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Equilibrium and Kinetic Studies on the Removal of Cu(II) from Aqueous Solution Using Acid Treated Modified Rice Husk: A Comparative Study

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Abstract

This study deals with the removal of Cu(II) using rice husk and its acid treated modified form as adsorbents under batch experiments. Different parameters have been investigated for the adsorption of copper metal. Equilibrium time (90 min) was found for copper adsorption. Maximum percentage for removal of Cu(II) was found at pH=4 both for raw rice husk and its treated form. Percentage removal of copper metal was up to 90% for treated rice husk and up to 70% for raw form of rice husk. Calculated saturation capacity of rice husk for Cu(II) were found as 36.587mg/g and 45.267 mg/g for raw and treated rice husk respectively. The amount of Cu(II) adsorbed increased with increase in their contact time. 40 to 50% metal ions were removed within 2030 min after the start of the adsorption. The pseudo second order kinetic model provided the best correlation of the used experimental data compared to the pseudo first model with a R^2 of 0.984 and 0.979 for raw rice husk and treated rice husk respectively.

Keywords: Rice husk; Copper biosorption; Kinetic model

1. Introduction:

From the last several years, water resources pollution by disposal of heavy metal ions becomes a worldwide problem[1]. Due to industrialization, major global problem has been created by the releasing of heavy metal in the environment [2]. Discharge of heavy metals by the industries contains hazardous elements such as zinc, chromium, nickel, cadmium copper and arsenic [3-6]. Aquatic living bodies can also be affected badly due to these soluble heavy metals in water [7]. Quality and purity of water is also affected by these heavy metals discharge into water. Discharge of heavy metals cause a water pollution problem. Quality of water, aquatic livings and health of

human being are threatened by increasing discharge of these heavy metals in the environment. Hence heavy metals should be prevented from reaching the environment.

Industrial discharge contains different metals like Cu, Ni, Cd, Al, Pb etc. Cu is harmful and toxic for living organism [8]. Its presence in drinking water can cause different diseases like nausea diarrhea. It can lead the way towards the failing of kidney and livers. It is very important to reduce the Cu level up to 2 mg/L. The amount of Cu present in an adult human body is 100-150mg if it is crossed it is then

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toxic [9].

Different method such as membrane process, dialysis, extraction of solvent, reverse osmosis is also used but most of them have many drawbacks such as high cost, high usage of chemicals, large amount of sludge formation [10].

Cost effective methods are needed to remove heavy metals from wastewater. Agricultural waste is also use for metal removal from waste water as a sorbent such as coconut husk, sawdust, rice straw, wheat straw etc. Advantages of using these materials cause saving in cost and utilization of wastes [11-12].

One of the strategic crops of the world is rice. A great amount of rice husk is produced every year in Pakistan. Rice husk is made up of crude protein, ash, lignin and cellulosic materials etc. Rice husk can be used to remove Cu from water.

From the last decade, focused has been made on use of rice husk in its different forms such as treated form, ash form or pyrolysis form as a bio sorbent for removal of heavy metals. Different treatments for rice husk were reported for the enhancement of adsorption capacities for metal ions and other pollutants [13].

In this study, rice husk was used as a bio sorbent in raw form and acid treated modified form to removed copper metal ions. Comparative performance evaluation of different forms of same biomass i.e., raw, chemically modified and ash is necessary. Rice husk and their modified forms have been tested for the wastewater treatment under different conditions under batch experiments.

2. Materials and Methods:

2.1 Materials:

Copper Sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) purity 99%, Nitric acid (HNO_3) purity 98.5% and sodium hydroxide (NaOH) purity 99% were procured from Sigma Aldrich, USA. Rice husk was obtained from Jeddah rice mill, Multan, Pakistan. Standard solution of copper Sulfate was prepared for atomic absorption spectrometry. Nitric acid was used for the preparation of treated rice husk. 0.1mol/L NaOH

and 0.1mol/L HNO_3 solution were also prepared to control pH of the wastewater. All analytical grade reagents were used in this study

2.2 Preparation of Bio-sorbent:

First of all, rice husk was washed with distilled water. Dried rice husk was crushed and passed through series of mesh size and collect the material retain on sieve of mesh size 42 of Taylor sieves of series. Rice husk was treated with 0.1N nitric acid solution and then washed with distilled water till neutral pH was obtained. Bio sorbents materials must be store in air tight vessels for its protection from humidity or moisture.

2.3 Cu(II) Contents Detection:

Flame atomic absorption spectrometry FAAS (Shimadzu 6800) with cathode lamp of 232nm and 15mA was use for the detection of contents of Cu contents.

2.4 Experiments:

Stock solution of copper sulfate (1000ppm) was made. Different synthetic samples of initial different concentrations were made by diluting 1000ppm this stock solution. 100 ppm of sample solution of copper was used for each experiment. Mixing was performed on vibratory shaker with 150 rpm. Effect of contact time, pH, adsorbent dosage and initial metal concentration on biosorption of copper have been investigated.

2.5 Uptake Of Copper By Bio Sorbent:

Amount of copper metal ions on rice husk bio sorbent is calculated [13] by using this equation 1.

$$q_e = \frac{C_o - C_e}{M} \times V$$

Where,

q_e = Metal uptake (mg/g)

V = Volume of Solution (Liter)

C_o = Copper ions initial concentration (mg/L)

C_e = Copper ions final concentration (mg/L)

M = Mass of bio-sorbent (gram)

3. Results and Discussion:

3.1 Effect of time:

Figure (1-2) represents the relationship between

contact time and Cu(II) metal uptake using raw rice husk and treated rice husk with biosorbent amount (0.2 gram) and temperature (30 ± 1) C and initial metal ion concentration (100mg/L).

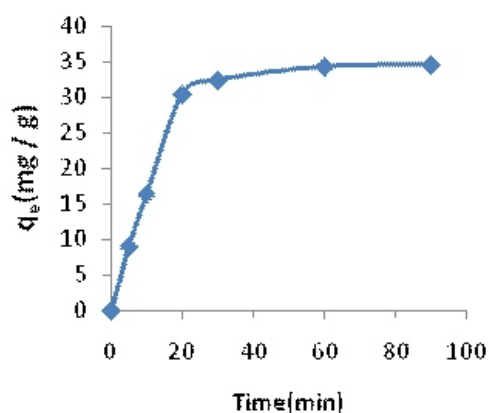


Figure 1: Time vs Metal uptake for equilibrium time determination for raw rice husk

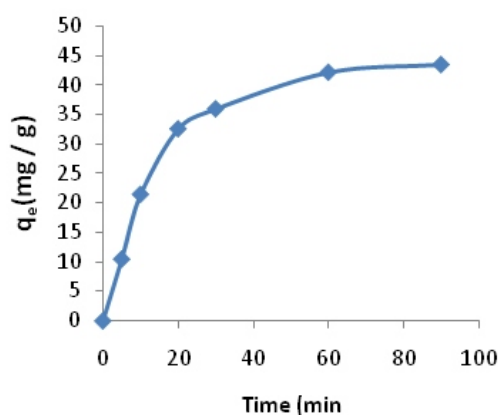


Figure 2: Time vs Metal uptake for equilibrium time determination for treated rice husk

Figure 1 revealed that no metal uptake after 90 minutes was take place. It was found that about 70% copper is adsorbed by the untreated rice husk. The reason behind that the vacant surfaces were available at the start of biosorption which is decreases with the passage of time due to occupancy of metals on the surface [14]. Figure 2 represents the 90% copper metal removal by the treated rice husk after 90 minutes. Treatment of rice husk with the nitric acid enhance the adsorption activity of the bio sorbents.

3.2 Effect of pH:

Figure (3-8) represents the relationship between

contact time and Cu(II) metal uptake using raw rice husk and treated rice husk at different pH with bio sorbent amount (0.2 gram) and temperature (30 ± 1) C and initial metal ion concentration (100ppm). Figure (3-4) depicted the copper metal uptake as 35mg/g and 40mg/g at pH=3 both for raw and treated rice husk respectively. On the other hand, Figure (5-6) revealed the copper metal uptake as 37mg/g and 45mg/g at pH=4 for both cases. While Figure (7-8) showed the copper metal uptake as 32mg/g and 38mg/g at pH=5 both for raw and acid treated of bio sorbent. It is concluded from the above discussion, the maximum removal of copper from water sample was found for pH-4 that may be due to high active sites present on the surface of bio sorbent [13].

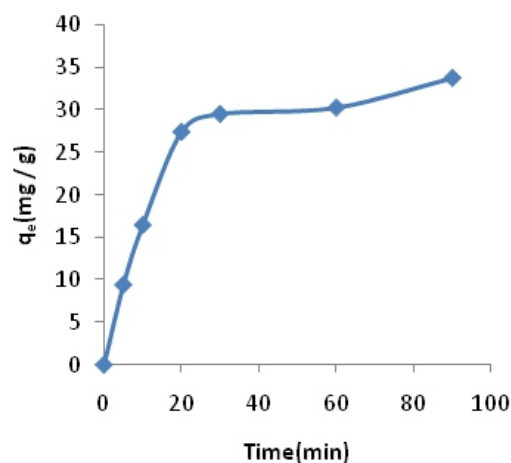


Figure 3: Effect of contact time on copper metal uptake at pH=3, dose=0.2g, concentration= 100ppm using raw rice husk

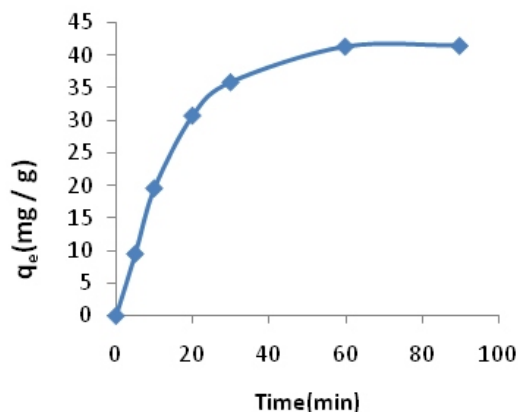


Figure 4: Effect of contact time on copper metal uptake at pH=3, dose=0.2g, concentration= 100ppm using treated rice husk

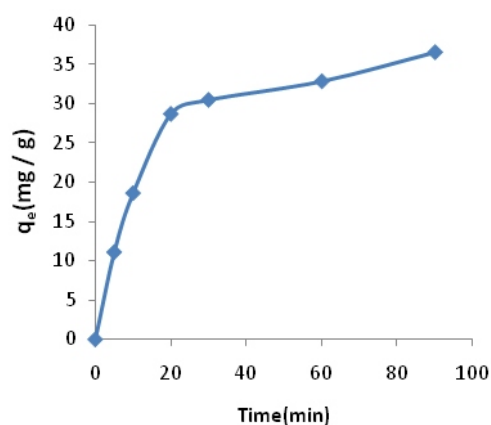


Figure 5: Effect of contact time on copper metal uptake at pH=4, dose=0.2g, concentration=100ppm using raw rice husk

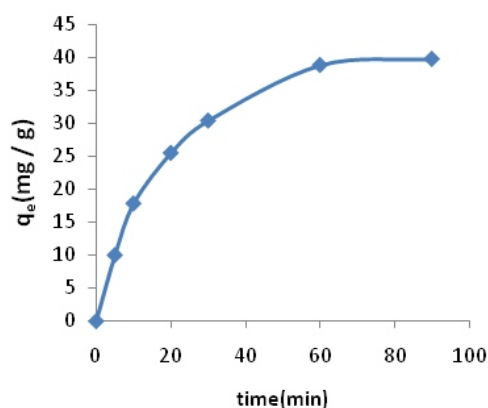


Figure 8: Effect of contact time on copper metal uptake at pH=5, dose=0.2g, concentration=100ppm using treated rice husk

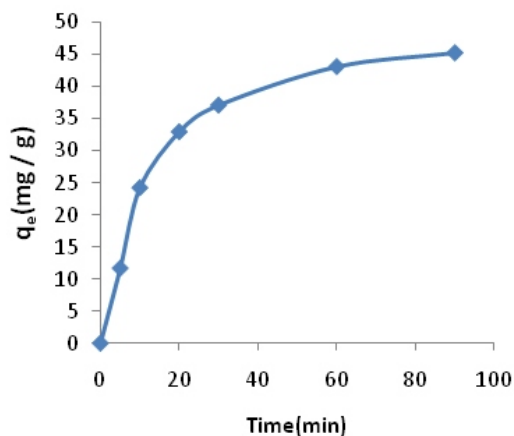


Figure 6: Effect of contact time on copper metal uptake at pH=4, dose=0.2g, concentration=100ppm using treated rice husk.

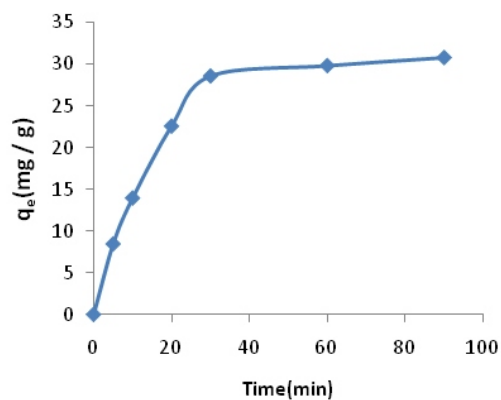


Figure 7: Effect of contact time on copper metal uptake at pH=5, dose=0.2g, concentration=100ppm using raw rice husk

3.3 Effect of initial metal concentration:

Figure (9-10) represents the relation of initial concentration of metal on the Cu (II) metal uptake using raw rice husk and treated rice husk with bio sorbent amount (0.2 gram) and temperature (30 ± 1) C and pH=4. Figure 9 depicted that the copper metal uptake was found maximum at an initial metal concentration of 100ppm for raw rice husk. While Figure 10 revealed the maximum removal of copper metal was found at near 90 ppm for acid treated form of rice husk.

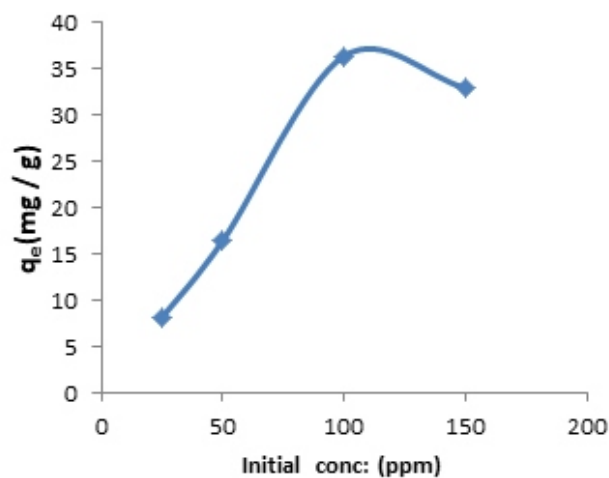


Figure 9: Effect of initial metal concentration on copper metal uptake at pH=4, dose=0.2g using raw rice husk

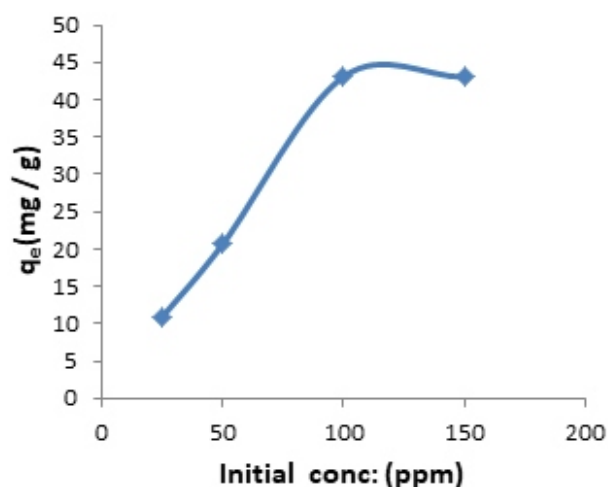


Figure 10: Effect of initial metal concentration on copper metal uptake at pH=4, dose=0.2g using treated rice husk

3.4 Effect of adsorbent dosage:

Figure (11-12) represents the effect of adsorbent dosage of bio sorbent on the Cu (II) metal uptake for raw and treated rice husk with initial metal concentration of 100ppm along with temperature (30±1) C and pH=4. Figure 11 showed that the copper metal uptake was decreases with the increase in the adsorbent dosage for raw rice husk. While on the other hand, Figure 12 revealed the maximum removal of copper metal at adsorbent dosage of 0.2 g.

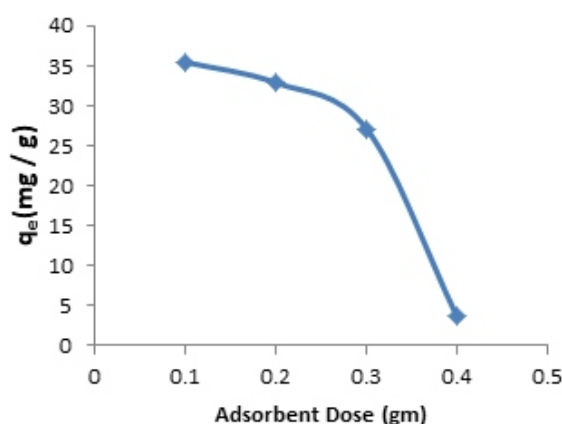


Figure 11: Effect of adsorbent dose on copper metal uptake at pH=4, dose=0.2g, concentration=100ppm using raw rice husk.

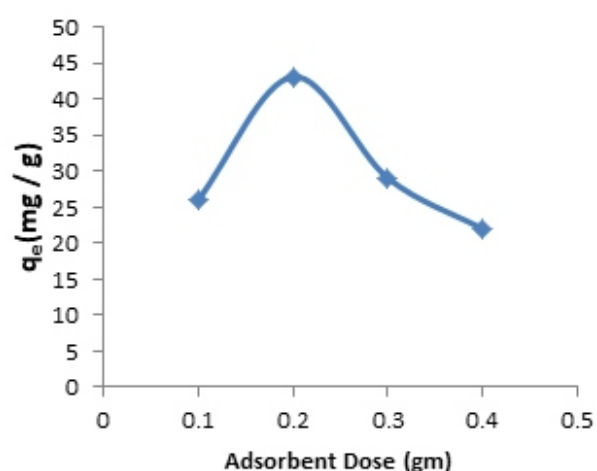


Figure 12: Effect of adsorbent dose on copper metal uptake at pH=4, dose=0.2g, concentration=100ppm using treated rice husk

3.5 Kinetic Modeling:

Kinetic model tells us about the mechanism of adsorption of metal [15-17]. Equation (2-3) represents the pseudo kinetic model of first order in its differential and integral form respectively [18]. Figure (13-14) revealed the first order kinetic model with R^2 values of 0.6568 and 0.6898 for raw and treated adsorbents respectively and these could not fit for both cases due to lesser values of R^2 .

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2)$$

$$\text{Log}(q_e - q_t) = \text{Log} q_e - \frac{k_1 t}{2.303} \quad (3)$$

Where

q_t = Uptake capacity (mg/g)

t = Time (min)

k_1 = Equilibrium rate constant (min^{-1})

q_e = Equilibrium capacity (mg/g)

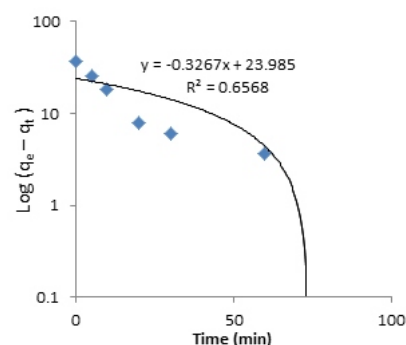


Figure 13: Pseudo first order kinetic model for raw rice husk.

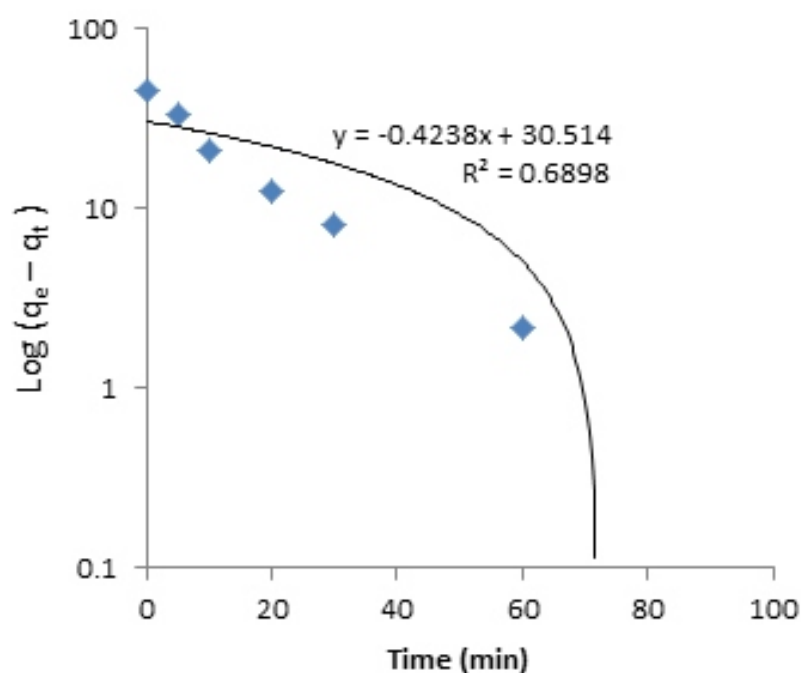


Figure 14: Pseudo first order kinetic model for treated rice husk.

On the other hand, equation (4-5) represents the pseudo kinetic model of second order in its differential and integral form respectively [18] Figure (15-16) represents the second order kinetics with R^2 (0.9840 and 0.9796) for raw and treated adsorbents respectively.

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

Where

q_t = Uptake capacity (mg/g)

t = Time (min)

k_1 = Equilibrium rate constant (g/mg.min)

Q_e = Equilibrium capacity (mg/g)

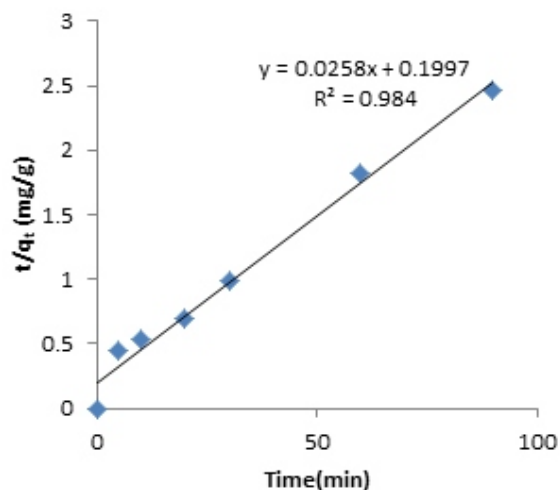


Figure 15: Pseudo second order kinetic model for raw rice husk.

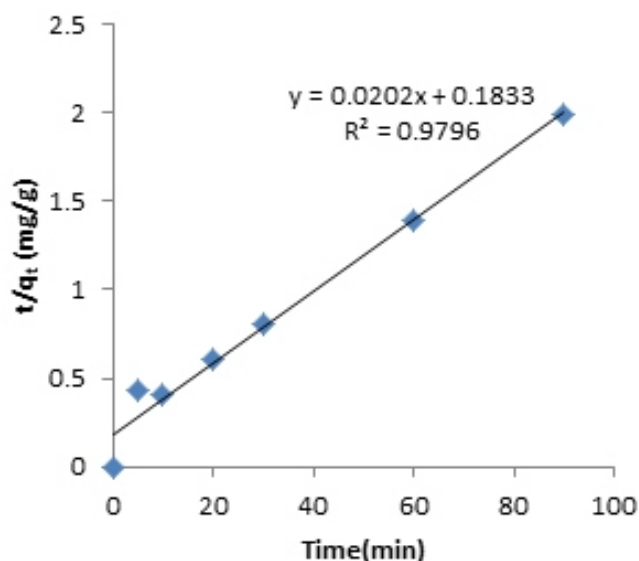


Figure 16: Pseudo second order kinetic model for treated rice husk.

Moval of Cu (II) from wastewater using rice husk as a bio sorbent in its raw and treated form. It is concluded that treated rice husk has more potential to remove copper metal than raw rice husk. Number of active sites, functional group enhancement and high ion-exchange properties were enhanced due to chemical treatment of rice husk. Equilibrium time for adsorption was achieved up to 90 mins. The adsorption was found maximum at pH=4 in both cases. Kinetic modelling revealed the pseudo model of second order was best fitted both for raw and treated form of rice husk. More comprehensive research should be done to find the most cost-effective method of rice husk treatment to improve its adsorption capacities.

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