amount of Ni(II) adsorbed decreases with increase in particle size of the adsorbent. Higher rate of removal by adsorbent with smaller particle size is due to availability of more surface area on the adsorbent [18].

### 3.6 Adsorption isotherm studies

#### 3.6.1 Freundlich isotherm

The data for the uptake of Ni(II) by esterified rice husk has been analyzed in the light of Freundlich model of adsorption. The linearised form of the Freundlich equation can be given as:

$$\log q_e = 1/n \log C_e + \log K_f$$

where  $C_e$  is the equilibrium concentration ( $\text{mg L}^{-1}$ ) and  $q_e$  is the amount adsorbed ( $\text{mg g}^{-1}$ ). The data follow the Freundlich adsorption isotherm model and the values of  $n$  and  $K_f$  determined from slope and intercept of the linear plot of  $\log q_e$  vs.  $\log C_e$  are 1.18 and 0.082. The value of  $1 < n < 10$  indicates the effectiveness of the adsorbent [19].

#### 3.6.2 Langmuir isotherm

The Langmuir isotherm is represented by the following equation

$$\frac{C_e}{q_e} = \frac{1}{bQ_m} + \left( \frac{1}{Q_m} \right) C_e$$

where  $C_e$  is the equilibrium concentration  $\text{mg/L}$ ,  $q_e$  is the amount adsorbed at equilibrium  $\text{mg/g}$  and  $Q^0$  and  $b$  are Langmuir constants related to adsorption capacity and energy of adsorption, respectively. The plot of  $C_e/q_e$  vs.  $C_e$  shows the applicability of Langmuir isotherm. The values of  $Q^0$  and  $b$  as determined from slope and intercept of the Langmuir plot are 8.82 and 0.38. The applicability of these isotherm models and the high values of the correlation coefficients ( $r^2$  values 0.97) suggests favourable and monolayer adsorption. The essential characteristics of Langmuir isotherm can be described by the dimensionless parameter  $R_L$ ; also known as the separation factor, given by equation

$$R_L = \frac{1}{1 + bC_0}$$

where  $C_0$  is the initial metal ion concentration. The factor  $R_L$  indicates whether adsorption is favourable or not. The values of  $R_L$  have been found to be 0.069. The values of  $R_L$  have been found between 0 and 1 which suggests favourable adsorption [20].

#### 3.6.3 Tempkin isotherm

The data has also fitted in Tempkin isotherm. The linear form of Tempkin equation is given by

$$q_e = B_T \ln A_T + B_T \ln C_e$$

Where,  $B_T = (RT)/b_T$ ,  $T$  is absolute temperature in Kelvin and  $R$  is universal gas constant,  $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ . The constant  $b_T$  is related to the heat of adsorption,  $A_T$  is the equilibrium binding constant ( $\text{l min}^{-1}$ ) corresponding to maximum binding energy [21]. The slope and intercept from a plot of  $q_e$  versus  $\ln C_e$  determines the isotherm

constants  $A_T$  and  $b_T$ . The constants  $A_T$  and  $b_T$ , obtained for Tempkin isotherm model are 20.2 and 6.46 respectively. The obtained regression correlation coefficient for Tempkin isotherm model is 0.978 which confirms the better fit of equilibrium data.

### **3.7 Adsorption kinetics**

#### **3.7.1 Rate equation**

Kinetic studies for the adsorption of Ni(II) ions on esterified rice husk has been carried out by using the rate equation [7].

$$R = K C^n$$

where R is rate of adsorption, K is rate constant, C is concentration and n is the order of the reaction. The linear form of rate equation is given by

$$\log R = n \log C + \log K$$

A straight line plot of  $\log R$  vs  $\log C$  indicates that the adsorption follows first order kinetics for the adsorption of Ni(II) on esterified rice husk and the values of n and K obtained from the slope and intercept of these plots are 0.72 and  $9.60 \times 10^{-2}$  respectively.

#### **3.7.2 Lagergren first order equation**

To verify first order kinetics Lagergren equation has been used and showed that the rate of adsorption of solute on the adsorbent is based on the adsorption capacity and followed a pseudo first order equation .The data was fitted to Lagergren first-order equation [7]

$$\log (q_e - q) = \log q_e - \frac{K_{ad} t}{2.303}$$

Where  $K_{ad}$  ( $l \text{ min}^{-1}$ ) is first order rate constant of adsorbent, q and  $q_e$  are amount of metal ions adsorbed ( $\text{mg/g}$ ) at time t (min) and equilibrium time respectively. Linear plots of  $\log (q_e - q)$  vs time (correlation coefficient 0.976) which shows the applicability of above equation for first order kinetics for the adsorption of Ni(II) on esterified rice husk. The value of  $K_{ad}$  ( $l \text{ min}^{-1}$ ), the first order rate constant has been found to be  $1.62 \times 10^{-2}$ .

#### **3.7.3 Pseudo second order equation**

The adsorption kinetics data were further analyzed using Ho and McKay's pseudo-second-order kinetic model [22]. The model is based on the assumption that the rate of sorption is proportional to the square of number of unoccupied sites. It is expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where  $k_2$  is equilibrium rate constant of pseudo-second order adsorption ( $\text{g mg}^{-1} \text{ min}^{-1}$ ). The slopes and intercepts of plots  $t/q_t$  versus t was used to calculate the pseudo second order rate constants  $k_2$  and  $q_e$  (correlation coefficient 0.997) and values are  $1.68 \times 10^{-3}$  and 15.8 respectively.

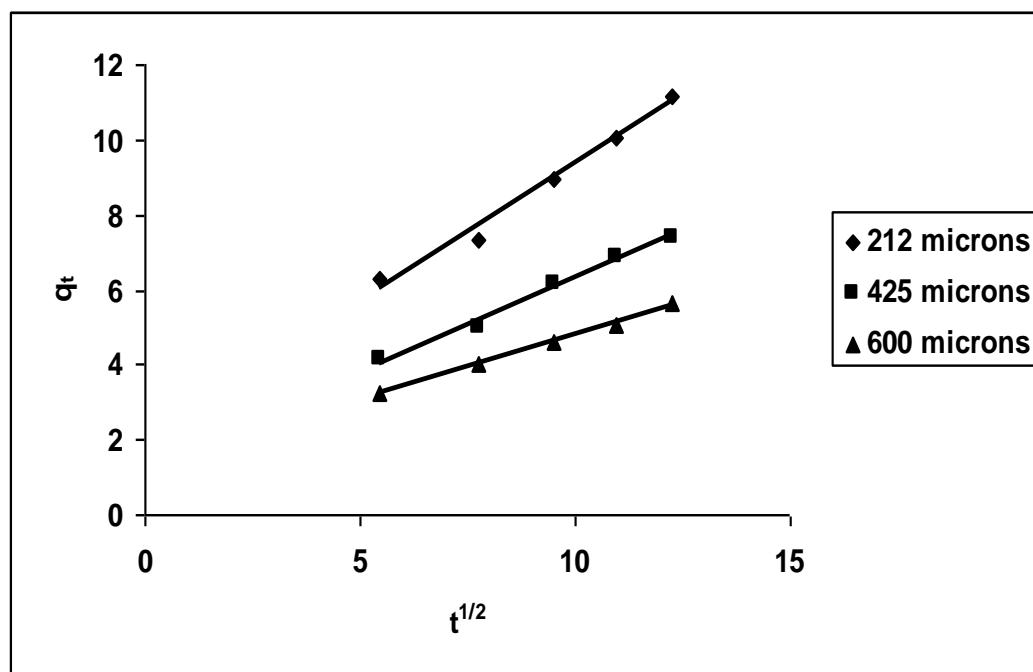
The time course data of Ni(II) adsorption were fitted to pseudo first order and second order Lagergren models to find out the order of reaction. If regression coefficient ( $R^2$ ) is taken as the parameter for model fitness,

it becomes apparent that both models very well define the present data. However for esterified rice husk the second-order kinetic model, with slightly higher  $R^2$  values, showed a little superiority over the first-order model.

### 3.7.4 Intra-particle diffusion study

Besides adsorption at the outer surface of esterified rice husk there is also possibility of intraparticle diffusion from the outer surface into the pores of the material. The possibility was explored by plotting amount of Ni(II) adsorbed vs.  $t^{1/2}$ , for different particle sizes of the adsorbent, according to Weber and Morris equation,  $q_t = K_p t^{1/2}$  [17] where  $q_t$  is amount of Ni(II) adsorbed at time  $t$  in mg/g,  $t$  is time of contact (min) and  $K_p$  is intra-particle diffusion constant ( $\text{mgg}^{-1}\text{min}^{-1/2}$ ).

Fig. 4 shows the plots of  $q_t$  against time with half power (i.e.  $t^{1/2}$ ) for different particle sizes of the adsorbent. The  $K_p$  values for three different particle sizes viz. 212, 425, 600 micron of esterified rice husk are 0.80, 0.66 and 0.56 respectively. This shows that increasing particle size decreases the adsorption of Ni(II) on esterified rice husk.  $K_p$  values give an idea about the surface porosity, higher the value of  $K_p$ , more porous is the surface. For large particles the diffusional resistance to mass transport is higher and most of the internal surface of the particle may not be utilized for adsorption and consequently the amount of Ni(II) adsorbed is small. Earlier studies have reported [17] similar conclusions.



**Fig.4. Weber-Morris plot for adsorption of Ni(II) on esterified rice husk at different particle size, temperature 298 K, initial metal ion concentration 300mg/l and pH 5**

## IV. CONCLUSIONS

Studies suggest that modified forms of agrobased byproducts can be effectively used as adsorbent for removal of Ni(II) ions from aqueous medium. Batch adsorption studies show that removal is dependent upon process parameters like contact time, metal ion concentration, pH and temperature. Maximum removal by chemically

modified adsorbents at pH 5 in 2.5 hr have been achieved for the concentration range 30 to 300 mgL<sup>-1</sup>. The sorption data obtained at optimized conditions have been subjected to Freundlich, Langmuir, Tempkin isotherm studies. The data fits well to both the Freundlich and Langmuir isotherm models indicating favorable and monolayer adsorption. The values of 1<n<10 indicate the effectiveness of the adsorbent. The values of R<sub>L</sub> have been found to be between 0 and 1 which suggests favorable adsorption. Kinetic studies carried out using the rate equation, the Lagergren first order equation, the pseudo second order equation and a study of intraparticle diffusion by the Morris Weber equation show that the mechanism of adsorption of Ni(II) ions by the selected adsorbents is complex and both the surface adsorption and intraparticle diffusion contribute to the rate determining step. From the results it is evident that adsorption of Ni(II) follows pseudo second order kinetics. Thus, the use of chemically modified agricultural based adsorbents may contribute to the sustainability of the surrounding environment. These adsorbents offer a lot of promising benefits for commercial purpose in the future for wastewater treatment due to their local availability, technical feasibility and cost effectiveness.

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