

ADSORPTIVE REMOVAL OF Fe (II) BY NaOH TREATED RICE HUSK: ADSORPTION EQUILIBRIUM AND KINETICS

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Abstract: The low cost adsorbents were prepared from raw rice husk (RRH) and NaOH treated rice husk (NRH). Then prepared materials were characterized by XRD, FTIR and surface area of rice husk adsorbent were determined by methylene blue adsorption method. XRD showed amorphous nature with low crystallinity of the material. The FTIR spectra showed the presence of oxygenated functional groups such as ester, phenol, carbonyl and silica on the material. The surface area of RRH and NRH were found to be 387 and 417 m²/g respectively. Thus, prepared adsorbents were used for the removal of Fe(II) ion from aqueous solution. The influence of various parameters like pH, adsorbent dose, and contact time were studied for the better adsorption of Fe(II) on rice husk adsorbents. Results revealed that the maximum efficiency was achieved at pH 3 for Fe(II). The adsorption process was found to be best fitted to Langmuir adsorption isotherm model controlled by pseudo-second-order kinetics with the rate constant value i.e. 0.0218 and 0.0235 g/(mg·min) for RRH and NRH respectively. The χ^2 values of pseudo second order was found to be lower which confirmed chemisorption, involving ion exchange and valence forces through sharing or exchange of electrons between adsorbent and adsorbate. The maximum adsorption capacity for Fe(II) on RRH and NRH was found to be 2.9 mg/g and 5.6 mg/g respectively. The positive ΔG value represents the randomness of the system during adsorption process. The slope of the linear plot of Q_t vs $t^{0.5}$ was linear but not passed through the origin, which indicates that, the intraparticle diffusion was not only rate controlling step. Temkin value showed the maximum binding energy (K_T) for NRH was 16.4 L/g and for RRH it was 12.2 L/g.

Key word: Rice husk; Iron; Langmuir adsorption.

INTRODUCTION

Metals of having relatively high densities ($> 5 \text{ g/cm}^3$) and high atomic weights simply means heavy metals¹. Copper, aluminium, iron, zinc, platinum, arsenic, chromium, etc are some of the examples. Heavy metals are either essential nutrients like iron, cobalt and zinc or relatively harmless such as ruthenium, silver and indium while other are highly poisonous such as arsenic, cadmium, mercury and lead¹. Among the wide variety of heavy metals, iron is one of the most common heavy metals that is found in nature. The magnetite [Fe₃O₄, 72.4 % Fe], hematite [Fe₂O₃, 69.9% Fe], goethite [FeO(OH), 62.9% Fe], limonite [FeO(OH).n(H₂O)] or siderite [FeCO₃, 48.2% Fe] are the most common ore of iron that is found in earth's crust.

Among them, hematite and magnetite are found in the form of rocks² which during demineralization introduced in ground water by leaching and percolation. It also introduced from anthropogenic sources specially from industrial sector³.

Heavy metals have become one of the major causes of concern for water pollution¹. In ground water, iron exists in ferrous state and remains dissolved in water. Nonetheless when it is exposed to atmosphere, it gets oxidised to ferric ion. The iron in ferric state does not dissolved in water and forming reddish brown colour². The relatively high content of iron levels in water can cause stains in plumbing, laundry and cooking utensils that can impart objectionable tastes and colours to foods³. Additionally, excessive

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concentration of iron intake causes life threatening issues such as diabetes, heart failure, under developed growth³, haemochromatosis², anorexia, oliguria etc^{4,5}. According to WHO, 0.3 mg/L of iron in drinking water is the water permissible level². When it is higher than permissible level, one has to remove iron from drinking water for health purposes. In these days, different methods has been adopted such as chemical precipitation, lime coagulation, ion exchange, reverse osmosis, solvent extraction, reduction, electro dialysis, evaporation, electrochemical precipitation⁴, oxidation with oxidising agent such as chlorine and potassium permanganate and treatment with lime stone⁵. However, these methods are not widely acceptable due to high capital, operational costs and problem in disposal of residual metal sludge. Taking these into considerations, the adsorption process thus appeared as one of the most promising methods⁶. It is considered as an efficient, convenient and economic method for waste water treatment.

In present study, rice husk was used as an adsorbent. Rice husk is actually the outer most covering of the rice grain. It contains 15-20% hemicellulose, 28-30% cellulose, 25-30% lignin, 15-20% silica and 10-15% moisture⁷. This composition of rice husk makes it possible to be regarded as an adsorbent and the large amount of silica in the rice husk means that it could provide sufficient structural strength without cross linking⁸. Previous researchers has used rice husk for the removal of ionic dyes, basic dyes and variety of metal cations⁹⁻¹¹.

In this context, the activated carbon (AC) was commonly used as an adsorbent. However, due to its high cost and its high affinity towards high molecular weight organic molecules, it is unable to adsorb heavy metal ions. To overcome this problem, many researchers have shown interest to search and explore on other potential adsorbents to replace AC⁶ synthesized and chemically modified adsorbent have been used.

In the present research work, the rice husk waste collected from rice mills of Kathmandu valley and used for the adsorptive removal of Fe (II) from aqueous solution.

MATERIALS AND METHODS

Instruments

The X-Ray Diffractometer (D2-Phaser, Bruker, Germany) was used to study the phase state of rice husk. It was operated at an accelerating voltage of 40 KV and current 40 mA with Cu-K α radiation ($\lambda=1.5418\text{\AA}$) in the diffraction angle of 10 to 50 degrees. Likewise, the surface functional group was studied by Fourier Transmission Infrared Spectroscopy (Shimadzu, Model No. IRTracer-100, Japan) and FTIR spectra were recorded at 4000-400 cm^{-1} wave number. The spectrophotometric analysis was carried out by using 2306 visible Spectrophotometer, (AB1211010, Electronics India) and with the help of deluxe pH meter (Max Electronics, India) pH of solution was measured.

Reagents

Analar grade (AR) reagents such as Ferrous ammonium sulphate, hydroxylamine hydrochloride, ammonium acetate, 1,10 Phenanthroline monohydrate, NaOH, and methylene blue were procured from Merck Company India.

Preparation of Adsorbents

Fresh rice husk was collected from a local rice mill of Kathmandu. It was washed with distilled water and dried in sunlight and finally dried in oven at 60°C. The rice husk was grounded into fine powder and sieved through 75 μm mesh size. Thus, obtained adsorbent was designated as Raw Rice Husk (RRH).

Preparation of NaOH treated rice husk (NRH)

Raw rice husk powder was treated with (0.5 N) NaOH solution at room temperature for 4 hour⁹. Excess of NaOH was removed by washing with distilled water and the material was dried at 40°C. Thus, obtained base treated rice husk was designated as NRH.

Determination of surface area by Methylene blue (MB) adsorption method

Surface area of adsorbent is generally done by methylene blue adsorption method using equation (1).

$$S_{MB} = (Q_m \cdot a_{MB} \cdot N \times 10^{-20}) / M \dots\dots\dots(1)$$

Where, S_{MB} = surface area (m^2/g), Q_m = Maximum loading (mg/g), a_{MB} = Cross section area of one molecule of MB = 197.2 \AA^2 , N = Avogadro's No. = 6.023×10^{23} , M = Molecular weight of MB = $319.84 \text{ g}/\text{mol}$.

The amount of methylene blue adsorbed from each adsorbent was calculated by using equation (3). Where, C_0 (mg/L) is the concentration of the methylene blue solution at initial time ($t=0$), C_e (mg/L) is the concentration of the methylene blue solution at equilibrium time which can be calculated by equation (2), V (L) is the volume of the solution treated and M (g) is the mass of the adsorbent. To determine the Q_m , Q_e was plotted as a function of C_e .

$$C_e = \text{Absorbance/Slope} \dots \dots \dots (2)$$

$$Q_e = (C_0 - C_e) \times V/M \dots \dots \dots (3)$$

By using the Langmuir adsorption isotherm, maximum loading (q_m) of MB on adsorbent sample was obtained. Then surface area was calculated by using equation (1)

Batch adsorption study

The batch adsorption study was used to access the adsorption capacity of adsorbent. The amount of metal ion adsorbed onto adsorbent was determined by using following equation (4).

$$Q_t = (C_i - C_e/W) \times V \dots \dots \dots (4)$$

Where, C_i = Initial concentration of metal ion (mg/L), W = Weight of adsorbent (g). Likewise metal ion removal percentage was calculated by using the following equation.

$$R\% = (C_i - C_e/C_i) \times 100 \dots \dots \dots (5)$$

C_e = Equilibrium concentration of metal ion (mg/L). Q_t = Amount of metal ion adsorbed onto adsorbent at time 't' (mg/g), V = Volume of metal ion solution (L).

Adsorption Isotherm

Langmuir, Freundlich and Temkin adsorption isotherm models were used to evaluate the adsorption efficiency. Likewise, error analysis for the isotherm and kinetics studies, analysis of intraparticle diffusion (Weber and Morris model) as well as influence on the removal of Fe(II) from aqueous solution by adsorbent was also studied.

RESULTS AND DISCUSSION

X-Ray Diffraction Analysis

The X-Ray diffraction spectrum of raw rice husk sample is presented in Fig. 1. In spectra, a peak at 23° degree was observed which represents the low crystallinity of the material. It is assigned for silica present in raw rice husk. There are no other sharp peaks identified. The broad peaks

could be seen which indicated for the typical amorphous form of the material¹².

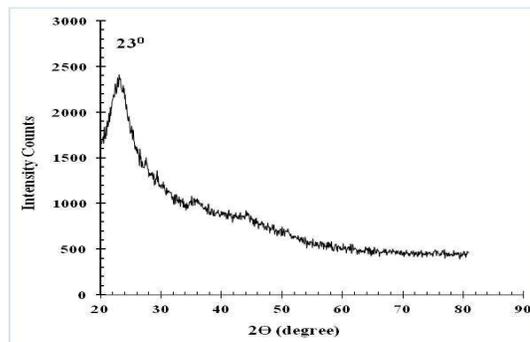


Figure 1: XRD spectrum of raw rice husk

Fourier Transfer Infrared Spectroscopy Analysis

FTIR spectra of raw rice husk, NaOH treated rice husk is shown in Error! Reference source not found., (a) represents the spectra of RRH whereas (b) spectra represents for NRH. In Fig. 2, the broad bands at around 3724, 3296 cm^{-1} is assigned to -OH stretching vibration. Similarly, the next broad band at around 2872 cm^{-1} was observed which is assigned for the C-H group. The band at 2349 and 2328 cm^{-1} has been assigned to symmetric or asymmetric stretching of aliphatic band of -CH, -CH₂ or -CH₃. Another small band at 2013 cm^{-1} may represent residual water. Similarly, the band observed at the region around 1749, 1637, 1508 cm^{-1} is assigned for the presence of C=O stretching or C=C stretching vibration of aromatic ring structure from lignin¹³. The small C-OH bending bands were also observed at 1361 cm^{-1} which is attributed to ester. The major peak appeared at 1045 cm^{-1} ascribed for the bending vibration of -CH₃ group or stretching Si-O-Si bond of siloxane¹⁴.

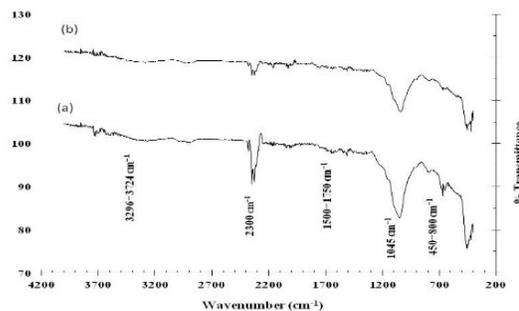


Figure 2: FTIR spectra of (a) RRH and (b) NRH

Characteristic bands near 783, 669 and 451 cm^{-1} were assigned to the bending vibration of Si-O bond from amorphous silica^{15,16}. Another small band at 418 and 399 cm^{-1} are assigned for C-C stretching bond.

Spectra (b) of NRH shows the similar bands at same wavenumber (cm^{-1}), however at 2300, 1045, 669 and 451 cm^{-1} , the peak of intensity found to be reduced. This may be due to removal of lignin, cellulose by NaOH treatment on RRH. The increase of surface area of adsorbent, may be due to the formation of porosity on surface^{17,18}.

Determination of specific surface area of adsorbents

Specific surface area of adsorbent was determined and are shown in table 1.

Table 1. Surface area of RRH and NRH

Adsorbents	Specific surface area (m^2/g)
RRH	387
NRH	417

As can be seen in Table 1, the specific surface area of the NRH was found to be higher than RRH due to the more adsorption site formed with more numbers of pores in NRH than RRH. Surface area of rice husk is compared with other previous literature^{15, 19, 20} and was found to be in good agreements. It can be observed that the variation of surface area may be due to variation of temperature on the process of heating, stage of preparation, retention time for activation and pyrolysis.

Study on the removal of Fe(II) from solution by rice husk samples: Effect of initial pH of Fe(II) solution

The optimal pH for the removal of Fe(II) from aqueous solution by rice husk sample was found to be 3. The optimum uptake of Fe^{++} by RRH and NRH was found to be 91.5% and 95.5% respectively at pH 3. Among these two adsorbents, NaOH treated adsorbent showed better result. It may be due to formation of porosity on surface by base treatment where removal of low molecular weight cellulose and lignin may occur^{17, 18}.

Effect of Adsorbent Dose and Contact Time

The 1.5 g of RRH adsorbent and 1.0 g of NRH adsorbents were found to be optimum adsorbent dose to carry out adsorption studies.

Similarly, the effect of contact time was studied. The

equilibrium time for 99.4% Fe(II) adsorption on NRH was found to be 60 min whereas equilibrium time for 98.35% adsorption of Fe(II) by RRH was found to be 180 min.

Adsorption Kinetics Studies: Adsorption kinetics provides a deeper insight into how the amount of adsorbate changes with time and information about the equilibrium time. The pseudo first order kinetic model was studied for the reversible reaction when an equilibrium being established between liquid and solid phase. The linearized form of pseudo first order model is generally expressed as follows:

$$dQ_t / dt = K_1(Q_e - Q_t) \dots\dots\dots (6)$$

Where, Q_e (mg/g) is the amount of metal ion adsorbed at equilibrium, Q_t (mg/g) is the amount of metal ion adsorbed at any time 't' and K_1 is the Lagergren rate constant for pseudo first order adsorption reaction. After integration and applying boundary conditions, $t = 0$ to $t = t$ and $Q_t = 0$ to $Q_t = Q_t$, the linear form of equation (6) becomes;

$$\text{Log} (Q_e - Q_t) = \text{log} Q_e - (K_1 t / 2.303) \dots\dots\dots (7)$$

The plot of $\text{Log} (Q_e - Q_t)$ vs t should give a straight line from which K_1 and Q_e can be determined from slope and intercept of the plot. The Kinetic parameters obtained are tabulated in Table 2 where low correlation coefficient (R^2) value for both the adsorbents i.e. 0.8294 for RRH and 0.8643 for NRH could be seen. The χ^2 value was also noted which was found to be 1.26 for RRH and 28.94 for NRH.

By observing the parameter obtained from the pseudo first order, the process of removal of Fe(II) was not clear so further pseudo second order rate equation has been studied which may help to study the kinetics of adsorption of heavy metals onto adsorbent according to equation (8).

$$dQ_t / dt = K_2 (Q_e - Q_t)^2 \dots\dots\dots (8)$$

Where, K_2 (mg/g/min) is the pseudo second order rate constant and Q_e and Q_t are the amount of metal ion removed at equilibrium and at time 't', respectively, in (mg/g). On integration and applying boundary conditions, $t = 0$ to $t = t$ and $Q_t = 0$ to $Q_t = Q_t$, the above equation (8) becomes,

$$t/Q_t = 1 / K_2 Q_e^2 + (1/Q_e) \times t \dots\dots\dots (9)$$

$$t/Q_t = 1/v_0 + (1/Q_e) \times t \dots\dots\dots (10)$$

Where, v_0 is the initial adsorption rate in mg/g/min and is equal to $K_2 Q_e^2$.

Table 2. Kinetic parameter

Adsorbents	Pseudo first order			Pseudo second order		
	K_1 (min^{-1})	R^2	χ^2	K_2 ($\text{mg g}^{-1}\text{min}^{-1}$)	R^2	χ^2
RRH	0.0218	0.8294	1.26	2.504	1	7.25×10^{-5}
NRH	0.0235	0.8643	28.94	3.081	0.9998	5.91×10^{-5}

From the data of kinetic parameters, it can be seen that K^2 and χ^2 value was found to be higher which implies that the removal of Fe(II) by RRH sample follows pseudo second order kinetics model with better R^2 value 1 and 0.9998 for NRH sample as compared with pseudo first order kinetic models.

Error analysis for kinetics studies

In order to conform the observations, error analysis was carried out using the chi square test (χ^2) for experimental data as well as the calculated data in given time interval and in different concentration. The mathematical expression is;

$$\chi^2 = \sum [(q_t - q_{tm})^2 / q_{tm}] \dots\dots\dots(11)$$

Where, q_t = adsorption capacity obtained by experimental value (mg/g) and q_{tm} = adsorption capacities obtained by using the model (mg/g).

If the calculated data from model are similar to the experimental data, the value of χ^2 will be smaller, while if these values differ, then the value of χ^2 will be larger⁵. Here, the corresponding values of χ^2 are tabulated in Table 2 which showed that χ^2 values is lower for pseudo second order compared to pseudo first order.

Hence, the adsorption of Fe(II) onto rice husk sample follows pseudo second order kinetics. The pseudo second order confirmed the chemisorption, involving ion exchange and valence forces through sharing or exchange of electrons between adsorbent and adsorbate²¹.

Analysis of intraparticle diffusion (Weber and Morris model)

Intraparticle diffusion model was applied to determine the mechanism and the rate determining step in adsorption process. The rate constants of intraparticle diffusion (K_{id}) are determined by using the following Weber–Morris equation (12)^{22,23}.

$$Q_t = K_{id}t^{0.5} + C \dots\dots\dots(12)$$

Where, K_{id} (mg/g. $\text{min}^{0.5}$) represents the intraparticle diffusion rate constant and its values are obtained from the plot of Q_t versus $t^{0.5}$ and value of ‘C’ is obtained from the intercept of the plot and represented the boundary layer effect. The larger the value of C, the greater is the boundary layer effect.

Here (Fig. 3), the intraparticle diffusion curve was found to be linear and was not passed through the origin showing the intercept C. It was described that the adsorption was partly controlled by intraparticle diffusion¹⁴. Therefore, the adsorption here was also controlled by external adsorption.

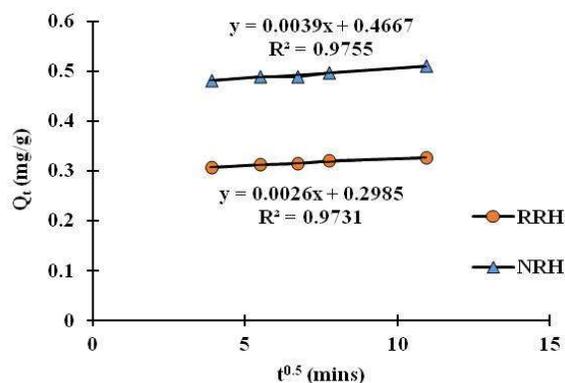


Figure 3: A plot of Q_t versus $t^{0.5}$

Table 3. Langmuir parameters, Freundlich parameter and Temkin parameter

Adsorbents	Langmuir parameters					Freundlich parameters			Temkin parameters	
	b	Q _m	R ²	K _L	G ⁰	1/n	K _F	R ²	B	K ^T
RRH	0.3	2.9	0.996	0.017-0.257	3.1	0.46	1.98	0.9677	0.24	12.4
NRH	0.9	5.6	0.997	0.006-0.107	0.2	0.54	1.42	0.9741	0.98	16.4

Adsorptions Isotherm Studies

To evaluate the feasibility, three different isotherm models have been tested.

a. Langmuir isotherm model

It is widely applied model to describe experimental adsorption data based on the assumption that maximum adsorption corresponding to saturated monolayer of adsorbate molecule on adsorbate surface with a constant energy and no further adsorption. The Langmuir adsorption equation can be represented as; $Q_e =$

$$\frac{Q_m b C_e}{1 + b C_e} \dots \dots \dots (13)$$

The linear form of Langmuir expression is expressed as;

$$\frac{C_e}{q_e} = \frac{1}{Q_m b} + \frac{1}{Q_e} C_e \dots \dots \dots (14)$$

Where, Q_e (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent; C_e (mg/L) is the equilibrium concentration of the adsorbate in solution after adsorption; Q_m (mg/g) is the maximum adsorption capacity corresponding to monolayer coverage of adsorbents and b (L/ mg) is the adsorption equilibrium constant.

Here, the value of Q_m and b are presented in Table 3 which was calculated from the slope and intercept of the C_e/Q_e versus C_e plot. The chemical modification of RRH resulted in enhancing the sorption capacity from 2.9 mg/g to 5.6 mg/g which was compared with various literature^{5,10,22} and found to be good agreement with literature values of wooden charcoal⁵ and calabrian pine bark²². Langmuir isotherm constant (b) was found to be 0.9 and 0.3 L/mg for NRH and RRH respectively which indicates free energy of adsorption. Here, the value of G^0 represents the randomness of the system during adsorption process where it was found to be 3.1 for RRH and 0.2for NRH. The essential feature of Langmuir adsorption isotherm can be expressed in terms of dimensionless constant called

separation factor or Langmuir parameter (K_L) which was found to be 0.006–0.107 for NRH and 0.017 – 0.257 for RRH. These values of K_L lies between 0 and 1 indicating the favourability of adsorption. Here, K_L was calculated by equation (15);

$$K_L = 1/(1 + bC_i) \dots \dots \dots (15)$$

Where, C_i = Initial concentration (mg/L) and b = Langmuir constant.

The correlation coefficient R^2 value are closer to unity for NRH and RRH which indicated that linear isotherm is fitted for both NRH and RRH sample.

b. Freundlich isotherm model

The adsorption data was also tested through Freundlich Adsorption Isotherm model. The model explains the non-ideal sorption that involves heterogeneous surface energy system and is expressed by equation (16).

$$Q_e = K_F C_e^{\frac{1}{n}} \dots \dots \dots (16)$$

The linear form can be written as; $\log q_e = \log K_F + \frac{1}{n} \log C_e \dots \dots \dots (17)$ where, K_F and n (dimensionless constants) are the Freundlich adsorption isotherm constants, K_F indicates adsorption capacity which was found to be 1.98 mg/g for RRH and 1.42 mg/g for NRH. The slope $1/n$ ranging between 0 and 1, is favourable adsorption condition and was found to be 0.54 and 0.46 for NRH and RRH respectively (Table 3) which indicates the favourable adsorption behaviour of Fe(II) from aqueous solution by RH sample however the correlation coefficient value obtained from Freundlich isotherm for RRH and NRH was found to be 0.9677 and 0.9741 which appeared to be lower than the Langmuir isotherm value i.e. 0.996 (RRH) and 0.997 (NRH). It clearly revealed that Langmuir model was best fitted one.

c. Temkin isotherm model

After observing these two models, the effect of interaction of adsorbate and adsorbent was studied by Temkin adsorption isotherm model. This model assumes that heat of adsorption of all the molecules in the layer would decrease linearly rather than logarithmically with coverage due to adsorbate adsorbent interaction and adsorption is characterized by uniform distribution of binding energy up to some maximum binding energy. The linearized Temkin equation is given by the following equation.

$$Q_e = (RT/b) \log K_T C_e \dots \dots \dots (18)$$

$$Q_e = B \ln K_T + B \ln C_e \dots \dots \dots (19)$$

Where, $(RT/b) = B$, $K_T =$ Temkin isotherm equilibrium binding constant (L/g), which corresponds to maximum binding energy, $b =$ Temkin isotherm constant, $R =$ Universal gas constant (8.314 J/ mol/K), $T =$ temperature at 298K, $B =$ constant related to heat of sorption (J/mol)

The Temkin constants K_T and b is calculated from the slope and intercept of Q_e as a function of $\ln C_e^{24}$ and the data are presented in Table 3, where heat of sorption (B) was found to be 0.24 J/mol for RRH and 0.98 J/mol for NRH. The maximum binding energy (K_T) was found to be 12.2 L/g for RRH and 16.4 L/g for NRH indicates greater interaction of adsorbate and adsorbent in NRH

CONCLUSION

It is concluded that simple and low cost bio adsorbents can be prepared from rice husk and chemical modification can be done by base (NaOH) treatment. Both adsorbent samples were able to uptake maximum Fe(II) at 3.0 pH. Adsorption capacity of rice husk sample was enhancing from 2.9 mg/g to 5.6 mg/g after chemical treatment by NaOH. The adsorption capacity of NRH was found to be 2 times greater than RRH. Then, experimental data were better fitted for Langmuir isotherm model which indicates the homogenous distribution of active sites on the surface of adsorbent and from the Temkin model it was concluded that maximum binding energy was greater for adsorption of Fe(II) onto NRH. Similarly, the kinetics for uptake of Fe(II) by RH sample has followed the pseudo second order kinetic model which indicated the chemisorption occurred as the rate limiting mechanism. And from intraparticle diffusion

model, it is concluded that the adsorption was partly controlled by intraparticle diffusion and also controlled by external adsorption.

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