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Adsorption isotherms and Kinetics for the Adsorption of Ni(II) onto Coconut Shell Based Activated Carbon

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Abstract

Adsorption isotherms and kinetics studies for the adsorption of Ni(II) have been investigated onto activated carbon prepared from Coconut shell by using phosphoric acid as an activating agent. The structure of the activated carbon has been characterized by SEM, XRD and FTIR.The optimum conditions for the adsorption of Ni(II) have been studied by varying the parameters such as solution pH, contact time of adsorbate and adsorbent and adsorbent dose. The optimum conditions of the adsorption have been found to be 5,180 minutes and 2g/L respectively. The Langmuir and Feundlich adsorption isotherms have been utilized to verify the adsorption performance. The Langmuir isotherm equation best described the experimental data with higher value of coefficient of correlation as compared to that of Freundlich isotherm showing a maximum uptake of 30.77 mg/g. The adsorption data have been analyzed by two mostly applied Kinetics models- Pseudo first order and Pseudo second order models. The represented adsorption kinetics model exhibited good agreement between the experimental data and the pseudo-second-order kinetic model. The results show the activated carbon prepared from waste material Coconut shell successfully adsorbed the heavy metal from wastewater.

Keywords: *Activated carbon, Coconut shell, Adsorption, Adsorption isotherms Adsorption kinetics, Nickel*

1. Introduction

Water contamination caused by heavy-metals released from nuclear power plant operations, aerospace industries, electrical contacts, alloys, pigments, electroplating, mining, metallurgical activities, printing, and the manufacture of paper, rubber, plastics, and batteries [1,2] is a global problem receiving worldwide attention. Nickel, one of toxic heavy metals, is released into water by anthropogenic activities such as manufacturing process of

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stainless steel, super alloys, metallic alloys, coins, batteries etc. and the presence of Ni(II) ions in drinking water in concentrations that exceed the permissible limit of 0.02 mg/L may cause adverse health disorders such as anemia, diarrhea, encephalopathy, hepatitis, lung and kidney damage, gastrointestinal distress, pulmonary fibrosis, renal edema, skin dermatitis, and central nervous system dysfunction [3,4,5].

Many conventional methods such as precipitation, coagulation, ion exchange, membrane separation, lime softening and adsorption have been applied to remediate Ni (II) from water. Among other removal methods adsorption technology has received much more attention because it is convenient and economical for the removal of trace quantities of heavy metals. Many recent researches utilized different inexpensive and locally abundantly available materials such as Lapsi seed stone [6], apricot stone [7], olive stone [8], date stone [9], rice husk [10], palm shell [11], coconut shell [12], peanut shell [13], corn stalk [14], peanut hull [15], hazelnut shell [16], saw dust [17] etc. for the preparation of activated carbons.

Ni (II) from aqueous media by adsorption. The isotherms of Ni (II) adsorption on the activated carbon have been studied by Langmuir and Freundlich adsorption isotherms. Similarly, the kinetics of Ni (II) adsorption onto the activated carbon has also been investigated through a pseudo-first-order [10, 11] and a pseudo-second-order [12, 13] model.

2.EXPERIMENTAL

2.1 Materials

The precursor used in this study is Coconut shell, the waste product of Coconut. The coconut shells were collected from the temples of Lalitpur, Kathmandu, Nepal. The coconut shells were first washed well tap water and then with distilled water. The shells were dried in an oven at 105 ° C for 24 hours and ground by Crusher and electric grinder. The particles were sieved to get the fraction of 300 µm and were mixed with 50% H3PO4 in the ratio of 1:1 and dehydrated at 100 ºC for 24 hours in a hot box oven and then carbonized at 400 º C for four hours in a horizontal tube furnace under flow of (75 ml / min) nitrogen. The activated carbon thus prepared was cooled at room temperature and was washed several times with warm distilled water. The materials were then dried at 110 ºC for 24 hours, cooled and sieved to obtain the particles of size106 µm and were used for adsorption study.

2.2 CHEMICALS AND EQUIPMENT

The chemicals and equipment used in the research works are of analytical grade (Merck and Qualigens Company). Test solutions of Ni (II) ions were prepared from nickel sulphate in distilled water. The pH value of the solution was measured by digital pH meter. The adsorption experiments were carried out by using Shaker (Digital VDRL Rotator RPM-S). The concentration of Ni (II) after adsorption onto the activated carbon was determined by Atomic absorption spectrophotometer (AAS–VARIAN-AA240FS). Solutions of 0.1 N NaOH and 0.1 N HCl were used to adjust pH. All the working solutions were prepared by diluting the stock solutions with distilled water.

2.3 ADSORPTION EXPERIMENTS

In order to study the adsorption of Ni (II) onto activated carbon batch mode of experiments were carried out in 50 ml Borosil stoppered conical flasks. The flasks were stirred well using Digital VDRL Rotator- RPM-S at 225 rpm for identifying time intervals. Each experiment was carried out by suspending 0.05 g of adsorbent in 25 ml adsorbate solution taken in the conical flasks under the optimum conditions set out for the experiment. The amount of Ni (II) ions adsorbed was determined by atomic absorption spectrophotometer (AAS –VARIAN-AA240FS). The equation given below has been used to calculate the amount of metal ions uptake [22].

$$q_e = \frac{(C_o - C_e) \times V}{W} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where Co and Ce = initial and equilibrium concentration of adsorbate solution.

V = the volume of solution in Liter and W is the mass of the adsorbent in gram.

The percentage removal of metal ions (Rem %) can be calculated by using following equation 2

$$\text{Rem}(\%) = \frac{(C_o - C_e) \times 100}{C_o} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

2.4 Scanning Electron Microscope (SEM)

The surface morphology of Activated carbon (AC) was analyzed by scanning electron microscope (SEM). For the SEM image the carbon tape was cut into small pieces and fixed on the disc. Then the upper layer of the disc was removed and very small amount of carbon was placed on the black carbon tape, well fixed just pressing on a clean silicon wafer. The images were recorded in U-8000 Hitachi Co.Ltd., Japan at 5KV.

2.5 X-ray diffraction

X-ray diffraction analysis was done to determine the degree of crystalline or amorphous nature of the activated carbon. Activated carbon was homogenously spread on the groove of the glass slide and mounted on Rigaku X-ray diffractometer RINT, Japan. The measurement was carried out at 40 kV and 40 mA with Cu-Kα radiation at room temperature for the scanning angle (2θ) range of 3 to 85 ° at scanning speed of 5°/min.

3.RESULTS AND DISCUSSION

3.1 Effect of pH

The percentage removal of removal of metal ions against pH is shown in Fig 1. pH is one of the major parameters and a great significance effect on rate of adsorption and the degree of ionization of adsorbate. The effect of pH on the adsorption of Ni(II) was investigated by varying pH from 2 to 7 because of precipitation of metallic hydroxides beyond pH 7. With the increase in the pH of the solution, the removal percentage of Ni(II) considerably increased. The percentage removal of the metal ions is found to be low at lower pH. This lower percentage removal of metal ions may be due to the fact that at lower pH there is higher concentration of hydrogen ions and that competes with metal ions. Due to this the percentage removal of metal ions from aqueous solution is low.

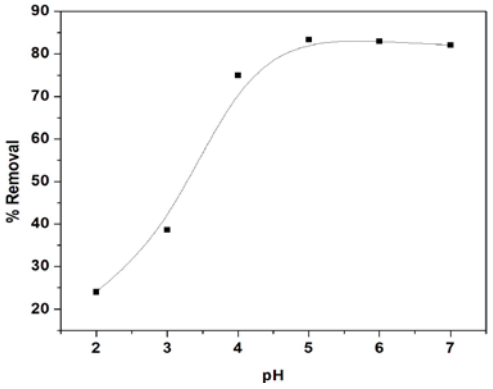


Figure 1. Effect of pH

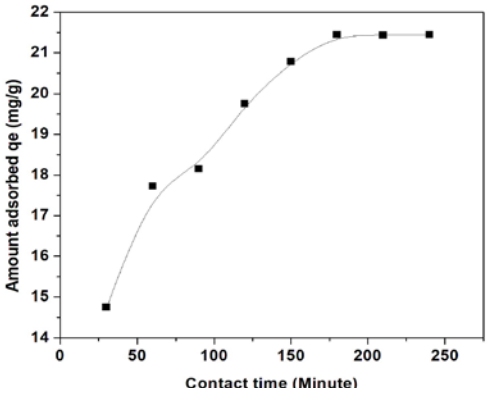


Figure 2. Effect of Contact time

3.2 Effect of Contact time

The plot of percentage removal of all the three metal ions onto activated carbon against time is shown in Fig. 2. The effect of contact time is another one of the effective parameters on adsorption Ni (II)).The results showed that the adsorption rate is found to be very fast initially up to 100 minutes and then after the time attains equilibrium value slowly.100 minutes onwards, the removal percentage increases gradually and attains plateau value at 180 minutes. At equilibrium all the active sites will be covered by the metal ions and no further adsorption of metal ions occurs. Thus equilibrium time for adsorption of Ni(II) ions was found to be180 minutes.

3.3 Effect of Adsorbent dose

Fig. 3 shows the effect of adsorbent dose on percentage removal of the metal ions. The percentage removal increased with increase in adsorbent dose from 0.5 g/L to 2 g/L. The increase in percentage removal of metal ions with the increase in adsorbent dose is obviously due to the availability of larger adsorption sites due to increase in adsorbent dose. The percentage removal of the heavy metal ions remains constant when adsorbent dose is more than 2g/L. Adsorbent dose of 2 g/ L has been observed as sufficient for effective removal of Ni(II) ions from the aqueous solutions.

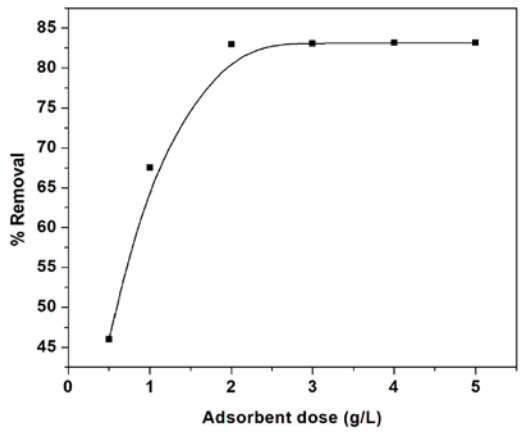


Figure 3. Effect of Adsorbent dose

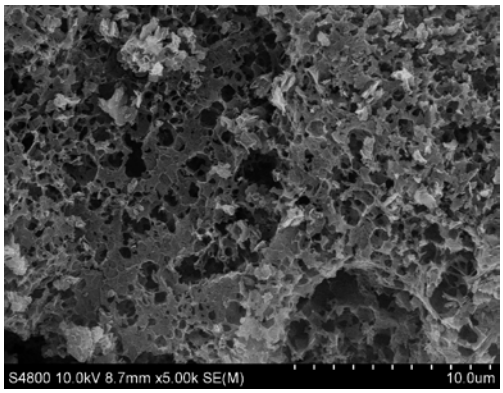
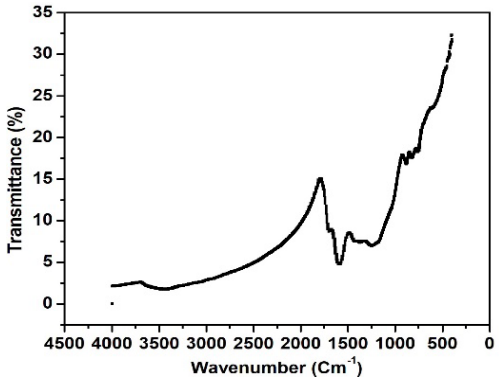
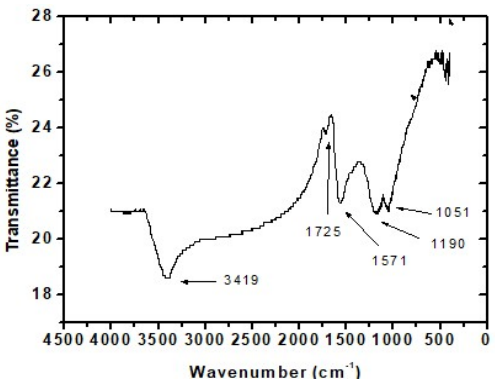


Figure 4. SEM of Activated carbon

3.4 Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR spectra of activated carbon as shown in Fig 6 shows a broad band at 3419 cm-1due to the presence of hydroxyl groups on the adsorbent surface. The band located at1725 cm-1is ascribed due to the stretching vibrations of carboxylic groups or conjugated carbonyl groups (C=O in carboxylic and lactone groups). Asymmetric stretching vibrations of ionic carboxylic groups (-COO -) appeared at 1571 cm−1.The functional groups play important role in the adsorption of the metal ions by donating electrons to heavy metal ions. These bands observed in the activated carbon are not seen in the carbon prepared without activating agent as shown in Fig 5.





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Figure 5. FTIR of Carbon without Activating agent

Figure 6. FTIR of Activated carbon

Asymmetric stretching vibrations of ionic carboxylic groups (-COO -) appeared at 1571 cm−1.The functional groups play important role in the adsorption of the metal ions by donating electrons to heavy metal ions. These bands observed in the activated carbon are not seen in the carbon prepared without activating agent as shown in Fig 5.

3.5 SEM (SCANNING ELECTRON MICROSCOPE)

Fig.4 shows SEM image of activated carbon. The SEM shows no. of pores with different diameters. The formation of porous structure may be due to the dehydrating effect of H3PO4. Phosphoric acid being a strong dehydrating agent removes oxygen and hydrogen from the waste material as water, and that promotes the development of porous structure

3.6 XRD (X-RAY DIFFRACTION)

Fig.5 exhibits XRD of activated carbon. XRD shows two broad diffraction peaks located near at 2θ = 25.5 o and 43o reflected from 002 and 001 planes. The appearance of broad peaks shows amorphous nature of the activated carbon which is the one of the good properties of activated carbon.

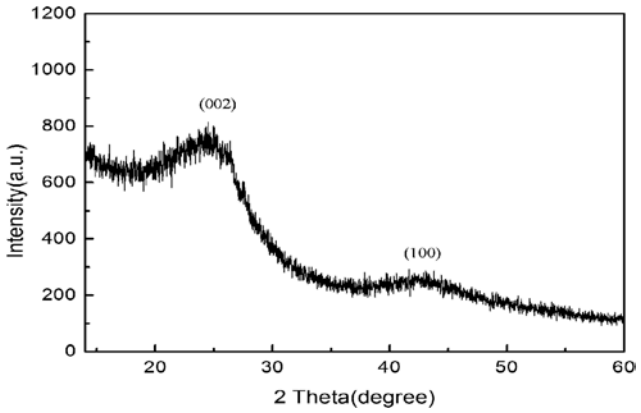


Figure 5. XRD of Activated carbon

3.7 ADSORPTION ISOTHERM

Adsorption isotherm is a curve obtained by plotting at constant temperature the quantity of adsorbate against the concentration of the substance in the original solution. Adsorption isotherms characterize the interaction behavior of gases or solute with solids. Langmuir and Freundlich isotherms are most commonly applied isotherms. Hence the adsorption data have been analyzed by Langmuir and Freundlich isotherm models.

3.7.1 LANGMUIR ISOTHERM

The Langmuir isotherm is used to characterize the monolayer adsorption, which is represented by the following linear form equation.

$$\frac{Ce}{qe} = \frac{1}{bqm} + \frac{Ce}{qm} \quad \text{.....(1)}$$

Where Ce is the equilibrium concentration of the adsorbate (mg/L) and qe is the amount of the adsorbate

adsorbed at equilibrium while qm is the monolayer adsorption capacity (mg g-1) and b is the Langmuir constant [23,24].

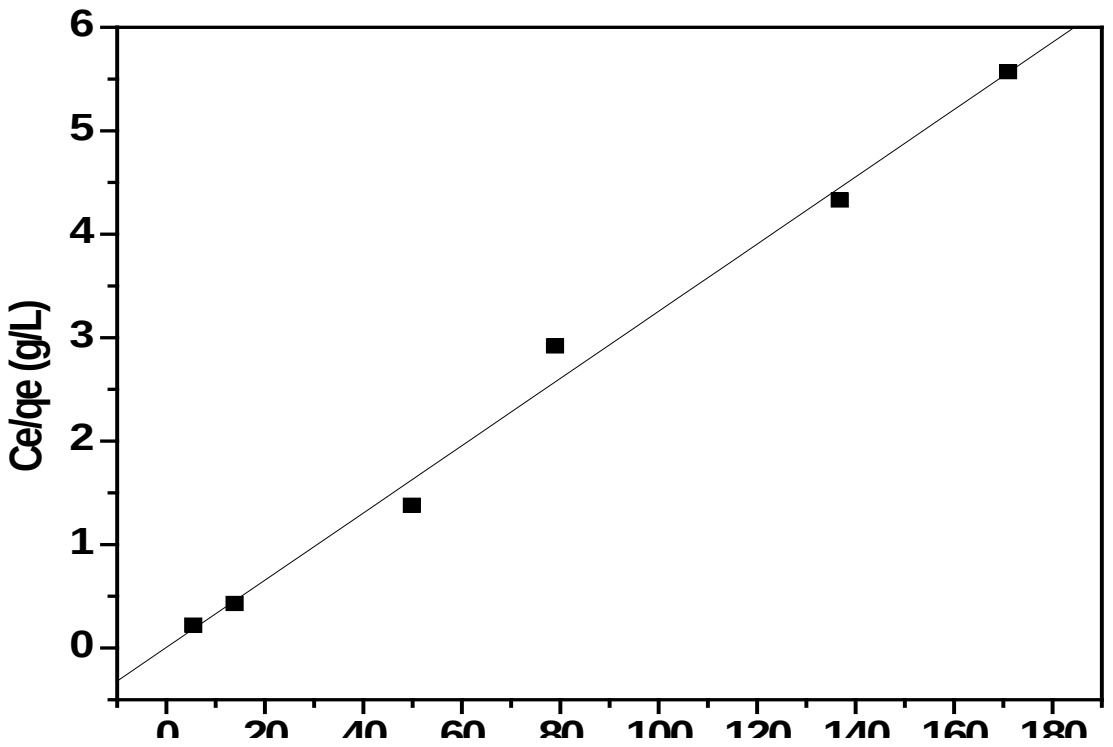


Figure 6. Langmuir adsorption isotherm

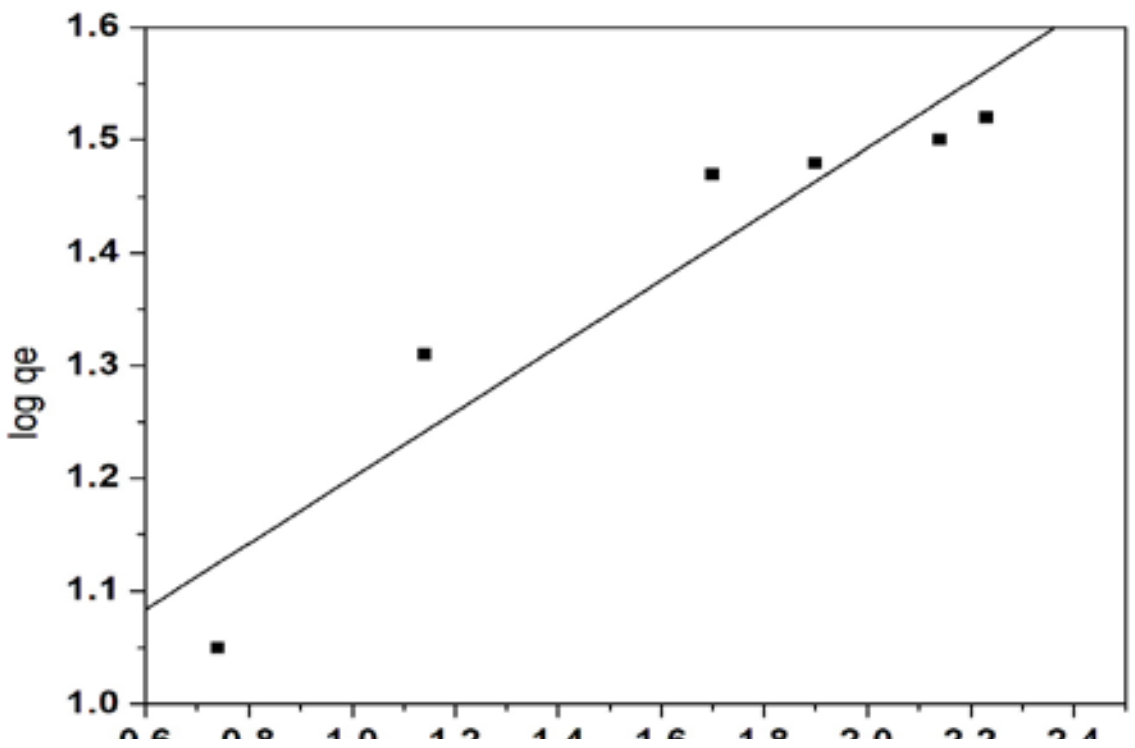


Figure 7. Freundlich adsorption isotherm

A

Fig. 6.

3.7.2 Freundlich isotherm

The Freundlich isotherm is generally applicable to the adsorption occurred on heterogeneous surface and can be applied to multilayer adsorption [25]. The isotherm was applied to determine adsorption intensity of adsorbent for the adsorbate. The linear form of Freundlich isotherm equation can be represented by following equation.

$$\log qe = \log Kf + \frac{1}{n} \log Ce \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where Kf and n are the Freundlich constants related to adsorption capacity and intensity. qe and Ce are the amount of adsorbate adsorbed and equilibrium concentration of the adsorbate respectively. The values of Kf and 1/n can be determined from intercept and slope of the plot of log qe versus log Ce as shown in Fig. 9. Langmiur and Freundlich parameters are shown in Table 1.

Table 1. Langmiur and Feundlich parameters

Heavy metal ions	Langmuir parameters		R^2	Freundlich parameters		R^2
	Q_{max} (mg/g)	b		K_f (mg/g)	n	
Ni (II)	30.77	0.00546	0.996	0.908	3.413	0.945

3.8 Adsorption kinetics

Adsorption kinetics is the measure of the adsorption uptake with respect to time at a constant pressure or concentration and is employed to measure the diffusion of adsorbate in the pores of activated carbon. Pseudo first order and second order kinetic models are the most commonly used kinetic models which have been applied to the adsorption kinetic data to analyze rate of adsorption.

3.8.1 Pseudo First Order

Pseudo first order kinetics was given by Legergren in 1898 [26]. The first order equation can be represented as follows.

$$\frac{dqt}{dt} = K_1(q_e - q_t) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Where qe is equilibrium concentration of the metal ions adsorbed (mg/g), qt is the amount of the metal ions adsorbed at time't' (mg/g) ,k1 is the pseudo –first order rate constant (Lmin-1).

On integration the equation (3) will take the form as follows:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}\,t \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots . (4)$$

The plot of value of log (qe - qt) against 't' as shown in Fig. 8 has been applied to test the validity of the kinetic model.

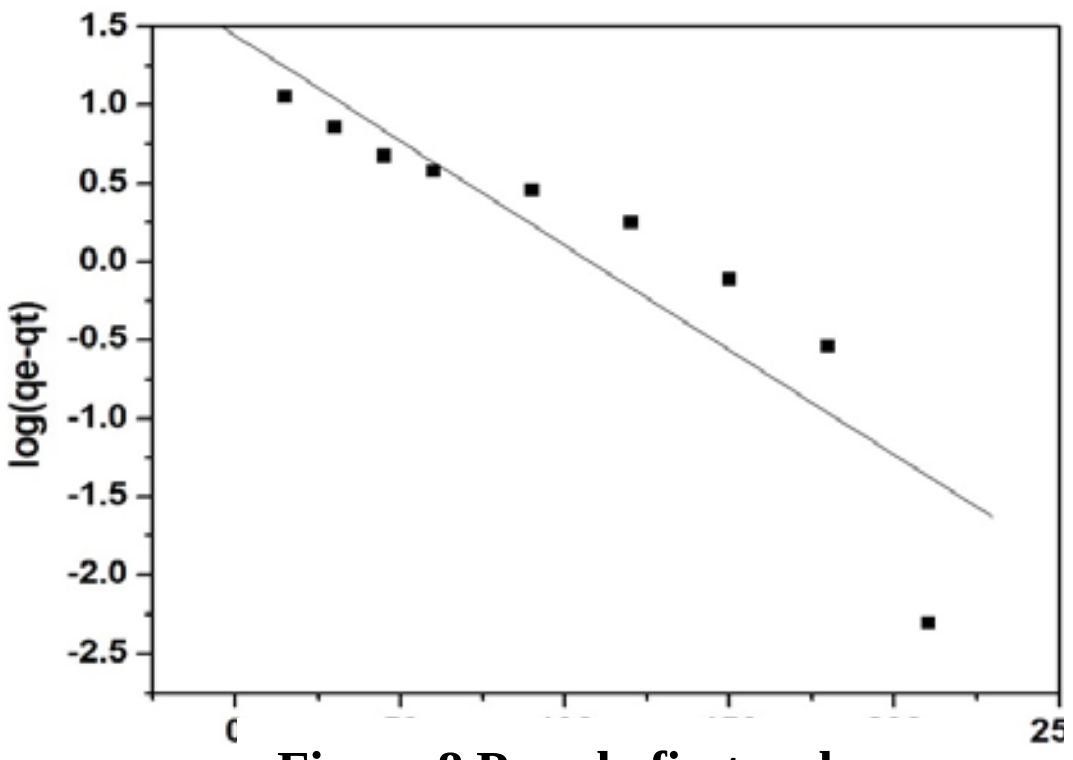


Figure.8 Pseudo first order

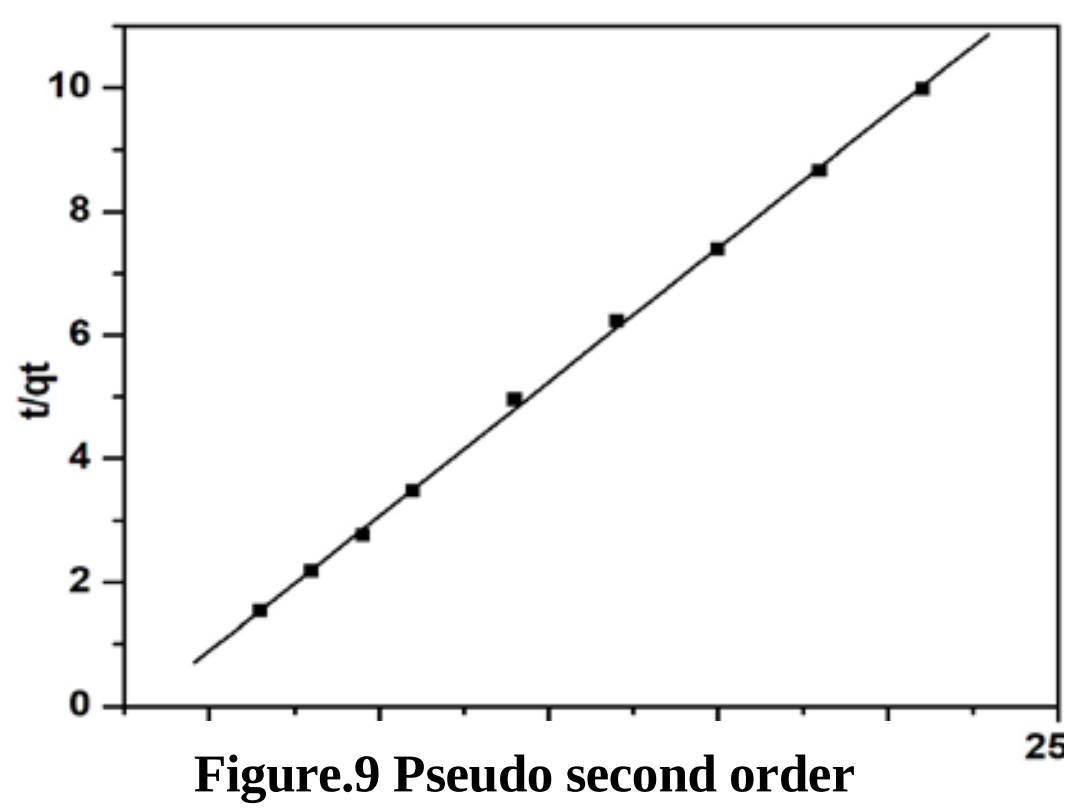


Figure.9 Pseudo second order

3.8.2 Pseudo Second Order

Pseudo second order model is also called Ho second order model. The rate equation of pseudo second order model is represented by following equation

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Where k2 = second order rate constant of adsorption (g mg -1 min -1).

The equation (7) after integration takes the form as follows.

$$\frac{1}{(qe - qt)} = \frac{1}{qe} + k_2\,t \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

By rearranging the equation (8) will be as follows

$$\frac{t}{qt} = \frac{1}{qe^2}\frac{1}{k_2} + \frac{t}{qe} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

The plot of value of 't/qt' against 't' as given in Fig. 9 has applied to test the validity of the kinetics.

The slopes and intercepts of the curves have been applied to calculate the kinetic parameters such as K1 and equilibrium adsorption capacity. The constants of the kinetics models are presented in Table 2.

Table 2 Parameters of Pseudo first and second order kinetics

Heavy metal ions	Pseudo First order			Pseudo Second order		
	qe(mg/g)	k_1(1/min)	R^2	qe(mg/g)	k_2(1/min)	R^2
Ni(II)	27.67	0.03079	0.8119	23.015	2.09856×10^{-3}	0.9993

4. CONCLUSION

The present study explored the investigation of adsorption isotherms and adsorption kinetic for the adsorption of Ni (II) using the activated carbon prepared from Coconut shell. The adsorption of the metal ions has been found to be dependent on pH and the maximum adsorption has been observed at pH 5. Optimum contact time and adsorbent dose have been found to be 180 minutes and 2 g/L respectively. The SEM of the activated carbon has

shown the pores of different diameters. XRD analysis has shown the appearance of broad peaks. Surface functional groups on the surface of the activated carbon has been analyzed by FTIR and the analysis shows the presence of surface functional groups such as carboxyl, phenols and lactones. The adsorption data was best described by Langmuir adsorption isotherm with higher correlation coefficient (R2=0.996) than that of Freundlich isotherm (R2=0.945) showing a maximum adsorption uptake of 30.77 mg/g. Analysis of adsorption kinetic data has shown that the Pseudo second- order model was found to describe adsorption much better with high correlations coefficient (R2= 0.999) than that of Pseudo first- order model (R2= 0.811). The results exhibit that Coconut shell based activated carbon can be used as an efficient adsorbent for removal of cadmium ions from aqueous solution.

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