

## Removal of Ni (II) ions from aqueous solution using chitosan and activated carbon: isotherms and kinetics

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### Abstract

The present study deals with adsorption of Ni (II) ions from aqueous solution using chitosan (CHI) and activated carbon (ACC) as adsorbents. Several parameters such as pH, contact time, adsorbent dosage, concentration of adsorbate and radiation dose were varied to achieve an optimized adsorption of the metal ions. It was concluded that maximum removal of Ni (II) ions (92.2%) using CHI was observed at pH 3, dosage 1 g and contact time 240 min. Maximum removal of Ni (II) ions (82.3%) was achieved using ACC at pH 2, dosage 2.5 g for 120 min. The percentage removal of Ni (II) ions increases slightly after irradiation with Co-60. The adsorbents were characterized before and after irradiation and adsorption using FTIR and SEM techniques which clearly indicated the occurrence of adsorption of metal ions. Harkin-Jura and Jovanovic isotherms study indicated multilayer adsorption. The adsorption process follows pseudo-second-order kinetics.

### Introduction

In the modern civilization and progressive industrialization, the level of nickel pollution is intensifying in water bodies like surface water, soil water, and shallow groundwater. Wastewater from electroplating and battery production industries are common sources as waste for nickel. Some other sources are metal mining, vehicle emission, smelting, fossil fuel combustion, domestic, municipal and industrial waste disposal, fertilizer applications and organic fertilizers<sup>1</sup>.

Nickel shows many adverse effects on human beings, for instance, it is responsible for most common skin allergies called dermatitis, cardiovascular and kidney diseases, lung fibrosis and lung and upper respiratory cancer<sup>2</sup>. Nickel is considered as the most hazardous element to the environment due to its toxicity and carcinogenicity. Generally, the levels of Ni (II) ions in air is 5-40 ng/m<sup>3</sup>, in agricultural soils is 3-1000 mg/kg and less than 2 µg/L in fresh water and oceans. (WHO). It has become essential to explore all its sources so that new efficient technologies can be developed for decreasing its concentration. Some of the existing methods which are routinely used for removal of nickel ions are ion-exchange, precipitation, reverse-osmosis and more. The reason for not choosing these techniques are the high cost and foul smell of loaded resins, expensive chemicals and membranes for long-term investment, respectively. Adsorption is found to be the cost-effective technique compared to other ones and this is the reason for choosing it for the study of removal of Ni (II) ions. Nowadays, more and more importance are being given on research into materials suitable for cheap and efficient removal of nickel ions from the environment. In addition, there is high availability of the adsorbents. Few of the adsorbents are organic, mineral sources biomass<sup>3</sup>, agricultural waste or synthetically developed material are being used for removal of metallic ions.

This research is devoted to the study of adsorption of nickel ions on chitosan and activated carbon. CHI and ACC are comparatively cheaper and thus they were selected for this study. Chitosan is obtained from chitin by enzymatic or chemical deacetylation of chitin (removal of -COCH<sub>3</sub> group). Chitin is a biopolymer of the exoskeleton of living organisms such as shrimps, crabs, lobsters, beetles and in the cell walls of certain fungi. Therefore, β-D glucosamine is the monomer unit present in chitosan which is soluble in dilute acids and hence helps in enhancing the complexation with metals compared to chitin<sup>4-6</sup>. Chitosan is in a form of a white powder and is commercially available.

Globally, adsorbent activated carbon has been widely used in wastewater treatment. The process for production of activated carbon is to dehydrate, carbonize and activate raw materials. The starting material is dehydrated and carbonized by slowly heating it in the absence of air. During the step of carbonization, organic material is converted to primary carbon forming a mixture of ash, tars, amorphous carbon and crystalline carbon where some decomposition products or tars are deposited in the pores, which are later removed during the activation step. The current research gives an overview on adsorption of Ni (II) ions from aqueous solution using chitosan (CHI) and activated carbon (ACC) as adsorbents. In literature, there exists more data on types of modifications of CHI and ACC while only few work has been done on the

modification using gamma irradiation. The adsorbents were irradiated with Co-60 gamma chamber 900A in order to examine any structural change responsible for increased adsorption. The effect of pH, contact time, adsorbent dosage and initial concentration of Ni (II) ions on the process of adsorption were monitored. Adsorbents were characterized using FTIR and SEM techniques. Isotherm and kinetic studies were performed on the obtained data.

## 2. Experimental

### 2.1. Adsorbate and adsorbent material

AR Grade nickel sulphate ( $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ ) was purchased from Sisco Research Laboratories Pvt. Ltd. Chitosan of Otto brand was purchased from S. D. Fine-Chem Ltd., India. It is a fine powder of off-white color. Activated charcoal was supplied by S. D. Fine-Chem Ltd. It is in the form of black color powder. The commercially obtained CHI and ACC were irradiated in Co-60 gamma chamber 900A for three different doses 1, 5 and 9 kGy with a dose rate of 2.0838 Gy/min, estimated by Fricke Dosimetry.

### 2.2. Batch adsorption process

Adsorption was performed by batch adsorption process at room temperature. In this process, aliquot of 25 mL of 2000 ppm of Ni (II) ion solution was placed in a round bottom flask at the pre-determined pH of the solution. An initial dosage of 1.0 g of adsorbent was added to the flask and was agitated on magnetic stirrer for 1 h at room temperature. The solution was then centrifuged and the supernatant solution was analysed for Ni (II) ions concentration using UV-Vis spectrophotometer. The experiment of the adsorption batch were repeated three times and mean values were presented.

The amount of nickel ions adsorbed by the adsorbent is given by equation (1)

$$q = \frac{C_0 - C}{m} \times V \quad (1)$$

where  $q$  is the amount of metallic ion adsorbed by the adsorbent (mg/g);  $C_0$  is the initial concentration of Ni (II) ions in contact with the adsorbent (mg/L),  $C$  is the equilibrium concentration of Ni (II) ions in aqueous solution (mg/L) after batch adsorption.  $V$  is the volume of Ni(II) ions solution (L) in contact with the adsorbent and  $m$  is the mass (g) of adsorbent.

The various parameters *viz* pH, contact time, dosage with initial concentration of metal ion were optimized for achieving maximum removal of Ni (II) ions.

### 2.3. Irradiation of adsorbents

The adsorbents (ICHI and IACC) were irradiated using a Cobalt 60 Gamma Chamber 900A. The  $\gamma$  radiation dose was measured using Fricke Dosimeter. The effect of radiation dose (1, 5 and 9 kGy) on removal of Ni (II) ions was studied to examine the changes in the structure of CHI and ACC induced by  $\gamma$ -radiation which may increase the percentage removal.

### 2.4. Characterization of adsorbent

FTIR spectra of virgin adsorbent, irradiated virgin adsorbent and loaded irradiated adsorbent obtained by using FTIR spectrophotometer (Shimadzu 8400) in the range 4000-400  $\text{cm}^{-1}$  having KBr disk as reference. were analyzed for their vibrational frequency (transmittance) changes in the functional groups of the adsorbents.

Scanning electron microscope (SEM - JEOL, JSM 6360 LV) was used to investigate the texture and porosity of the adsorbents before and after adsorption at the optimized conditions. A thin layer of platinum was sputter-coated on the samples for charge dissipation during SEM imaging. The sputter coater (Eiko IB-5 Sputter Coater) was operated in an argon atmosphere. The coated samples were then transferred to the SEM specimen chamber and observed at an accelerating voltage of 20 kV.

## 3. Results and discussion

### 3.1. Effect of pH

One of the most significant aspects in adsorption studies is effect of pH of the medium. The percentage removal of Ni (II) ions with pH is shown in Fig. 1. The range of pH was varied from 2 to 7. In case of CHI, the adsorption was found to be almost constant from pH 2 to 7 and a slight increase at pH 3. This increase could be by the fact that total number of negative groups available for binding of metal ions increased and therefore competition between proton and metal ions became less pronounced and thus indicated higher adsorption. pH 2 shows a higher percentage removal of the metal ions onto ACC. The removal was found to be almost constant from pH 3 to 7. For further studies, pH 3 for CHI and pH 2 for ACC were used as optimized pH.

### 3.2 Effect of contact time

The effect of contact time for adsorption of Ni (II) ions was studied by varying the agitating time from 60 to 240 min (Fig. 2). As the contact between adsorbate and adsorbent increases, efficiency of removal also increases in the case of CHI. While in case of ACC, the percentage removal was almost constant (slightly higher at 120 min). After the adsorbed material form one molecule/ ion thick layer, the capacity of adsorbent gets exhausted and the metal adsorbed rate is controlled by the rate at which the adsorbate is transported from the exterior to interior sites of the adsorbent particle. In further study, 240 and 120 min are taken as equilibrium time for CHI and ACC, respectively.

### 3.3 Effect of adsorbent dosage

The effect of adsorbent dosage was studied by varying its amount from 1 to 2.5 g (Fig. 3). Adsorbent dosage seems to have great effect on adsorption process. It was found that 1 g of CHI was sufficient to achieve maximum removal of Ni (II) ions (92.2%) whereas 2.5 g of ACC shows maximum percentage removal of Ni (II) ions (82.3%). The phenomenon of increase in percentage removal of Ni (II) ions with increase in adsorbent dosage of adsorbent ascribed to the availability of surface area for the solute to adsorb.

### 3.4 Effect of concentration

The initial concentration of Ni (II) ions was varied between 400 to 2000 mg/ L at 25 °C at optimum pH, adsorbent mass and contact time. The percentage removal of Ni (II) ions with initial concentration remains almost unchanged for CHI and found to decrease for ACC (Fig. 4). The higher initial metal ion concentration provides a strong driving force between the liquid/ solid phases as reported by Mustapha et. al<sup>7</sup>. At lower concentrations, the ratio of available binding sites to the initial metal ion concentration appeared to be larger, while at higher concentrations overloaded adsorption sites could have been formed. This behavior is attributed to less availability of surface-active sites.

### 3.5 Effect of radiation dose

The percentage removal of Ni (II) ions using ICHI and IACC at optimized condition is illustrated in Fig. 5. It was found that in case of irradiated CHI there was slight increase of 0.2 % at 9 kGy dose and 3.38 % at 1 kGy for irradiated ACC in removal of Ni (II) ions. This is attributed to the insignificant changes in terms of structure for better adsorption of adsorbate

ions on CHI and ACC. Similar results were observed for irradiated bentonites studied for adsorption properties as reported by M. Galamboš *et. al*<sup>8</sup>.

### 3.6 Characterization studies

The spectra of the adsorbents were obtained by using FTIR. Fig. 6. shows that the adsorption peak for CHI is nearly at 2400 cm<sup>-1</sup> which is responsible for combinations of C-H and C-C bonds for binding of Ni (II) ions. Few peaks are observed in the range of 1700 – 1500 cm<sup>-1</sup>. This is attributed to the presence of double bond of C=C, C-O, and C-N of bond order 2, which vibrates to higher frequencies. For ACC, peaks around 2400 and 1500 cm<sup>-1</sup> are responsible for alkyl groups and more specifically methyl group (-CH<sub>3</sub>) (Fig. 7). Further examination of Fig. 6 and 7 shows slight change in peak intensity which indicates only slight increase in adsorption.

Morphological characteristics of adsorbents were studied with SEM and the corresponding micrographs are shown in Fig. 8 and 9. SEM micrograph (Fig. 8 (a)) of virgin CHI possesses irregular cavities of variable sizes from small to large. The surface areas seem highly porous with mean surface area of 6194 μm<sup>2</sup> and with mean length of 40.6 μm (measured by ImageJ software). These pores seem occupied after adsorption of Ni (II) ions on CH surface as shown in Fig. 8 (b) as no empty cavities are observed. Micrograph of virgin ACC (Fig. 9 (a)) shows homogeneous tiny size pores of mean surface area of 20.92 μm<sup>2</sup> with mean length of 5.65 μm. As the pores seem tiny, adsorption found to be occurred on the surface of ACC (layers) (Fig. 9(b)).

### 3.7 Adsorption Isotherms

An adsorption isotherm is the relationship between the adsorbate in the liquid phase and the adsorbate adsorbed on the surface of the adsorbent at equilibrium at constant temperature. The equilibrium adsorption is essential in designing the adsorption systems. For solid-liquid systems, several isotherms are available in the literature.

#### Langmuir isotherm

Langmuir isotherm represents equilibrium distribution of metal ions between solid and liquid phases. The linear Langmuir isotherm is expressed as follows<sup>9</sup>.

$$\frac{1}{q_e} = \frac{1}{ab} \times \frac{1}{C_e} + \frac{1}{b} \quad (2)$$

where  $q_e$  is the amount of adsorbate at equilibrium (mg/g);  $a$ , Langmuir adsorption constant related to the affinity of the binding sites (mL/g);  $b$ , the adsorption capacity (mg/g);  $C_e$ , the equilibrium concentration of Ni (II) ions in the solution after adsorption (mg/L). The essential characteristics of Langmuir isotherm can be expressed in terms of dimensionless separation factor,  $R_L$  which is defined as equation (3)<sup>9</sup>.

$$R_L = \frac{1}{1+aC_0} \quad (3)$$

where  $C_0$  is the initial concentration (mg/L). The value of  $R_L$  indicates the shape of isotherms to be either unfavourable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favourable ( $0 < R_L < 1$ ) or irreversible ( $R_L = 0$ ).

It was observed that CHI follows Langmuir isotherm (Fig. 10). The constant,  $b$  (67.11 mg/g) (Table 1) indicates the good relation with the variation of suitable area and porosity of CHI which implies that large surface area and pore volume resulted in moderate adsorption capacity. The constant,  $R_L$  (1) (Table 1) indicated that the adsorption of Ni (II) ions on CHI is favorable<sup>9</sup>. It was observed that the adsorption of Ni (II) ions on ACC did not fit Langmuir isotherm and thus was not shown in article.

### Harkin-Jura Isotherm

The model assumes the possibility of multilayer adsorption on the surface of adsorbents having heterogeneous pore distribution<sup>10</sup>. It is expressed as follows:

$$\frac{1}{q_e^2} = \frac{B}{A} - \left(\frac{1}{A}\right) \log C_e \quad (4)$$

where  $B$  and  $A$  are Harkin-Jura constants which can be obtained from the plot  $1/q_e^2$  versus  $\log C_e$ . It was observed from Fig. 11 and Table 1 that the adsorption of Ni (II) ions on CHI fit well the Harkin-Jura model. It can then be concluded that the adsorption of Ni (II) ions is a multilayer adsorption applicable to heterogeneous surfaces of CHI. Similar results were reported by Foo and Hameed<sup>11</sup> for adsorptive removal of reactive black 5 from wastewater using bentonite clay.

### Jovanovic Isotherm

The model is based on the assumptions of Langmuir model and in addition, it explains the possibility of some mechanical contacts between adsorbate and adsorbent<sup>11</sup>. The linear form of Jovanovic isotherm is expressed as follows<sup>12</sup>

$$\ln q_e = -K_J C_e + \ln q_{max} \quad (5)$$

Where  $q_e$  is the amount of Ni (II) ions adsorbed by the adsorbents at equilibrium (mg/g),  $q_{max}$  is maximum uptake of adsorbate and  $K_J$  is Jonanovic constant obtained from plot  $\ln q_e$  versus  $C_e$ .

The adsorption of Ni (II) ions on CHI and ACC were tested Jonanovic. It was found from the correlation coefficients (0.9228) that adsorption of Ni (II) ions on ACC followed Jovanovic isotherm better than the others (Fig. 12 and Table 1).

### 3.8 Adsorption kinetics

Adsorption kinetics was studied by using pseudo-first-order and pseudo-second-order kinetics. It was observed that the adsorption of Ni (II) ions did not follow pseudo-first-order kinetics.

#### Pseudo-second-order:

The pseudo-second-order model is represented as follows<sup>13</sup>

$$\frac{t}{q_t} = \frac{1}{(K_2 q_e^2)} + \frac{t}{q_e} \quad (6)$$

where  $K_2$  is pseudo-second-order rate coefficient (g/mg/min) and  $q_e^2$  (mg/g) is the maximum adsorption capacity. A graph (Fig. 13 and Fig. 14) of  $t/q_t$  versus  $t$  is plotted from which the intercept and slope can be determined and they are presented in Table 2.

The adsorption of Ni (II) ions using both the adsorbents CHI and ACC obeys pseudo-second-order model (0.993 and 0.9074, respectively). This concludes that the overall rate of Ni (II) ion adsorption process seemed to be controlled by the chemical process through sharing of electrons or by covalent forces through exchange of electrons between adsorbent and adsorbate.

### Conclusions

The current research showed the effectiveness of both adsorbents CHI and ACC in the removal of Ni (II) ions from aqueous solution. The study of adsorption of Ni (II) ions concluded that the maximum removal of metal ions (92.2 %) was observed at pH 3 with 1 g of CHI in contact for 240 min. 82.3 % removal of Ni (II) ions was achieved using pH 2 with 2.5 g of ACC in contact 120 min with the adsorbate. The percentage removal of Ni (II) ions increases slightly after irradiation with Co-60. FTIR and SEM studies clearly indicated the occurrence of adsorption of metal ion. Langmuir, Harkin-Jura and Jovanovic isotherms study indicated



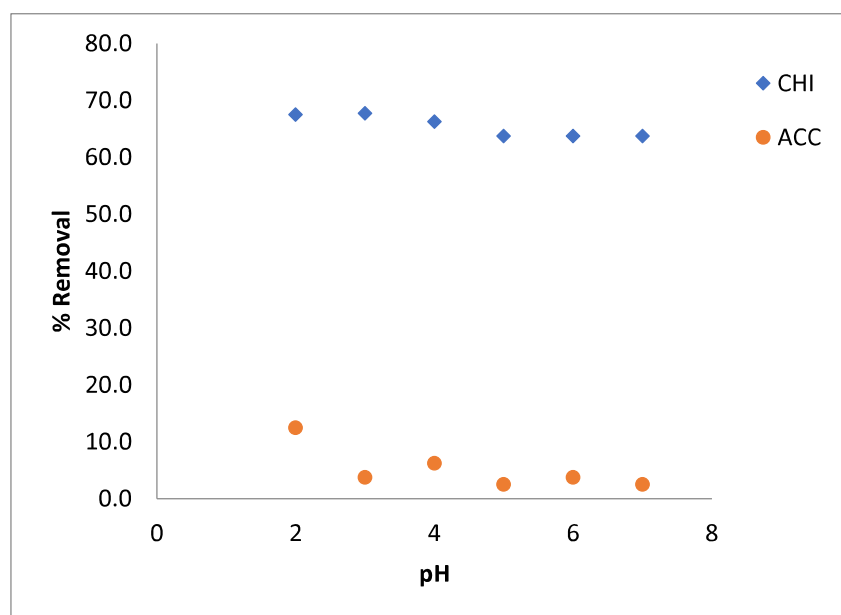
multilayer adsorption with adsorption capacity of CHI is found to be 67.11 mg/g for Ni (II) ions. Both the adsorption processes follow pseudo-second-order kinetics and the adsorption capacity for ACC was found to be quite less for Ni (II) ions (1.05 mg/g). It may be concluded that CHI may be used as a potential adsorbent for adsorption of Ni (II) ions (adsorption capacity 67.1 mg/g) compared to synthesized adsorbent developed with plant extract<sup>15</sup> (MWCNTs-KIAgNPs: 40.1 mg/g). However, ACC (1.0 mg/g) seems to have least (and closely to 4.0 mg/g-beech sawdust) adsorption capacity as compared to other adsorbents.

This work concludes that CHI can be used as a potential adsorbent compared to ACC for effective removal of Ni(II) ions and can also be applied to industrial effluents for treatment.

### Acknowledgement

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### Figures:



**Fig. 1.** Effect of pH of solution on adsorption of Ni (II) ions using CHI and ACC

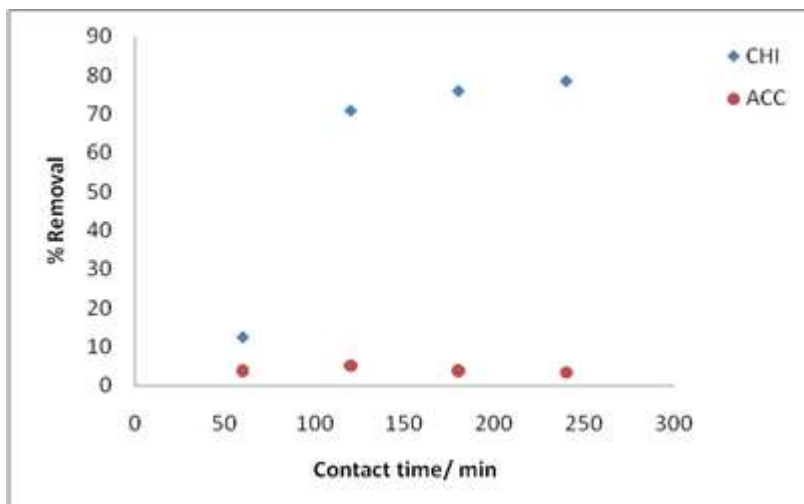


Fig. 2. Effect of contact time on adsorption of Ni (II) ions using CHI and ACC

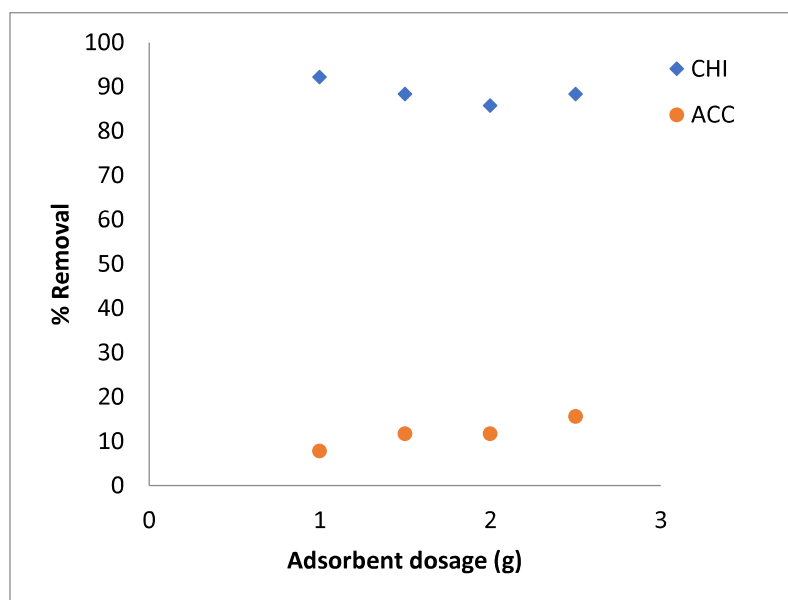


Fig. 3. Effect of adsorbent dosage on adsorption of Ni (II) ions using CHI and ACC

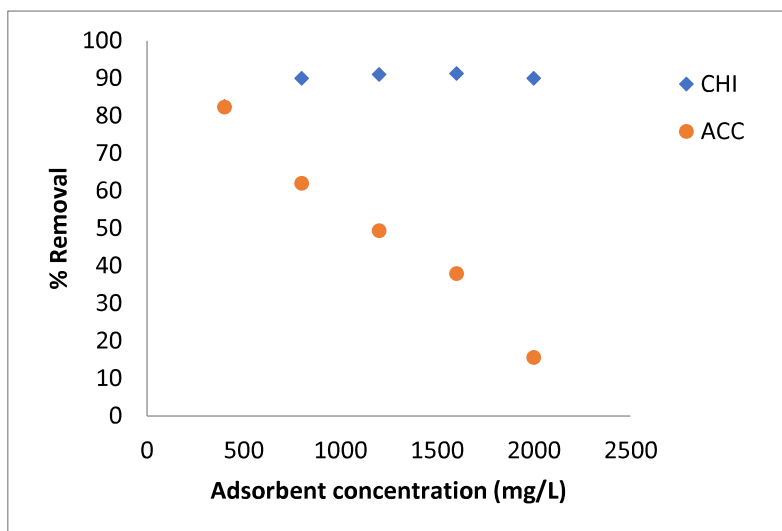


Fig. 4. Effect of adsorbate concentration on adsorption of Ni (II) ions using CHI and ACC

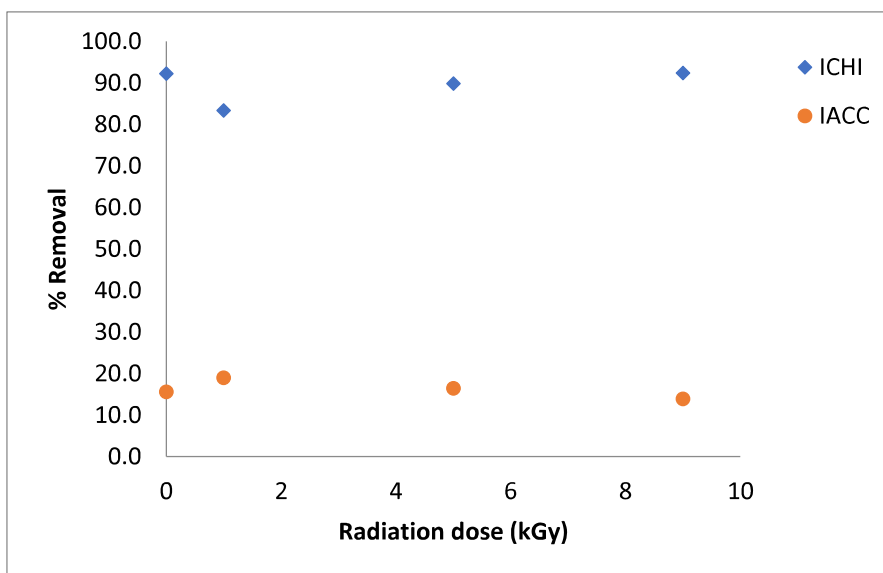


Fig. 5. Effect of radiation dose on removal of Ni (II) ions using ICHI and IACC

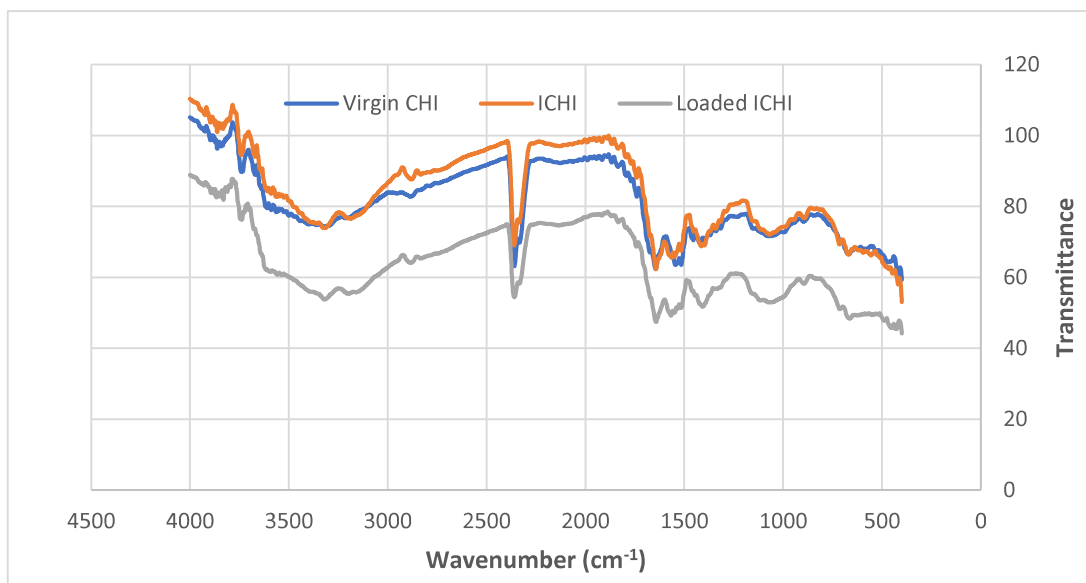


Fig. 6. FTIR spectra for CHI

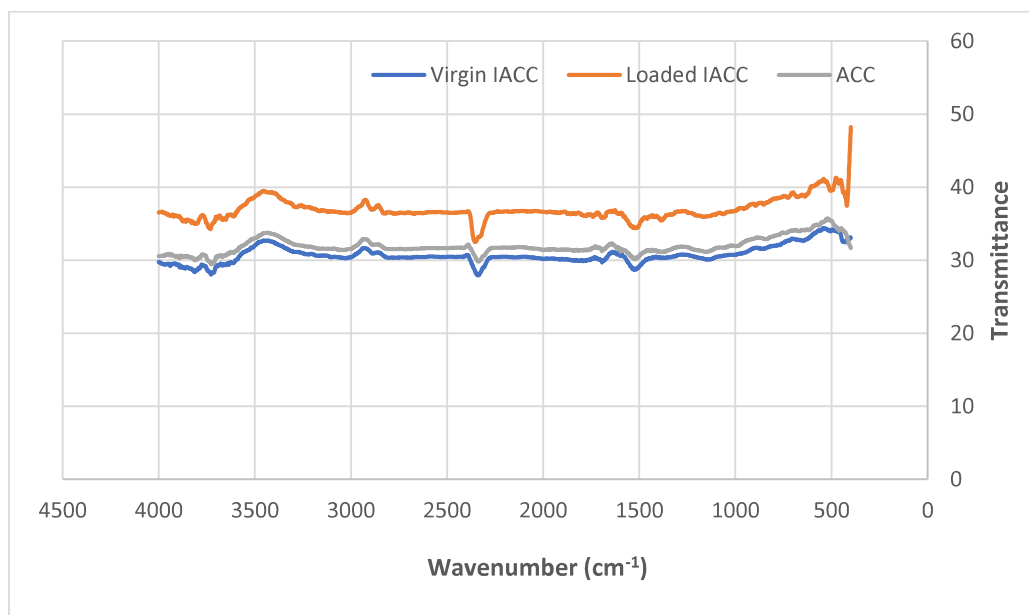
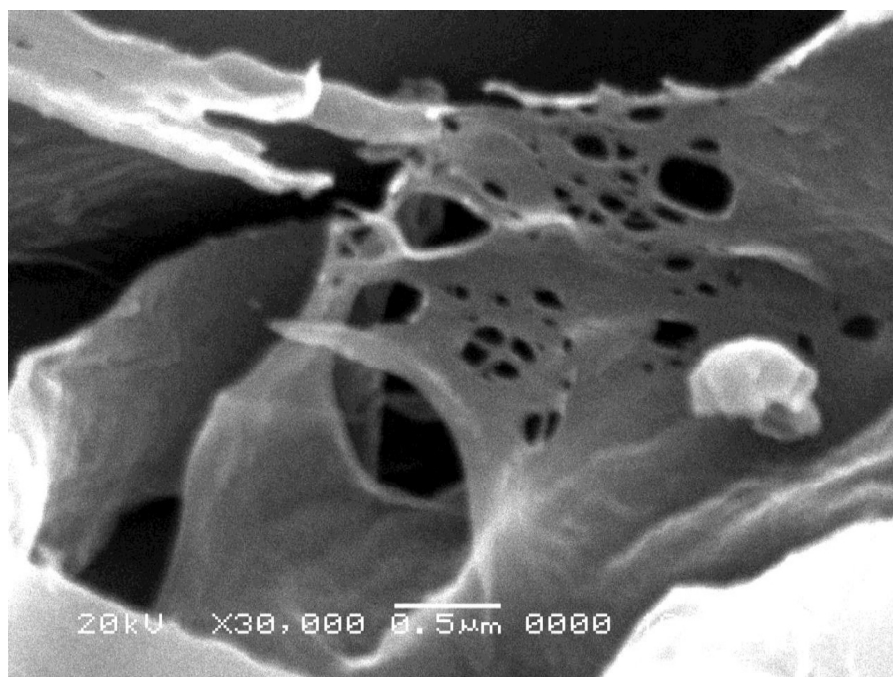
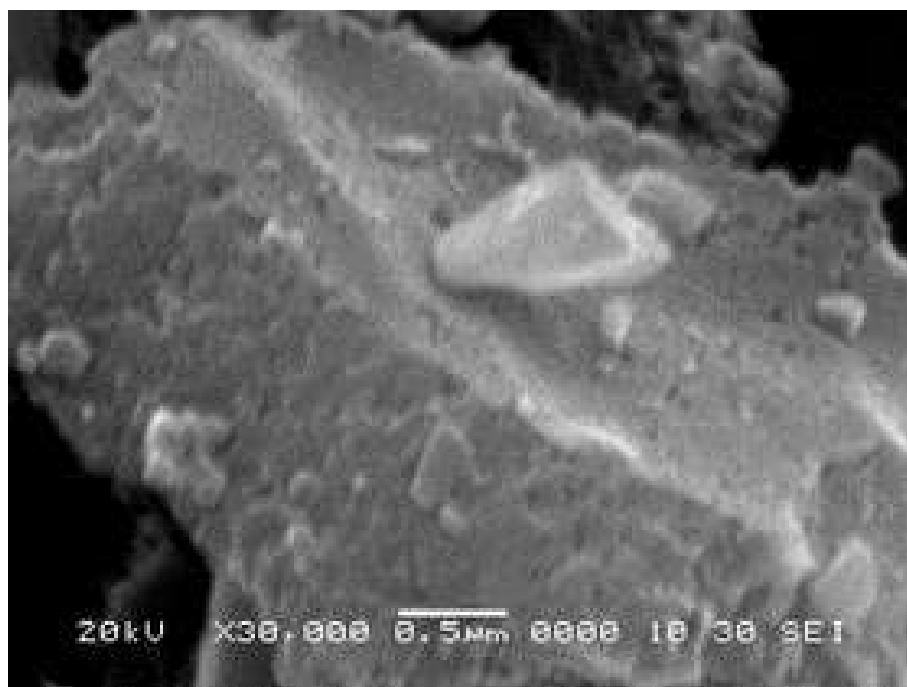


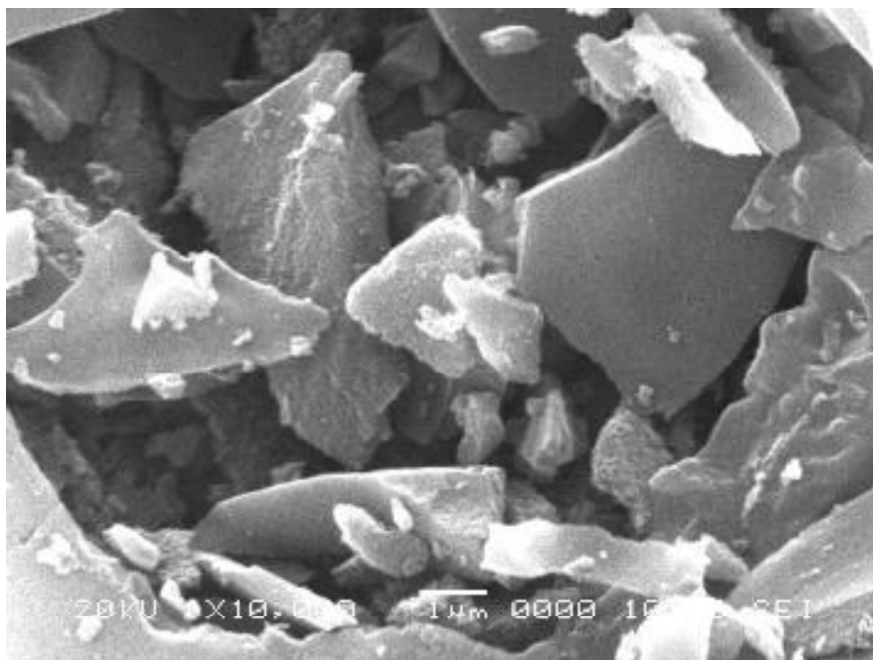
Fig. 7. FTIR spectra for ACC



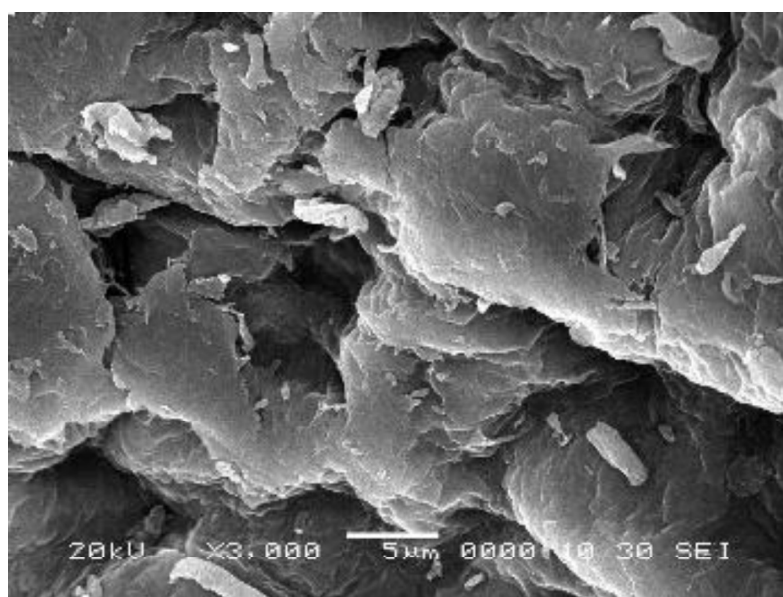
**Fig. 8.** SEM micrograph of (a). virgin CHI



**Fig. 8 (b)** Ni (II) loaded CHI



**Fig. 9.** SEM micrograph of (a) virgin ACC



**Fig. 9.** (b) Ni (II) loaded ACC

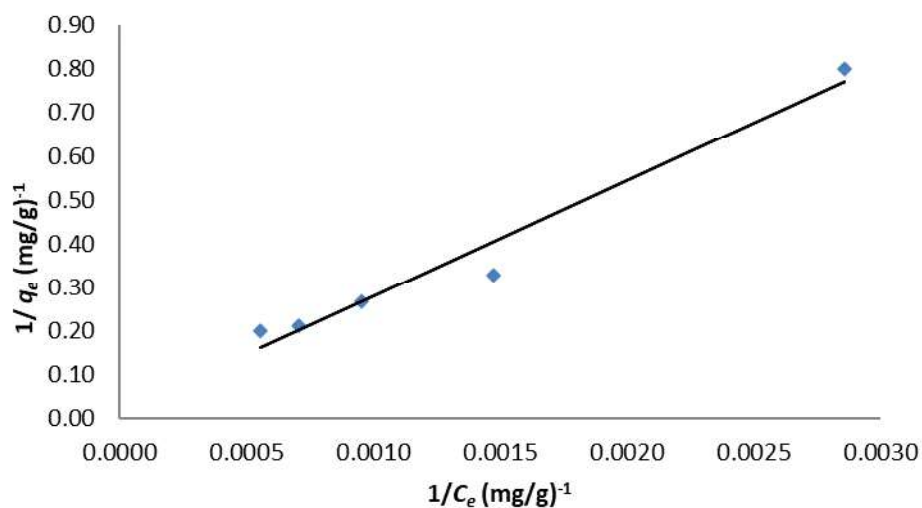


Fig. 10. Langmuir isotherm for adsorption CHI

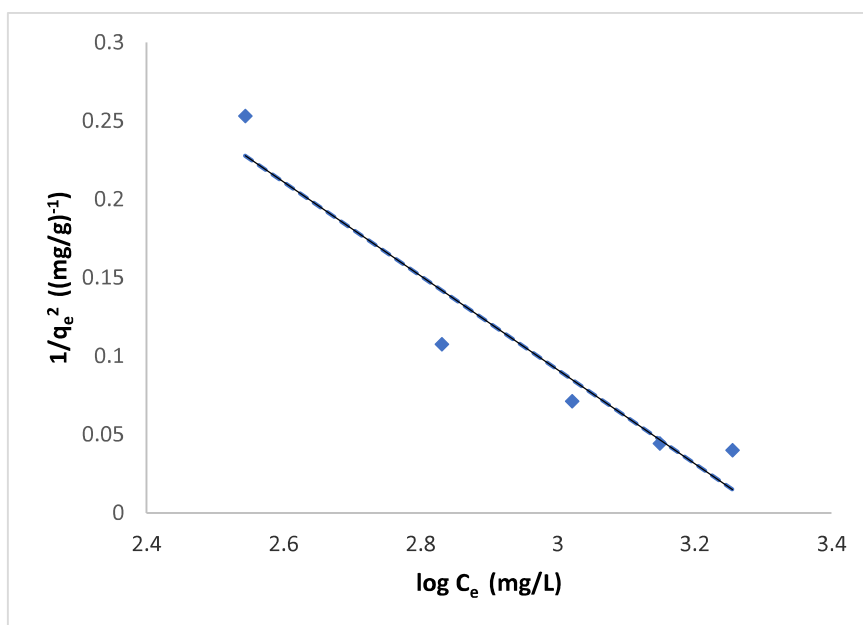


Fig. 11. Harkin-Jura isotherm for adsorption CHI

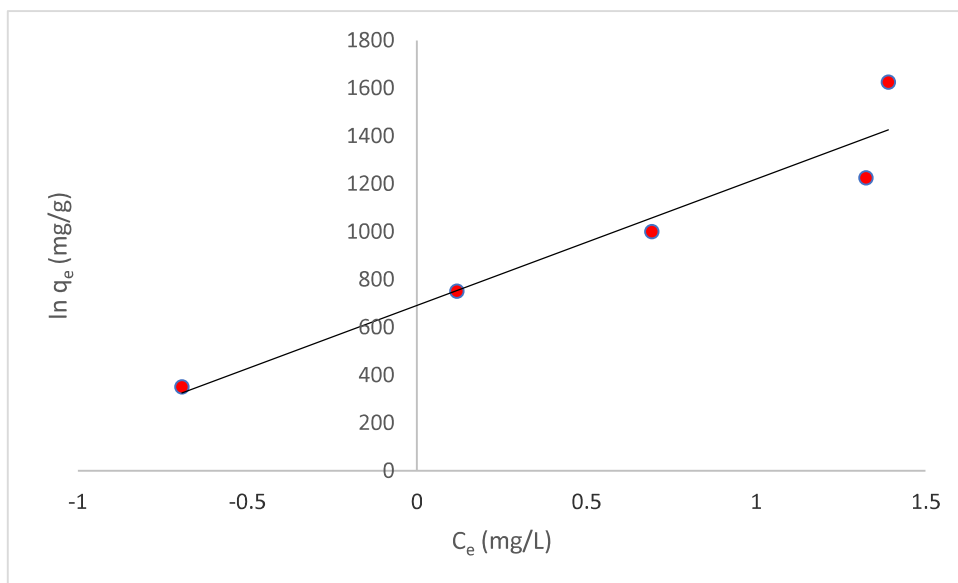


Fig. 12. Jovanovic isotherm for adsorption of Ni (II) ions on ACC

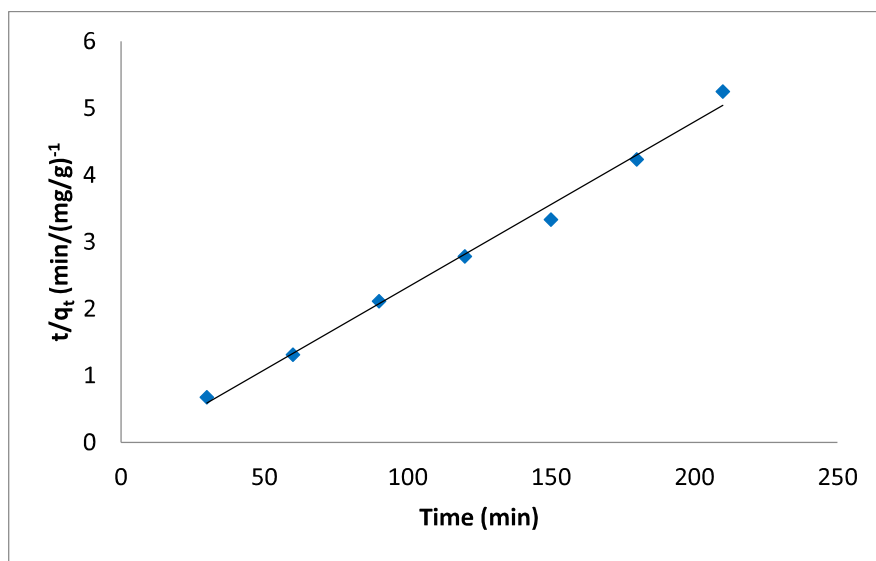
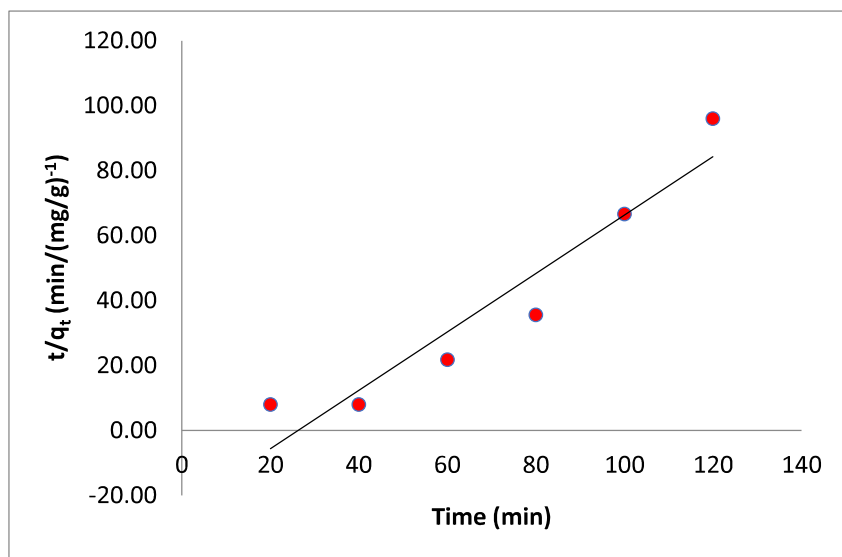


Fig. 12. Second-order kinetic plot of adsorption of Ni (II) ions on CHI





**Fig. 13.** Second-order kinetic plot of adsorption of Ni (II) ions on ACC

**Tables:**

**Table: 1.** Adsorption isotherm parameters for adsorption on Ni (II) ions on CHI and ACC

<b>Langmuir</b>				
<b>CHI</b>	<b>a (10<sup>-5</sup>) mL/g</b>	<b>b (mg/g)</b>	<b>R<sub>L</sub></b>	<b>R<sup>2</sup></b>
	5.64	67.11	1.00	0.9668
<b>Harkin-Jura</b>				
	<b>A</b>	<b>B</b>	<b>R<sup>2</sup></b>	
<b>CHI</b>	3.34	3.30	0.9146	
<b>Jovanovic</b>				
	<b>K<sub>J</sub></b>	<b>q<sub>max</sub></b>	<b>R<sup>2</sup></b>	
<b>ACC</b>	-528.51	2.04	0.9228	

**Table 2. Kinetics Parameters for adsorption of Ni (II) ions using CHI and ACC**

<b>Pseudo-second-order</b>			
	<b>q<sub>e</sub><sup>2</sup> (mg/g)</b>	<b>K<sub>2</sub> (g/mg/min)</b>	<b>R<sup>2</sup></b>
<b>CHI</b>	40.49	-3.938x10 <sup>-3</sup>	0.9930
<b>ACC</b>	1.11	-34.24x10 <sup>-3</sup>	0.9074

**Table 3. Comparison on adsorption capacities of adsorbents for removal of Ni (II) ions**

<b>Adsorbents</b>	<b>Adsorption capacities (mg/g)</b>	<b>Reference</b>
Composite-CaCO <sub>3</sub>	769.2	14
Composite-biopolymer base material	500	14
MWCNTs-KIAgNPs	40.1	15
Sodium hydroxide treated rice bran	153.6	16
Acid treated sawdust	74.1	17
Beech sawdust	4	18
Chitosan (CH)	67.1	This study
Activated carbon (ACC)	1.0	This study

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