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Environmental health and toxicology
Evaluation of carbon-based nanosorbents synthesised by ethylene decomposition on stainless steel substrates as potential sequestrating materials for nickel ions in aqueous solution


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Abstract
The present work covers the preparation of carbon-based nanosorbents by ethylene decomposition on stainless steel mesh without the use of external catalyst for the treatment of water containing nickel ions (Ni^{2+}). The reaction temperature was varied from 650 to 850°C, while reaction time and ethylene to nitrogen flow ratio were maintained at 30 min and 1:1 cm^3/min, respectively. Results show that nanosorbents synthesised at a reaction temperature of 650°C had the smallest average diameter (75 nm), largest BET surface area (68.95 m^2/g) and least amount of impurity (0.98 wt.% Fe). A series of batch sorption tests were performed to evaluate the effects of initial pH, initial metal concentration and contact time on Ni^{2+} removal by the nanosorbents. The equilibrium data fitted well to Freundlich isotherm. The kinetic data were best correlated to a pseudo second-order model indicating that the process was of chemisorption type. Further analysis by the Boyd kinetic model revealed that boundary layer diffusion was the controlling step. This primary study suggests that the prepared material with Freundlich constants compared well with those in the literature, is a promising sorbent for the sequestration of Ni^{2+} in aqueous solutions.

Key words: adsorption; nanosorbent; nickel ions; isotherms; kinetics
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Introduction
Nickel ions (Ni^{2+}) are one of the most toxic heavy metal ions and are utilised in a wide range of industries including nickel alloys production, battery manufacturing, industrial plumbing, machinery parts and electroplating. Wastewaters discharge by these industries often contain Ni^{2+} in a wide range of concentrations which exceed the permissible discharge limit; for example, the wastewaters from metal plating, paint formulation and porcelain enamelling have been found to contain Ni^{2+} in concentrations ranging from 2–900, 0–40 and 0.25–67 mg/L, respectively (Patterson, 1997). Ingestion of water contaminated with Ni^{2+} by humans can lead to health issues such as damage to the kidneys and lungs, pulmonary fibrosis, gastrointestinal distress, dermatitis and cancers as a result of its accumulative and non-biodegradable properties (Padmavathy, 2008). The detrimental effects of Ni^{2+} necessitate its level in the aquatic environment to be controlled within the acceptable limit.

Several methods are available for the treatment of industrial effluents containing Ni^{2+} and these include ion-exchange, chemical precipitation, electro-dialysis, reverse osmosis and adsorption. Among these methods, adsorption is most commonly used due to its process simplicity and cost-effectiveness. Adsorption of Ni^{2+} onto various solid materials such as activated carbon (Hasar, 2003), bagasse fly ash (Gupta et al., 2003) and activated sludge (Aksu et al., 2000) have all been reported, however, their low removal capacities and efficiencies restrict their applications. Therefore, new adsorbents with enhanced removal properties are being investigated by many researchers.

Carbon-based nanosorbents such as carbon nanotubes (CNTs) and nanoparticles have attracted much attention due to their high specific surface area, excellent chemical resistance and mechanical strength, and good adsorption capacity. CNTs can be single-walled or multi-walled depending on the number of graphene layers found in their structures, and these materials have been tested for the removal of a range of pollutants including dioxins (Long and Yang, 2001), fluoride (Li et al., 2001), pesticides (Asensio-Ramos et al., 2008) and cationic dyes (Gong et al., 2009). Although CNTs can be synthesised by several methods such as arc discharge, laser ablation or chemical vapour deposition (CVD), the most popular method is CVD as it can be easily scaled up (Coleman et al., 2006).

This work covers the synthesis of carbon nanosorbents using a CVD apparatus adapted from a piece of equipment.
used for previous work on the carbonisation of agricultural (Foo and Lee, 2010). The representative sources of carbon and catalyst are ethylene gas and stainless steel mesh, respectively. This method does not require any addition of particulate metal catalyst as the steel mesh acted as both the catalyst and supporting material. The effect of reaction temperature on the formation and morphology of nanosorbents were investigated. Batch adsorption studies were performed at different initial pH, initial Ni$^{2+}$ concentrations and contact time in order to determine the capabilities of the prepared materials to remove Ni$^{2+}$. Experimental data were analysed to determine the adsorption isotherm, kinetics and mechanism of Ni$^{2+}$ sorption onto the synthesised nanosorbents.

1 Materials and methods

1.1 Synthesis of nanosorbents

A commercial grade stainless steel mesh (type 304; mesh size 0.074 mm; wire diameter 0.040 mm) selected as the catalyst cum supporting material was cut into square pieces of 20 by 20 mm$^2$. The pieces were placed in an ultrasonic bath (Kerry Ultrasonic, UK) filled with acetone for 30 min for the removal of microscopic impurities. The cleaned steel substrates were etched in 1 mol/L HCl for an hour and then heated in a muffle furnace (Carbolite, UK) at 850°C overnight. After cooling, the substrates were stored in a desiccator.

The synthesis of nanosorbents was performed under atmospheric pressure in a stainless steel tubular reactor (type 316; internal diameter 40 mm; length 1220 mm) mounted horizontally in an electrical tube furnace (Carbolite, UK). Figure 1 shows the schematic of the apparatus which was connected to a gas flow system. The stainless steel substrates held in ceramic crucibles were placed in the middle of the reactor. Nitrogen gas was introduced into the reactor at 30 cm$^3$/min and the furnace was heated to 650°C. Upon reaching the desired temperature, ethylene was fed into the reactor at 30 cm$^3$/min to initiate the growth of nanosorbent. The synthesis process occurred for 30 min before the ethylene supply was stopped and the reactor was cooled down to room temperature (about 30°C) under the same nitrogen flow. The products formed were removed from the reactor and kept in a desiccator for further experimental work. The above synthesis procedures were repeated at different reaction temperatures.

1.2 Characterisation of nanosorbents

The morphological properties of the synthesised materials were examined using a scanning electron microscope equipped with energy dispersive X-ray spectrometry (SEM-EDS) (FEI Quanta 400 with EDS, USA). A representative sample was sprinkled onto a double-sided carbon tape mounted on a SEM stub. Sample analysis was carried out by the bombardment of electrons of 15–20 kV on target sample particle at various magnifications (20,000–80,000×).

The specific surface area of the adsorbents was determined by nitrogen adsorption using Accelerated Surface Area Porosimeter (ASAP, Micromeritics 2010, USA). Prior to analysis, about 80 mg of a sample was de-gassed at 200°C and under vacuum (300 mmHg) for 3 hr to remove moisture and volatile contaminants. The sample was then allowed to cool down to room temperature and its weight was measured. The BET surface area was calculated using nitrogen adsorption data at −196°C in the relative pressure range of 0.05–0.30, and taking the molecular cross-sectional as 0.162 nm$^2$. The total pore volume was based on adsorption data at −196°C and relative pressure of 0.05. The determination of average pore size was based on uniform cylindrical pores.

The point of zero charge (PZC) of the adsorbent was evaluated by the method described by Oladoja and Aliu (2009). Twenty milliliters of 0.1 mol/L KNO$_3$ solution was poured into a series of 100 mL conical flasks. The initial pH (pH$_0$) of the solutions was adjusted from 2 to 11 by adding either 0.1 mol/L HNO$_3$ or 0.1 mol/L KOH. After recording the solution pH$_0$ using a pH meter (Schott Inst, Lab 860, Germany), adsorbent (20 mg) was added to each flask and the mixture was agitated in a water-bath shaker (Protech, Malaysia) for 24 hr at 30°C. Thereafter, the final pH (pH$_f$) of the supernatant liquid was recorded. The difference between the values of pH$_0$ and pH$_f$ ($\Delta$PH) was plotted against pH$_0$. The point at which the plot intersects with the X-axis represents the PZC.
1.3 Experimental procedure for adsorption study

Batch sorption tests were conducted on the synthesised nanosorbents and a commercially available CNT (Global Science Resources, Malaysia). Prior to the study, the adsorbents were heated at 300°C for 3 hr in a muffle oven (Carbolite, UK) to remove amorphous carbon.

A stock solution of 1000 mg/L of Ni²⁺ was prepared by dissolving 4.05 g of nickel(II) chloride hexahydrate (analytical grade, Merck Germany) in 1.0 L of distilled water. The stock solution was diluted with distilled water to the desired concentrations in separate volumetric flasks.

The effect of initial pH on the adsorption of Ni²⁺ was investigated in the pH range of 2.0–11.0. A series of 250 mL conical flasks were filled with 100 mL solution of concentration 100 mg/L Ni²⁺. The pH of the solutions, measured by a pH meter (Schott Inst. Lab 860, Germany), was adjusted at the start of the experiment to the desired value by adding either 0.1 mol/L HCl or 0.1 mol/L KOH. Then, a precisely measured amount of adsorbent (20 mg) was added to each flask. After covering with rubber stoppers, the flasks were placed in a water-bath shaker (Protech, Malaysia) at a constant temperature of 30°C. The mixtures were agitated at 125 r/min for 24 hr to ensure equilibrium was attained. Thereafter, the mixtures were filtered and Ni²⁺ concentration in the filtrate was determined by an atomic adsorption spectrometer (AAS, PerkinElmer AAAnalyst 400, USA). The pH values of the solutions were not controlled during the experiment. A control test was also carried out at 30°C without the addition of any adsorbents.

To determine the effect of initial Ni²⁺ concentration on its adsorption, the above procedures were repeated using a series of solutions of different initial metal concentrations while other parameters such as adsorbent dosage, temperature, agitation speed and contact time were kept the same. This study was performed at the original pH of the solutions without any pH adjustment. The amount of Ni²⁺ adsorbed at equilibrium per unit mass of adsorbent (\( q_e \)) was determined by Eq. (1):

\[
q_e = \frac{(C_0 - C_e) V}{W}
\]

where, \( C_0 \) (mg/L) and \( C_e \) (mg/L) are the initial and equilibrium Ni²⁺ concentration, respectively, \( V \) (L) is the solution volume and \( W \) (g) is the mass of the adsorbent.

Kinetic studies of Ni²⁺ adsorption were conducted by contacting 20 mg of adsorbent with a 200 mL solution of initial concentration 100 mg/L Ni²⁺ at 30°C and at the original pH of the solution. Agitation was performed at 125 r/min and samples were withdrawn at regular time intervals for the determination of Ni²⁺ concentration by AAS. The procedure was repeated using a different initial metal concentration. The amount of Ni²⁺ adsorbed per unit mass adsorbent at a certain time \( t \) (\( q_t \)) was calculated by Eq. (2):

\[
q_t = \frac{(C_0 - C_t) V}{W}
\]

and the percentage removal (\( R, \% \)) of Ni²⁺ was determined by Eq. (3):

\[
R = \frac{(C_0 - C_t)}{C_0} \times 100\% \tag{3}
\]

where, \( C_i \) (mg/L) is the Ni²⁺ concentration at time \( t \) (hr).

1.4 Calculations on adsorption isothermal and kinetic parameters

1.4.1 Adsorption isotherms

The equilibrium distribution of Ni²⁺ between the solution and the adsorbent at a constant temperature may be represented by mathematical models such as the Freundlich and Temkin models. To identify which one of these models would accurately represent Ni²⁺ adsorption, the experimental data were fitted to the models.

The Freundlich isotherm describes an exponential decrease in the adsorption energy with an increase in the surface coverage. It is an empirical expression based on the assumptions that adsorption occurs on a heterogeneous surface and no interaction between absorbed molecules and hence, equal concentration on surface site. The logarithmic form of the Freundlich equation was expressed by Eq. (4) (Freundlich, 1906):

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}
\]

where, \( K_F \) (L/g) is the Freundlich constant related to the adsorption capacity and \( n \) (dimensionless) is the Freundlich exponent related to the adsorption intensity. By plotting \( \log q_e \) against \( \log C_e \), the values of \( K_F \) and \( n \) can be determined from the intercept and gradient of the straight line.

The Temkin isotherm model represents a linear reduction in the adsorption energy with an increase in the degree of completion of the sorption sites. This model assumes that the interactions between the adsorbate and adsorbent caused the adsorption heat of all molecules in the layer to reduce linearly with surface coverage, and adsorption is characterised by a uniform distribution of binding energies. The Temkin isotherm is normally used in the form given by Eq. (5) (Temkin and Pyzhev, 1939):

\[
q_e = B \log (A C_e) = B \log A + B \log C_e \tag{5}
\]

where, \( A \) (L/g) and \( B \) (= \( RT/h \), J/mol) are the Temkin constants related to maximum binding energy and heat of adsorption, respectively, \( R \) (8.314 J/(mol.K)) is the universal gas constant and \( T \) (K) is the absolute temperature. The Temkin parameters \( A \) and \( B \) are determined from the plot of \( q_e \) against \( \log C_e \).

1.4.2 Adsorption kinetics

Kinetic study involves the determination of the rate and mechanisms for the uptake of Ni²⁺ which are crucial for the evaluation of process efficiency. This study was performed by fitting the experimental data with two reaction rate models, namely pseudo first-order and pseudo second-order kinetics. The data were further examined...
with the intra-particle diffusion and Boyd kinetic models in order to determine the diffusion mechanisms governing the sorption process.

The pseudo first-order model is widely used to predict the kinetics for the initial stage of the adsorption process and is given by Eq. (6) (Lagergren, 1898):

\[
\log_{10}(q_e - q_t) = \log_{10} q_e - \frac{k_1}{2.303}t
\]  

(6)

where, \(k_1\) (L/hr) is the pseudo first-order adsorption rate constant. The values of \(q_e\) and \(k_1\) are found from the gradient and intercept of a plot of \(\log_{10}(q_e - q_t)\) versus \(t\).

The pseudo second-order model which cover the whole range of the adsorption process, assumes that the process was of chemisorption type (Ho and McKay, 1998). The model is given by Eq. (7):

\[
t = \frac{1}{k_2 q_e^2 + \frac{1}{q_e}}\left(\frac{t}{q_t}\right)
\]

(7)

where, \(k_2\) (g/(mg·hr)) is the pseudo second-order adsorption rate constant which is determined from the gradient of the plot of \(t/q_t\) versus \(t\).

Adsorption of Ni\(^{2+}\) onto the solid sorbents could be represented by the following mechanistic steps: (1) Transport from the bulk of the solution to the adsorbent surface. (2) Diffusion across the boundary layer to the adsorbent surface. (3) Transport from the surface to the interior pores of the sorbent (intra-particle diffusion). (4) Sorption at active sites within the adsorbent and on the external surface.

In this work, the effect of transport in the solution was suppressed by performing the batch experiments at high agitation speed so that the first step would not be rate limiting. The fourth step was considered negligible as it was fast and an equilibrium reaction. The overall adsorption rate would be controlled by the slowest step which could either be boundary layer or intra-particle diffusion.

The intra-particle diffusion model proposed by Weber and Morris (1963) was used to investigate the possibility of Ni\(^{2+}\) being transported in the internal pores of the adsorbents. It is expressed by Eq. (8):

\[
q_t = k_{pi}t^{1/2} + C_i
\]

(8)

where, \(k_{pi}\) (mg/(g·hr\(^{1/2}\))) is the intra-particle diffusion rate constant and \(C_i\) (mg/g) is the intercept value which reflects the boundary layer effect. The larger the intercept, the greater the diffusion effect due to the boundary layer. The values of \(k_{pi}\) and \(C_i\) were determined from the gradient and intercept of the plot \(q_t\) versus \(t^{1/2}\). The characteristic of the plot reveals the mechanisms which occur in the process; for example, if the plot is a straight line passing through the origin then intra-particle diffusion is the sole rate controlling. A linear plot which does not go through the origin means that the sorption dynamics may be due to several mechanisms such as boundary layer and intra-particle diffusions. To determine the actual rate controlling step in the adsorption process, the experimental data were further analysed by the Boyd kinetic model which is given by Eq. (9) (Boyd et al., 1947):

\[
B_i = -4.977 - \log(1 - F)
\]

(9)

where, \(F = q_t/q_e\) (dimensionless) is the fraction of Ni\(^{2+}\) absorbed at time \(t\) (hr) and \(B_i\) is a mathematical function of \(F\). The linearity of the experimental data was tested on the plot of \(B_i\) versus time \(t\). According to this model, a linear plot which passes through the origin indicates that intra-particle diffusion is rate controlling.

2 Results and discussion

2.1 Characterisation of nanosorbents

Figure 2 shows the SEM images of the nanosorbents prepared at reaction temperatures of 650, 750 and 850°C, respectively. The images reveal that the products formed were mainly tiny cylindrical conduits curled in random orientation. Material formed at 650°C (Fig. 2a), appeared to have smoother surface and more uniform diameter compared with those formed at higher reaction temperatures (Fig. 2b and c). With increasing temperature, the materials seem to contain more agglomerated particles which may be amorphous carbon. It has been demonstrated that during the CVD process, the hydrocarbon vapour decomposed when in contact with the hot nanometer-sized metal catalyst into carbon atoms and hydrogen species (Lupu et al., 2009). The carbon atoms then deposited on one side...
of the metal and diffused through the surface and bulk of the metal. Upon reaching the carbon-solubility limit in the metal at the specific temperature, as-dissolved carbon precipitated out and crystallised in the form of a tubular structure on the other side of the metal. To achieve a continuous growth of nanotubes, the hydrocarbon decomposition rate should balance well with the carbon atom diffusion rate. At high reaction temperatures, the rate of the former process was likely faster than the rate of later process. Therefore, the metal catalyst could be encapsulated by the excess of carbon atoms forming amorphous carbon at high temperatures. Similar observations to those shown here have been observed for different formation methodologies reported by Chen et al. (2008).

Estimation of the nanosorbents diameter was performed by selecting about 60 tubes per sample and measuring their external diameters from the respective SEM images. The distribution curves and average diameter are presented in Fig. 3. It was found that the average diameter became larger when the reaction temperature was increased. In CVD process, the size of active catalyst site usually determines the diameter of nanotubes formed. The acid pre-treatment performed on the steel mesh before the CVD stage would modify the external surface of the mesh, creating cracks and break-ups. Following high temperature treatment on the acid-treated mesh, the external nanoparticles of iron compounds were converted into active metallic sites for the CVD reaction (Martinez-Hansen et al., 2009). The observed rise in average diameter with reaction temperature could be the result of these active sites agglomerating together to form larger active metallic clusters, which in turn leads to the formation of thicker nanosorbents at higher reaction temperatures (Chen et al., 2008).

The composition of the nanosorbents was determined by energy dispersive X-ray spectrometer (EDS), and results are shown in Table 1. As can be seen, the nanosorbents prepared at 650°C (NS650) have the highest weight percentage of carbon. When the reaction temperature was increased, the weight composition of carbon decreases, while that of residual minerals increases (Table 1). These impurities originated from the stainless steel substrates used in the synthesis process. It is well known that iron, chromium and nickel are the main components of steel alloy. The growth of the nanosorbents may have occurred by extracting these metallic elements from the substrate surface. However, it is still unclear why the formation of nanotubes occurs only by extracting certain metals from the substrate surface while other metals on the substrate surface remained unreacted. It has been postulated that this observation could be due to the different diffusion kinetics of carbon atoms in iron or nickel lattice at the synthesis temperature (Camilli et al., 2011). The presence of impurities in the nanosorbents may also have an impact on the surface properties and therefore the adsorption behaviour (Liu et al., 2011).

Nitrogen adsorption is commonly used to study the porosity and surface area of adsorbing materials. The porous system of nanotubes is likely contributed by the hollow interior of the tubes, interstitial space between three or more neighbouring tubes, at grooves present on the periphery of nanotube bundles or on the curved surface of the periphery of a tube (Agnihotri et al., 2005). When the tubes were subjected to high temperature treatment, their internal pore volume would be affected. Table 2 shows the effect of reaction temperature on the porosity and surface area of the nanosorbents prepared in this work. The standard BET method was used to determine the specific surface area of the nanosorbents, and it can be seen that this surface area decreases with increasing reaction temperature. This decrease in surface area may be due to carbon sintering sealing off some pores due to excessive temperature (Zhao et al., 2007). A similar drop in pore volume is observed with increasing temperature, while the

![Fig. 3](https://jesc.ac.cn) Histogram of external diameter distribution for nanosorbents formed at reaction temperature of 650°C (a), 750°C (b), and 850°C (c).
individual pore size for the different temperatures remains relatively similar (to within approx 2%) and fall in the range for micropores (< 2.0 nm). Another possibility for the reduction in surface area is that at high reaction temperatures, some pores are occupied by residual minerals, and therefore show a small effective BET surface area. However, this would not account for the reduction in pore volume and these observations seem to indicate that while individual pore size is independent of reaction temperature, carbon sintering at higher temperatures can reduce access to the individual pore structures.

### 2.2 Adsorption studies

#### 2.2.1 Effect of initial pH

The result in Fig. 4a illustrates the effect of pH on the removal of Ni$^{2+}$ by nanosorbent prepared at 650°C (NS650). As shown, the Ni$^{2+}$ removal increases when the initial pH was increased from 2.0 to 9.0, and remained nearly constant with further increase in pH up to 11.0. This adsorption trend can be attributed to the degree of ionisation and speciation of nickel. Jinxing and Cooper (1996) reported that at pH below 9.0, the dominant species of nickel was Ni$^{2+}$ and removal of this metal species was achieved mainly by the adsorption process. The low Ni$^{2+}$ removal which occurred in the acidic region was due to competition between protons and Ni$^{2+}$ for the same adsorption sites on NS650. These sorption sites became more accessible to Ni$^{2+}$ as the proton concentration is reduced, therefore, an increase in Ni$^{2+}$ removal with increasing pH was observed as seen in other work (Rao et al., 2007). At pH above 9.0, insoluble nickel hydroxide, Ni(OH)$_2$ (s), starts precipitating from the solution, and both adsorption and precipitation processes were the effective mechanisms for the removal of Ni$^{2+}$. This observation was confirmed by results of control tests (without adsorbent) shown in Fig. 4a. The removal of Ni$^{2+}$ at low pH region was insignificant, but it increase notably at pH above 9.0 due to nickel precipitation.

The influence of pH on Ni$^{2+}$ removal can also be explained by considering the surface charge of NS650. The point of zero charge for NS650 was found to be about 6.3 as shown in Fig. 4b. That is to say, the sorbent surface is positively charged at pH below 6.3 and negatively charged at pH above 6.3. In the low pH region, both the sorbent surface and metal ion carried same positive charge (Fig. 4a and b) leading to electrostatic repulsion between them. This explained the low removal of metal at pH below 6.3. At pH above 6.3, the surface of NS650 became negatively charged and electrostatic attraction with Ni$^{2+}$ would result in an increase in metal removal, represented in Fig. 4a by an increase in gradient.

#### 2.2.2 Effect of initial Ni$^{2+}$ concentration

Figure 5 illustrates the effect of initial concentration on the amount of Ni$^{2+}$ adsorbed per unit mass of nanosorbents. This study was conducted at the natural pH of the solution which was recorded as 7.0. It had been shown in the study on the effect of initial pH (Section 2.2.1) that no precipitation of Ni$^{2+}$ would occur at this pH value.

![Fig. 5](image_url) Effect of initial concentration on adsorption of Ni$^{2+}$ onto nanosorbents (NS) formed at different temperatures (650, 750 and 850°C) and onto commercial CNT (C-CNT). Condition: 30°C; dosage 20 mg; pH 7; 100 mL solution.

![Fig. 4](image_url) Effect of initial pH on Ni$^{2+}$ removal by nanosorbent formed at 650°C (NS650) (a) and plot of ΔpH against initial pH for the determination of the point of zero charge of NS650 surface (b). Condition: 30°C, dosage 20 mg.
Figure 5 reveals that when the initial metal concentration was increased, the amount of Ni\textsuperscript{2+} adsorbed per unit mass increased. This increasing trend was due to the increase in driving force as the initial concentration was increased (Akar et al., 2009). The fact that the amount adsorbed at equilibrium increases with initial concentration indicated the potential application of the prepared adsorbents for the removal of Ni\textsuperscript{2+} in aqueous solution. In all cases, the nanosorbent generated at 650°C is the most effective.

### 2.2.3 Adsorption isotherms

The experimental data were fitted with Freundlich and Temkin isotherms to determine which model more accurately represented the adsorption process. Figure 6 shows the Freundlich and Temkin isotherm plots for Ni\textsuperscript{2+} adsorption. From these plots, the corresponding isotherm constants and correlation coefficients evaluated are presented in Table 3. The high values of correlation coefficients suggest that experimental data fits better to the Freundlich than the Temkin model for all the nanosorbents. The highest Freundlich constants $K_F$ and $n$ were found to be 7.099 mg/g and 1.016, respectively, suggesting that among the four nanosorbents under investigation, NS650 has the largest adsorption capacity and affinity for Ni\textsuperscript{2+}. The value of $n$ greater than unity implied that Ni\textsuperscript{2+} was favourably adsorbed onto the surfaces of NS650 which was heterogeneous in nature (Kandah and Meunier, 2007).

In Table 4, the results of the present study are compared with the literature data (Ho et al., 1994, Kandah and Meunier, 2007; Padmavathy, 2008; Lu et al., 2008; Kalavathy et al., 2010; Anoop Krishnan et al., 2011) for a range of other adsorbents evaluated for Ni\textsuperscript{2+} adsorption. It can be seen that the prepared nanosorbents have Freundlich constants $K_F$ and $n$, which are comparable with those of other adsorbents. The results indicate that the synthesised nanosorbents may be suitable for certain applications and further studies are needed to evaluate their potential for Ni\textsuperscript{2+} removal.

### Table 3: Freundlich and Temkin isotherm constants and correlation coefficients for Ni\textsuperscript{2+} adsorption onto prepared nanosorbents and commercial CNT

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>$K_F$ (mg/g)</th>
<th>$n$</th>
<th>$R^2$</th>
<th>$B$ (L/mol)</th>
<th>$A$ (L/g)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NS650</td>
<td>7.099</td>
<td>1.016</td>
<td>0.9460</td>
<td>231.07</td>
<td>0.1672</td>
<td>0.8129</td>
</tr>
<tr>
<td>NS750</td>
<td>6.561</td>
<td>1.009</td>
<td>0.9630</td>
<td>283.57</td>
<td>0.1821</td>
<td>0.7669</td>
</tr>
<tr>
<td>NS850</td>
<td>4.357</td>
<td>0.976</td>
<td>0.9650</td>
<td>245.58</td>
<td>0.1762</td>
<td>0.7394</td>
</tr>
<tr>
<td>C-CNT</td>
<td>1.557</td>
<td>0.851</td>
<td>0.9670</td>
<td>246.81</td>
<td>0.1641</td>
<td>0.6863</td>
</tr>
</tbody>
</table>

### Table 4: Comparison of Freundlich constants of Ni\textsuperscript{2+} adsorption onto various adsorbents

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>$K_F$ (mg/g)</th>
<th>$n$</th>
<th>$R^2$</th>
<th>$T$ (°C)</th>
<th>Initial concentration (mg/L)</th>
<th>Initial pH</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>NS650</td>
<td>7.099</td>
<td>1.016</td>
<td>0.9460</td>
<td>30</td>
<td>50–600</td>
<td>7.0</td>
<td>Present study</td>
</tr>
<tr>
<td>NS750</td>
<td>6.561</td>
<td>1.009</td>
<td>0.9630</td>
<td>30</td>
<td>50–600</td>
<td>7.0</td>
<td>Present study</td>
</tr>
<tr>
<td>NS850</td>
<td>4.357</td>
<td>0.976</td>
<td>0.9650</td>
<td>30</td>
<td>50–600</td>
<td>7.0</td>
<td>Present study</td>
</tr>
<tr>
<td>C-CNT</td>
<td>1.557</td>
<td>0.851</td>
<td>0.9670</td>
<td>30</td>
<td>50–600</td>
<td>7.0</td>
<td>Present study</td>
</tr>
<tr>
<td>MWCNT</td>
<td>2.267</td>
<td>1.510</td>
<td>0.9865</td>
<td>Room temp.</td>
<td>10–200</td>
<td>6.0</td>
<td>Kandah and Meunier, 2007</td>
</tr>
<tr>
<td>Oxidised MWCNT</td>
<td>2.921</td>
<td>1.725</td>
<td>0.9821</td>
<td>Room temp.</td>
<td>10–200</td>
<td>6.0</td>
<td>Kandah and Meunier, 2007</td>
</tr>
<tr>
<td>Bakers yeast</td>
<td>3.730</td>
<td>5.880</td>
<td>0.9800</td>
<td>27</td>
<td>10–400</td>
<td>6.7</td>
<td>Padmavathy, 2008</td>
</tr>
<tr>
<td>SWCNT</td>
<td>15.05</td>
<td>3.496</td>
<td>0.9747</td>
<td>25</td>
<td>10–80</td>
<td>7.0</td>
<td>Lu et al., 2008</td>
</tr>
<tr>
<td>MWCNT (NaOCl)</td>
<td>10.75</td>
<td>3.413</td>
<td>0.9926</td>
<td>25</td>
<td>10–80</td>
<td>7.0</td>
<td>Lu et al., 2008</td>
</tr>
<tr>
<td>AC (sawdust)</td>
<td>5.95</td>
<td>3.195</td>
<td>0.9920</td>
<td>25</td>
<td>10–80</td>
<td>7.0</td>
<td>Lu et al., 2008</td>
</tr>
<tr>
<td>AC (SBP)</td>
<td>2.206</td>
<td>2.910</td>
<td>0.9750</td>
<td>30</td>
<td>50–1000</td>
<td>6.5</td>
<td>Anoop Krishnan et al., 2011</td>
</tr>
</tbody>
</table>

are worthy of further study.

2.2.4 Effect of contact time

The adsorption of Ni\textsuperscript{2+} onto NS650 as a function of time at two different initial Ni\textsuperscript{2+} concentrations is presented in Fig. 7. For all concentrations studied, the adsorption of Ni\textsuperscript{2+} increases rapidly as the contact time is increased to 2.0 hr, and thereafter increases slowly approaching equilibrium between 4.0–6.0 hr. The fast uptake rate at the initial stage of the process may be due to high availability of adsorption sites for binding Ni\textsuperscript{2+}, however, as contact time increases, the availability of adsorption sites decreased causing a reduction in sorption rate (Chakravarty et al., 2010). These results have been published for the adsorption of Ni\textsuperscript{2+} onto cashew nut shell (Kumar et al., 2011) and onto Acacia leucocephala bark (Subbaiah et al., 2009).

To examine the kinetics of Ni\textsuperscript{2+} adsorption, the pseudo first-order and pseudo second-order equations were used to fit the experimental data. The plots for the pseudo first-order and second-order models are shown in Fig. 8. From these plots, the parameters of the models were determined and presented in Table 5. As can be seen, the correlation coefficients for pseudo second-order model are higher than those for the pseudo first-order model. Therefore, the present system is better described by pseudo second-order than by pseudo first-order model. This result shows that the assumption of chemisorption nature made by the pseudo second-order model is valid for the Ni\textsuperscript{2+} adsorption process. Similar findings were reported for the uptake of Ni\textsuperscript{2+} by biomass Oedogonium sp. (Gupta and Rastogi, 2008); by carrot weed based activated carbon (Lata et al., 2008) and by sugarcane bagasse (Homagai et al., 2010).

2.2.5 Kinetics of adsorption

To determine the slowest step involved in the present process, the kinetic data were further tested on the Boyd kinetic model. Figure 9a illustrates that the Boyd plots for Ni\textsuperscript{2+} adsorption are linear but they do not go through the origin, indicating that intra-particle diffusion was not the only controlling step. The plots did not go through the origin because the uptake rates at the beginning and end stages of the adsorption process were different. Similar results have been published for the adsorption of Ni\textsuperscript{2+} onto nanosorbent NS650 at different initial concentrations. Condition: 30°C; dosage 20 mg; pH 7; 200 mL solution.

<table>
<thead>
<tr>
<th>( C_0 ) (mg/L)</th>
<th>Pseudo first-order model</th>
<th>Pseudo second-order model</th>
<th>Intra-particle diffusion model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( q_{e,calc} ) (mg/g)</td>
<td>( k_1 ) (1/hr)</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>100</td>
<td>126.47</td>
<td>0.78</td>
<td>0.9591</td>
</tr>
<tr>
<td>400</td>
<td>452.38</td>
<td>0.71</td>
<td>0.9227</td>
</tr>
</tbody>
</table>

2.2.6 Mechanism of adsorption

The intra-particle diffusion plot for Ni\textsuperscript{2+} adsorption on NS650 is illustrated in Fig. 9a, and the values of the rate constant and intercept are shown in Table 5. As shown in Fig. 9a, the plots have two distinct phases suggesting that the uptake of Ni\textsuperscript{2+} proceeds by boundary layer and intra-particle diffusion. The first phase represents the boundary layer effect while the second phase represents the intra-particle diffusion. Figure 9a also reveals that the linearly regressed plots of \( q_t \) versus \( t^{1/2} \) did not pass through the origin, indicating that intra-particle diffusion was not the only controlling step. The plots did not go through the origin because the uptake rates at the beginning and end stages of the adsorption process were different. Similar results have been published for the adsorption of Ni\textsuperscript{2+} onto nanosorbent NS650 at different initial concentrations. Condition: 30°C; dosage 20 mg; pH 7; 200 mL solution.
boundary layer.

3 Conclusions

Carbon-based nanosorbents have been successfully developed directly on stainless steel mesh placed in a simple CVD apparatus without the use of an external catalyst using ethylene as the carbon source. The active catalytic sites needed for nanosorbents growth were provided by the steel mesh which at the same time served as the final product support. The effect of reaction temperature on the average diameter, purity and BET surface area of the nanosorbents were examined. Within the temperature range studied (650–850°C), the products were found to have diameters between 75–180 nm, BET surface area range studied (650–850°C), the products were found to the nanosorbents were examined. Within the temperature on the average diameter, purity and BET surface area of

Acknowledgment

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References


