Adsorption and desorption studies of Ni$^{2+}$ ions on to coconut shell char

M S Abesekara, K N R Kosvinna and B M W P K Amarasinghe$^1$

Department of Chemical and Process Engineering, University of Moratuwa, Moratuwa, Sri Lanka

Email: padma@uom.lk

Abstract. Heavy metal discharge with wastewater (WW) is a major environmental concern, widely discussed today. Heavy metals in WW can be removed by several methods including adsorption. Activated carbon (AC) derived from coconut shells is widely used, but expensive adsorbent. In this study coconut shell char (CSC) was tested as an effective low-cost adsorbent for heavy metal removal from aqueous solutions. Batch adsorption experiments were conducted using CSC as the adsorbent to remove Ni$^{2+}$ from water. CSC has 12% removal efficiency for a solution of 25 mg Ni$^{2+}$/L with a dose of 2 g adsorbent/200 mL solution. The isotherm results have shown that, equilibrium data best obey to Langmuir monolayer model. The adsorption kinetics studies revealed, that adsorption behave according to the pseudo-second order model. It was identified that adsorption process has two steps as external diffusion and intraparticle diffusion. Furthermore, desorption abilities of H$_2$SO$_4$, NaOH, NaCl and Distilled water as desorbing agents were analysed and found H$_2$SO$_4$ to be the most effective desorbing agent.

1. Introduction

In an industry, waste generation is unavoidable and heavy metals are one of the most disastrous pollutants, which continuously releases to water bodies. They are highly toxic and their entry into the food chains leads to severe health problems through bio magnification and bio accumulation [1]. Furthermore, they induce adverse effects on the growth of aquatic organisms [2]. Electroplating, battery manufacturing, mining and textile industry can be named as the main industries that are responsible for the discharge of heavy metals. In industry, various techniques such as chemical precipitation, solvent extraction, ion exchange and electrochemical removal have been used to remove heavy metals from wastewater (WW) [3]. Due to the advantages as low cost, easy operation, wide pH range, high metal binding capacity and reusability of adsorbents, adsorption has become a more preferred method [1][4]. Among common heavy metals present in WW, Ni$^{2+}$ was used for the studies. It is a non-biodegradable contaminant which is largely generated in textile industry and causes health effects such as lung cancer, liver diseases, nephrotoxic and hair loss [2][4].

Activated carbon (AC) is a popular adsorbent due to its high adsorption capacity owing to its porous structure and surface chemical groups [5]. However, utilizing AC for WW treatment is limited in developing countries due to its high preparation cost [6]. WW treatment is less economical unless that large quantity of adsorbents were reused. Hence, industry prefers to use low cost adsorbents. Over the last decade numerous studies have been conducted to reduce the cost of AC, through altering the

$^1$ Author to whom any correspondence should be addressed.
activation process and using different waste materials for derivation. Several researchers have determined that AC from coconut shell is a promising adsorbent [7][8][9]. Furthermore, it is already using commercially in WW treatment plants [3][5]. However, it will be more economical if coconut shell char (CSC) could be used as an adsorbent without undergoing the activation process. Considering that, AC derived from coconut shell has good adsorption properties; this study was conducted to investigate the adsorption ability of CSC.

Adsorption is a reversible process if chemisorption is not involved [2]. Desorption ability add more value to an adsorbent in both cost and sustainability wise. It shows that acidic solutions are effective desorbing agents for both AC and biochar. However, desorbing agent should be cheap, non-polluting, easily regenerative and non-damaging to the structure of the adsorbent [10]. Desorption properties of CSC were investigated with different desorbing agents: H2SO4, NaOH, NaCl and distilled water.

The main objective of the study was to evaluate Ni2+ adsorption and desorption properties of CSC while, identifying a suitable desorption agent.

2. Methodology

2.1. Material preparation

2.1.1. Preparation of the adsorbent. CSC was obtained from a small-scale local supplier in Gampaha, Sri Lanka. The char was cleaned using water to eliminate soluble and coloured components. Then, they were solar dried for two days before size reduction process. Next, dried char was ground into small particles within the range 500 - 1000 µm. Then, adsorbents were washed with distilled water subsequent to normal water. Cleaned adsorbents were oven dried at 50 – 60 °C until weight become a constant.

2.1.2. Preparation of solutions. 200 mg Ni2+/L solution was prepared by dissolving analytical grade Ni(NO3)2.6H2O (obtained from Sigma Aldrich Corporation) in distilled water and stored in a clean glass bottle for future use. Solutions for experiments were prepared by dilution with distilled water.

0.1 M H2SO4, 0.1 M NaOH, 0.5 M NaCl and distilled water were selected as desorption agents. 1 L solutions of each agent were prepared using analytical grade solutions or chemicals.

2.2. Characterization

Under characterization, true density and bulk density of the adsorbent were measured using an electronic density meter and packing adsorbents in a density bottle, respectively. Furthermore, a scanning electron microscope (SEM) image and Fourier transform infrared (FTIR) spectrums covering the wave number range in between 600 cm-1 and 4000 cm-1 were taken to identify surface properties.

2.3. Adsorption studies

Batch experiment process parameters such as pH (5), stirrer speed (150 rpm) and time to equilibrium (180 min) were determined according to the previous studies on CSC [11]. Test method used to determine heavy metal concentrations is APHA 23rd ed: 2017: 3125 B with ICP-MS (Inductively Coupled Plasma Mass Spectrometry).

2.3.1. Equilibrium experiments. The effect of initial concentration on percentage removal and equilibrium concentration was investigated at the concentrations of 25, 50, 75, 100, 150 and 200 mg Ni2+/L. Each sample of 200 mL was mixed with dry adsorbent dosage of 2 g at 150 rpm stirrer speed for 2 hours in room temperature of 30 °C. Finally, sample solutions were filtered using a filter paper and Ni2+ concentration in the filtrate was determined.

2.3.2. Kinetic experiments. 2 L of 50 mg Ni2+/L solution with pH 5 was prepared. Sample was loaded with 20 g of adsorbent and mixed at 150 rpm stirrer speed. Samples were withdrawn at time 0, 1, 2, 3, 5, 10 and 20 minutes for the study.
2.4. Desorption studies
Spent adsorbents were prepared by mixing 2 L of 50 mg Ni\(^{2+}\)/L solution with 20 g of CSC in room temperature. pH, stirrer speed and contacting time were maintained as 5, 150 rpm and 2 hours, respectively. After the adsorption, adsorbents were filtered, and oven dried at 80 - 100 °C. 0.1 M H\(_2\)SO\(_4\), 0.1 M NaOH, 0.5 M NaCl and distilled water were used as desorption agents. For 4 g of adsorbent, 100 mL of desorption agent was used with stirring speed of 150 rpm and 2 hours contacting time.

3. Equilibrium and Kinetic Models

3.1. Adsorption Equilibrium
Percentage removal of Ni\(^{2+}\) (E) and adsorption capacity of CSC at equilibrium \((q_e)\) were determined as equation (1) and equation (2), respectively. \(C_0\) and \(C_e\) are the initial and equilibrium concentrations of Ni\(^{2+}\) in the solution (mg/L). \(V\) is the volume of the sample and, \(w\) is the dry weight of adsorbent.

\[
E = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}
\]

\[
q_e = \frac{(C_0 - C_e)V}{w} \tag{2}
\]

The Langmuir and the Freundlich models are widely used to describe the interaction between adsorbate and adsorbent. Langmuir model assumes that there is limited number of active sites on the adsorbent surface, at which the monolayer adsorption occurs. The linear form of Langmuir model can be formulated as equation (3). Here, \(q_m\) is the maximum monolayer adsorption capacity (mg/g) and \(K_L\) is the dimensionless Langmuir constant [12].

\[
\frac{C_e}{q_e} = \frac{1}{q_mK_L} + \frac{C_e}{q_m} \tag{3}
\]

Freundlich model is obtained based on the assumption that multilayer adsorption occurs on a heterogeneous surface. The logarithmic form of Freundlich equation is,

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

where, \(K_F\) is a constant that indicates the relative adsorption capacity ((mg/g)(L/mg)\(^{1/n}\)) and \(1/n\) is the dimensionless constant, which indicate the intensity of the adsorption process [12].

3.2. Adsorption Kinetics
The concentration of adsorbate in solid phase \(q_t\) at time \(t\) was calculated by,

\[
q_t = \frac{(C_0 - C_t)V}{w} \tag{5}
\]

where \(C_0\) and \(C_t\) are the concentration of adsorbate in liquid phase (mg/L) at time 0 and time \(t\) (min), respectively. \(V\) is the volume of the solution and \(w\) is the weight of dry adsorbent [13].

\[
\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{6}
\]

\[
\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{7}
\]

\[
q_t = k_i t^{0.5} + c \tag{8}
\]

\[
F(t) = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \left(\frac{1}{n^2}\right) \exp(-n^2Bt) \tag{9}
\]

Four kinetic models were used to study dynamics of Ni\(^{2+}\) adsorption on to CSC. Lagrange’s pseudo first-order and second-order kinetic models can be expressed as equation (6) and equation (7), respectively. \(k_1\) and \(k_2\) are the respective rate constants of each adsorption model. The intraparticle diffusion equation is given as equation (8) where, \(k_i\) is the intraparticle diffusion rate constant. The Boyd’s film diffusion model can be expressed as equation (9), with \(F(t)\) as the fractional attainment of equilibrium at time \(t\) and \(Bt\) as a mathematical function of \(F(t)\) [13].
4. Results and Discussion

4.1. Characterization

True density and bulk density of CSC was observed to be 1217 kg/m$^3$ and 665 kg/m$^3$, accordingly. Furthermore, for a packed bed, bed porosity was 0.46. Adsorption is a surface phenomenon; the surface characteristics of the adsorbent assume an important influence on adsorption procedure [14]. Figure 1 shows the SEM image of fresh CSC at 1000 times magnification which was used to identify the morphology of fresh CSC. Surface is mostly irregular with cavities, which can facilitate ion binding active sites. Porous structure suggests the possibility of intraparticle diffusion in adsorption process.

FTIR analysis shown in figure 2 is essentially used to identify the useful functional groups on the surface of CSC before and after adsorption of Ni$^{2+}$. The sharp adsorption peaks, observed at 3430 - 3420, 2925 - 2855, 1570 - 1580 and 1164 cm$^{-1}$ are matching with groups as -OH stretching, -CH stretching, -C=O stretching and -CO stretching, respectively. The broad peak obtained between 1400 cm$^{-1}$ and 1160 cm$^{-1}$ represents -CH and -OH bending groups. After adsorption, height of the peaks has reduced as cations have chemically bound to functional groups. Surface area, pore size distribution and functional groups of the adsorbent determine the efficiency of adsorption process [4].

4.2. Adsorption Studies

4.2.1. Adsorption Equilibrium. Figure 3 shows the variation of % removal of adsorbate with initial adsorbate concentration in liquid phase. Ion removal percentage decreases when the initial ion concentration increases. The ratio of surface-binding sites to the initial metal ions in the solution is high in low ion concentrations. Therefore, metal ions may freely interact with the active sites and can be removed from the solution. At high concentrations, as adsorbent active sites get saturated, percentage ion removal decreases.

![Figure 1. SEM image of fresh CSC.](image1)

![Figure 2. FTIR analysis results of (a) fresh and (b) Ni$^{2+}$ adsorbed CSC.](image2)

![Figure 3. % removal of Ni$^{2+}$ with varying initial concentration: 2 g of CSC mixed with 200 mL of solution, room temperature 30 °C.](image3)

![Figure 4. Langmuir model and experimental data for adsorption of Ni$^{2+}$ onto CSC.](image4)
Predicted adsorption isotherm and isotherm parameters of Langmuir model are shown in figure 4 and table 1, respectively. Experimental data were hardly fitted to Freundlich model ($R^2 = 0.4299$) compared to Langmuir model ($R^2 = 0.9238$). Furthermore, table 2 consists of results of several adsorption isotherm studies carried out with coconut shell derivatives. As compared with maximum adsorption capacities of $\text{Ni}^{2+}$ adsorption, $q_m$ obtained in present study is lower than literature values. However, previous studies indicate that, CSC have higher maximum adsorption capacities for different metal ions subsequent to chemical activation.

| Table 1. Estimated numerical values for the Langmuir adsorption isotherm |
|-----------------------------|-----------------------------|
| Langmuir Isotherm Parameter | Value                       |
| $q_m$                      | 0.5777                     |
| $K_L$                      | 0.1344                     |
| $R^2$                      | 0.9238                     |

| Table 2. Maximum adsorption capacities obtained for different coconut shell derivatives |
|-----------------------------------------------|-----------------------------|
| Adsorbent                                | Adsorbate  | $q_m$ (mg/g) | Reference |
| Coconut shell char                        | $\text{Ni}^{2+}$ | 0.58        | Present work |
|                                            | $\text{Cr}^{6+}$ | 2.18        | [11]        |
| Chitosan coated coconut shell char        | $\text{Cr}^{6+}$ | 3.65        | [15]        |
| Chitosan coated coconut shell carbon      | $\text{Zn}^{2+}$ | 50.93       | [7]         |
| Acid treated coconut shell carbon         | $\text{Zn}^{2+}$ | 45.14       | [7]         |
| KOH treated coconut shell carbon          | $\text{Pb}^{2+}$ | 112.36      | [7]         |
|                                            | $\text{Pb}^{2+}$ | 8.65        | [7]         |
|                                            | $\text{Ni}^{2+}$ | 2.13        | [7]         |
|                                            | $\text{Cu}^{2+}$ | 0.84        | [16]        |
|                                            | $\text{Fe}^{2+}$ | 0.71        | [17]        |
| Coconut shell powder                      | $\text{Cu}^{2+}$ | 5.35        | [7]         |
|                                            | $\text{Pb}^{2+}$ | 3.07        | [7]         |
| Green coconut shell powder                | $\text{Ni}^{2+}$ | 2.98        | [7]         |
|                                            | $\text{Zn}^{2+}$ | 0.75        | [7]         |
| NaOH treated green coconut shell powder   | $\text{Ni}^{2+}$ | 2.98        | [7]         |

4.2.2. Adsorption Kinetics. Figure 5 shows the plot of $C_t/C_0$ vs t, where $C_t$ and $C_0$ are solute concentration in liquid phase at time t and time 0. It can be seen a rapid adsorption initially. Thus, within initial 3 minutes solution concentration has reached almost the equilibrium concentration. However, while reaching to the equilibrium, desorption can be dominant occasionally.

**Figure 5.** Variation of $C_t/C_0$ (instant/initial adsorbate concentration in liquid phase) with time: 50 mg $\text{Ni}^{2+}$/L, 20 g of CSC mixed with 2 L of solution, room temperature 30 °C.

**Figure 6.** Lagrange's kinetic models for adsorption of $\text{Ni}^{2+}$ onto CSC: 50 mg $\text{Ni}^{2+}$/L, 20 g of CSC mixed with 2 L of solution, room temperature 30 °C.
Table 3. Experimental and calculated equilibrium adsorption capacities and other kinetic model constants for Ni\textsuperscript{2+} adsorption onto CSC.

|                      | Experimental qₑ (mg/g) | 0.6050 |
|----------------------|------------------------|--------|
| **Pseudo First-Order Model** |                        |        |
| k₁ (1/min)           |                        | 0.1690 |
| qₑ (mg/g)            |                        | 0.1485 |
| R²                   |                        | 0.3769 |

| **Pseudo Second-Order Model** |                        |        |
| k₂ (g/mg min)              |                        | 1.5714 |
| qₑ (mg/g)                  |                        | 0.6212 |
| R²                         |                        | 0.9969 |

The experimental data of the adsorption kinetics were fitted to two Lagrange kinetic models - pseudo first-order model and pseudo second-order model as shown in figure 6 and, determined parameters for kinetic models are presented in table 3. There is a considerable difference between qₑ value obtained by experimental data and calculations in pseudo first-order model. However, calculated qₑ value of pseudo second order on par with experimental qₑ value. Further, coefficient of determination (R²) is closer to unity in pseudo second-order model. Hence, it can be determined that Ni\textsuperscript{2+} adsorption on to CSC behave better according to Lagrange’s pseudo second-order kinetic model. The pseudo second-order model assumes that two surface sites can be occupied by one adsorbate ion. Therefore, it is more appropriate to model the adsorption kinetics of divalent metal ion as Ni\textsuperscript{2+} [16]. Furthermore, fitting to pseudo second-order model suggests that adsorption is a chemisorption [19].

Mechanisms of the adsorption process were studied via intraparticle diffusion model, by plotting the graph of qₑ vs t\textsuperscript{0.5} as shown in figure 7. When intraparticle diffusion is the sole rate limiting step, plot goes through the origin. If film diffusion is also involved, there is an intercept, which gives an implication/indication on the thickness of film boundary layer [13]. According to figure 7, it is clear that adsorption process has two steps in adsorption. The initial sharper section is connected to faster external diffusion or faster mass transfer through the boundary layer and/or adsorption on the solid surface. Subsequent gradual adsorption stage is corresponding to the slow intraparticle diffusion [7][20]. Therefore, it can be concluded that, as the adsorption process reach equilibrium, the rate of adsorption will control by intraparticle diffusion.

Moreover, the plot of Bt vs t shown in figure 8, which is related to film diffusion model suggests that boundary layer around the adsorbent is the primary barrier to diffusion. According to this model, if intraparticle diffusion is the rate controlling resistance, line should pass through the origin [21]. Considering that experimental data have fitted to film diffusion model, it can be assumed that film resistance is the rate controlling factor of Ni\textsuperscript{2+} adsorption on to CSC.
4.3. Desorption studies

The study of desorption can successfully prevent the emergence of secondary pollution by waste adsorbents. At present, common adsorbent regeneration methods are solvent extraction, calcination, and bioremediation [10]. Figure 9 shows the % adsorbate desorbed by each desorption agent. Sulfuric acid is the best desorption agent with 44% desorption of adsorbed Ni\textsuperscript{2+}. This could be due to the protonation of the adsorbent surface under acidic conditions, which allows desorption of cations. However, complete desorption is prevented when low concentrations of desorbing agents result in the surface precipitation of metal ions [22]. As highest desorption is even lower than 50%, it again suggests that adsorption is a chemisorption process. Being basic, NaOH is the poorest desorption agent. As well, distilled water is a poor agent. According to results it can be identified that more ionic and acidic the agent, desorption ability is higher.

5. Conclusion

According to the study, it can be suggested that high dose of CSC is required for effective removal of heavy metals as in commercial scale, percentage ion removal should be at least higher than 80%. The isotherm results have shown that equilibrium data was best obeyed to Langmuir monolayer model. According to Lagrange’s adsorption kinetic models, processes was best fitted to pseudo second-order model suggesting adsorption is a chemisorption process. Furthermore, it was identified that adsorption mechanism has two steps as external diffusion and intraparticle diffusion, while both steps influence the rate of adsorption. Desorption studies as well indicate that adsorption is chemisorption and acids are the most suitable desorption agent. However, AC derived from coconut shell is one of the best commercial AC. Hence study can extend further to examine adsorption characteristic of CSC treated by various chemicals and temperatures.

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