Isotherm adsorption studies of Ni(II) ion removal from aqueous solutions by modified carboxymethyl cellulose hydrogel

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Abstract. This paper reports the removal of nickel ions from aqueous solutions using carboxymethyl cellulose-graft-poly(acrylic acid) CMC-g-PAA hydrogel as an adsorbent. The hydrogel was prepared through graft copolymerization of acrylic acid monomer onto a carboxymethyl cellulose backbone in the presence of N,N'-methylenebisacrylamide as a crosslinking-agent using benzoyl peroxide initiator system. Isotherm for the adsorption of nickel on CMC-g-PAA hydrogel was developed and the equilibrium data fitted to the Langmuir and Freundlich isotherm models. The result showed that at pH of 5 and shaker speed of 100 rpm, Freundlich model was better fitted than Langmuir model, of which \( R^2 = 0.999 \) and \( R^2 = 0.935 \), respectively. The constant of Langmuir model was \( K_L \) value = 0.003 and \( q_{\text{max}} \) = 1000 mg/g, whereas the constant of Freundlich model \( n = 1.2 \) and \( K_F = 4.614 \). The CMC-g-PAA hydrogel before and after Ni(II) adsorption were characterized using scanning electron microscopy (SEM) and Fourier transform infrared (FTIR).

1. Introduction

Environmental pollution by toxic metals arises from industries, agricultural effluents and waste disposal from various sources. Many industries such as metal plating facilities, mining operations and tanneries discharge waste containing heavy metal ions.

As pollutants, heavy metals were intensively studied due to their significance from the point of view of persistence and toxicity. These toxic metals can cause accumulative poisoning, cancer, and brain damage when present at above the tolerance levels. The agencies for the environmental monitoring have set permissible limits for heavy metals levels in drinking water because of their harmful effects. The removal and rapid decontamination of heavy metals such as Cd, Pb, Cu, Ni, Hg become very important for the environmental remediation [1]. The World Health Organization has recommended strict controls on the percentages of various heavy metals in effluent waters [2].

Hydrogels are water-swollen crosslinked network of hydrophilic polymer. Due to the hydrophilic groups in their backbone, hydrogels can imbibe large quantities of water and swells. The degree of hydrogel swelling is related to the degree of crosslinker, ionic strength of the solution, temperature, pH, and the presence and extent of hydrophilic groups such as –OH, -COOH, -NH₂, -CONH₂, and SO₃H. These functional groups in the hydrogel networks can be utilized for the toxic metal ion removal. Hydrogels can also be modified with new functionalities or prepared as composites with clays and with other materials to increase the metal ion absorption capacities [3–6].
Cellulose is renewable, and due to its abundance in nature it affords material for cost-effective hydrogel and ion exchange technologies. Cellulose and its derivatives have been used in metal ion adsorption. Sodium carboxymethyl cellulose (CMC) is an important biopolymer due to its high degree of solubility in water, biocompatibility, nontoxicity, and low cost [7]. Grafted cellulose products, when used as ion exchangers, have advantages over conventional ion exchangers due to chemical resistance, low cost of preparation, and they also offer considerable hydrophilic surface area. Acrylic acid and acrylamide monomers have been successively grafted onto a cellulose backbone. Grafting is a simple technique to incorporate desired active functional groups on the backbone of a polymer for absorption metal ions [8–10].

Adsorption techniques have been proved to be an excellent method for waste water, offering advantages over conventional processes. It is now recognized that adsorption using low cost-adsorbents is an effective and economic method for the removal of heavy metals in waste water. However, low-cost adsorbents with high adsorption capacities are still under development to reduce the adsorbent dose and minimize disposal problems. Much attention has recently been focused on biopolymers as bioadsorbent. They are naturally produced by all living organisms. Bioadsorbents are a useful option since they have no adverse impact on human or environmental health [11].

Isotherm adsorption models have been used in waste stream treatment to predict the ability of a certain adsorbent to remove a pollutant down to a specific discharge value. When a mass of adsorbent and waste stream are in contact for a sufficiently long time, equilibrium between the amount of pollutant adsorbed and the amount remaining in solution will develop. The Langmuir and Freundlich isotherm models are only applicable to batch adsorption systems where sufficient time is provided to allow equilibrium occurs between the pollutant in solution and the pollutant adsorbed on the media. During the flow through the adsorbent, a large amount of pollutants is expected to come into contact with active surface sites and thus be retained on the surface of the adsorbing media [12]. The Langmuir and Freundlich equations are most widely used. The Langmuir model assumes that the adsorption of metal ions is a process occurring on a homogenous surface without any interaction between adsorbed ions. The adsorption proceeds until a complete monolayer is formed. The Freundlich model is based on adsorption on a heterogeneous surface [1].

The aim of this work was to predict the ability of a certain adsorbent to remove a pollutant down to a specific discharge value by the Langmuir and Freundlich isotherm adsorption models.

2. Experimental

2.1. Material
Analytical reagent grade of nickel nitrate (\(\text{Ni(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}\)) was used as a source of \(\text{Ni(II)}\). Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were used pH adjustment. All these chemical were purchased from E-Merck Company Inc., Germany and used without further purification. Deionized water was used in this work. Hydrogel CMC-g-PAA was used as the adsorbent. \(\text{N,N'}\text{-methylenbisacrylamide was used as a crosslink agent whereas benzoyl peroxide was used as an initiator.}\)

2.2. Method
2.2.1. Preparation of CMC-g-PAA hydrogel. The graft copolymers CMC-g-PAA were synthesized by free radical and solution polymerization. CMC was dissolved in distilled water then stirred and purged by passing nitrogen gas. The solution was slowly heated up to the desired temperature then added with benzoyl peroxide (BPO) initiator and methylenebisacrylamide (MBA) crosslinker agent. The reaction was continued until the desired time and process of polymerization was achieved. The hydrogel adsorbent was oven-dried and washed with distilled water and acetone. This adsorbent was available from a previous study [13].
2.2.2. Nickel ions sorption. The experiments were carried out in 250 mL volumetric flasks, each using 100 mg of CMC-g-PAA hydrogel and 100 mL of 10 mg/L nickel-rich waste water. The flasks were placed on a Gallenkamp Orbital Incubator Shaker running at 300 rpm, 30°C for 10 h. Adsorption of nickel ion was determined by using Atomic Absorption Spectrophotometer (AAS) Varian Type.

The amount of Ni\(^{2+}\) ions adsorbed by the CMC-g-PAA hydrogel adsorbent \(Q_e\) was calculated for each run by the following equation:

\[
Q_e = \frac{(C_0 - C_e)W}{L} \tag{1}
\]

where \(Q_e\) (mg/g) was the adsorption capacity; \(C_0\) (mg/L) was the initial concentration of Ni\(^{2+}\); \(C_e\) (mg/L) was the equilibrium concentration of Ni\(^{2+}\); \(V\) (L) was the volume of the solution of Ni(II), and \(W\) (g) was the weight of adsorbent added [14, 15].

2.2.3. Equilibrium isotherm.

2.2.3.1. The Langmuir isotherm model. The Langmuir isotherm model equation was:

\[
q = q_{max} \left( \frac{C_e}{K_L + C_e} \right) \tag{2}
\]

where \(q\) (mg/g) was the amount of heavy metal ions adsorbed onto the unit mass of the polymeric beads; \(K_L\) was the Langmuir equilibrium constant which is related to the affinity of binding sites; \(C_{eq}\) was the equilibrium Ni\(^{2+}\) ion concentration, and \(q_{max}\) was the maximum adsorption capacity (theoretical monolayer saturation capacity) [16].

The main characteristics of the Langmuir equation, constants \(K_L\) and \(q_{max}\), could be determined from a linearized form of the Langmuir equation as follows:

\[
\frac{C_e}{q_e} = \frac{1}{q_{max}} \frac{1}{K_L} + \frac{C_e}{q_{max}} \tag{3}
\]

Therefore, a plot of \(C_e/q_e\) versus \(C_e\) gave a straight line with slope of \(1/q_{max}\) and intercept of \(1/(K_L \times q_{max})\).

The Langmuir isotherm was used to describe observed sorption phenomena. The Langmuir isotherm applies to adsorption on completely homogenous surfaces with negligible interaction between adsorbed molecules [17].

2.2.3.2. The Freundlich isotherm model. The Freundlich isotherm model was based on adsorption on a heterogeneous surface, developed an empirical equation [1]:

\[
q_e = K_f C_e^{1/n} \tag{4}
\]

where \(q_e\) is the adsorption (mg/g); \(C_e\) is the concentration of adsorbate in the solution (mg/L); \(K_f\) and \(n\) were empirical constants that are characteristics of the system, indicating the adsorption capacity and the adsorption intensity, respectively. The above equation can be linearized as the following form, also used to confirm the applicability of the model [1]:

\[
\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{5}
\]

where \(K_f\) was the measure of sorption capacity, and \(1/n\) was the sorption intensity. The plot of \(\ln q_e\) versus \(\ln C_e\) had a slope with the value of \(1/n\) and an intercept magnitude of \(\ln K_f\).

2.2.4. Fourier transform infrared spectroscopy (FTIR) analysis. FTIR analysis in the solid phase was performed using a FTIR spectrometer (Perkin Elmer). Adsorbent powders were blended with IR-grade KBr in an agate mortar and pressed into tablets. Spectra of the CMC-g-PAA hydrogel before and after Ni(II) sorption, and after desorption were recorded between 4000 and 400 cm\(^{-1}\).

3. Results and Discussion

3.1. Adsorption isotherm

To investigate the adsorption capacity as a function of aqueous concentration of the heavy metals, adsorption isotherms are widely employed for fitting the data using representation of the adsorption (expressed as mg metal adsorbed per g of solid adsorbent) versus concentration of the heavy metals at
equilibrium $C_e$. Adsorption isotherm for Ni$^{2+}$ ions on different CMC-g-PAA hydrogel are shown in Figure 1.

![Figure 1. Adsorption isotherms for Ni$^{2+}$ ions on CMC-g-PAA hydrogel.](image)

In batch adsorption processes, the initial metal ion concentration provided an important driving force to overcome the mass transfer resistance of Ni(II) ions between the aqueous solution and the CMC-g-PAA hydrogel surface. As a result, the amount of Ni(II) ions adsorbed was expected to be higher with a higher initial metal ions concentration, hence improving the adsorption process [14]. From Figure 1, we found that when the initial Ni(II) ion concentration increased from 4.18 to 166.11 mg/L, the uptake capacity of the CMC-g-PAA hydrogel for Ni(II) ions increased from 14.18 to 366.11 mg/g. This could be explained from two aspects. Firstly, the higher initial Ni(II) ion concentration increased the driving force to overcome the mass transfer resistance of Ni(II) ions between the aqueous and solid phases resulting in a higher probability of collision between the Ni(II) ions and the CMC-g-PAA hydrogel. Secondly, the increase of Ni(II) ion uptake capacity of the CMC-g-PAA hydrogel for Ni(II) ions with increasing initial Ni(II) ion concentration might also be attributed to a more intense interaction between the Ni(II) ions and the CMC-g-PAA hydrogel [14].

![Figure 2. The Langmuir adsorption isotherm for Ni$^{2+}$ ion adsorption by CMC-g-PAA hydrogel (adsorbent dosage 100 mg/L; pH 5; initial metal concentration 10 mg/L; 30°C).](image)

3.2. Langmuir model
The Langmuir equation has been frequently used to give the sorption equilibrium. The Langmuir model assumes that the uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between the adsorbed ions. All surface sites are alike and can only accommodate one
adsorbed molecule, the ability of a molecule to be adsorbed on a given site is independent of its neighboring sites occupancy, adsorption is reversible, and the adsorbed molecule cannot migrate across the surface or interact with neighboring molecules [9]. To get the equilibrium data, initial metal concentrations were varied while the adsorbent mass in each sample was kept constant [11]. The linearized Langmuir isotherm allows the calculation of adsorption capacities and Langmuir constant by Equation (3).

The adsorption constants of Langmuir isotherm model parameters, \( q_{\text{max}} \) and \( K_L \), were estimated from the intercept and slope of \( C_e/q_e \) versus \( C_e \) according to Equation (3) and obtained as 1000 mg/g related to adsorption capacity and 0.003 l/mg related to the rate of adsorption, respectively. The correlation coefficient of Langmuir isotherm \( (R^2) \) was 0.935 (Figure 2), which shows correlation or linear relationship. The relationship becomes more linear with \( R^2 \) values closer to 1. Thus, it was found that adsorption of Ni(II) onto CMC-g-PAA correlated well with Langmuir equation [1,11].

3.3. Freundlich model

The Freundlich isotherm was originally of an empirical nature, but was later interpreted as sorption to heterogeneous surfaces or surface supporting sites of varied affinities. It is assumed that the stronger binding sites are occupied first and that binding strength decreases with increasing degree of site occupation. The Freundlich isotherm can describe the adsorption of organic and inorganic compound on a wide variety of adsorbents [9].

On average, a favorable adsorption tends to have Freundlich constant \( n \) between 1 and 10. Larger value of \( n \) (smaller value of \( 1/n \)) implies a stronger interaction between the adsorbent and the adsorbate while \( 1/n \) equal 1 indicates linear adsorption leading to identical adsorption energies for all sites. Linear adsorption generally occurs at a very low solute concentration and low loading of the adsorbent [9].

The value of \( n \) of this model fell in the range of 1–10, indicating favorable biosorption. The numerical value of \( 1/n \) < 1 indicated that adsorption capacity was only slightly suppressed at lower equilibrium concentration. This isotherm did not predict any saturation of the adsorbent by the adsorbate. Thus infinite surface coverage was predicted mathematically, indicating multilayer adsorption on the surface. The present study results indicated that the Freundlich model fit the experimental data well.

In this study Freundlich model was the best-fit isotherm for adsorption of Ni(II) to CMC-g-PAA hydrogel. Freundlich isotherm model parameters \( K_F \) and \( n \), calculated according to Equation (5), were 4.614 for adsorption capacity and 1.2 for intensity of the adsorption. The correlation coefficient of Freundlich isotherm \( (R^2) \) was 0.999 (Figure 3).

![Figure 3. The Freundlich adsorption isotherm for Ni\(^{2+}\) ion adsorption by CMC-g-PAA hydrogel (adsorbent dosage 100 mg/L; pH 5; initial metal concentration 10 mg/L; 30°C.](image-url)
Table 1. Parameter for the Langmuir and Freundlich adsorption isotherms for Ni\(^{2+}\) on the CMC-g-PAA hydrogel adsorbent.

| Metal    | Adsorbent dosage (g/L) | Langmuir isotherm constants | Freundlich isotherm constants |
|----------|------------------------|-----------------------------|-------------------------------|
|          |                        | \(K_L\) \((1/\text{mg})\) | \(q_{\text{max}}\) \((\text{mg/g})\) | \(R^2\) | \(K_F\) \((1/\text{g})\) | \(n\) | \(R^2\) |
| Ni(II)   | 1                      | 0.003                       | 1000                          | 0.935   | 4.614                  | 1.2  | 0.999 |

The characteristics of Langmuir and Freundlich equations are shown in Table 1. In Table 1, Freundlich model seems to fit the experimental data well. It has been stated that magnitude of the exponent \(1/n\) gives an indication of the favorability or adsorption capacity of the solid adsorbent for the studied adsorbate. Values \(n > 1\) represented favorable adsorption conditions [1,15].

3.4. FTIR spectrum

Figure 4 shows the FTIR spectra of acrylic acid, the CMC-g-PAA hydrogel before adsorption, hydrogel after adsorption, and hydrogel after desorption. For FTIR spectra of acrylic acid (a) and cellulose adsorbent (b), there was a small shift of the ring vibration peak at 1712 \text{cm}^{-1}, 1626 \text{cm}^{-1}, 1425 \text{cm}^{-1}, 1299 \text{cm}^{-1}, 1240 \text{cm}^{-1}, 1060 \text{cm}^{-1}, and 983 \text{cm}^{-1} in acrylic acid to 1708 \text{cm}^{-1}, 1550 \text{cm}^{-1}, 1434 \text{cm}^{-1}, 1224 \text{cm}^{-1}, 1163 \text{cm}^{-1}, 1068 \text{cm}^{-1}, and 1002 \text{cm}^{-1} for carboxymethyl cellulose, which suggested a successful grafting. A new band at 1550 \text{cm}^{-1} was related to the stretching vibration of –C=O. The peaks at 1434 \text{cm}^{-1} and 1163 \text{cm}^{-1} in the spectrum of CMC-AA (acrylic acid) adsorbent were related to the stretching vibration and symmetrical stretching of –COO groups [19].

Figure 4. IR spectra hydrogel adsorbent: (a) acrylic acid; (b) CMC-g-PAA hydrogel before adsorption; (c) hydrogel after adsorption; (d) hydrogel after desorption.
To identify the possible functional groups on cellulose adsorbent involved in the binding of Ni(II), FTIR spectra were obtained before (b) and after (c) metal adsorption. If a ligand coordinated to a metal, the energy of the ligand material would most likely be perturbed, leading ultimately to subtle shifts in the absorption peaks in the FTIR spectra. These FTIR absorption bands were usually shifted to lower or higher frequencies. There was a small shift of the ring vibration peak at 1755 cm$^{-1}$, 1550 cm$^{-1}$, 1456 cm$^{-1}$, 1344 cm$^{-1}$, 1163 cm$^{-1}$, 1002 cm$^{-1}$, and 802 cm$^{-1}$ in carboxymethyl cellulose adsorbent to 1735 cm$^{-1}$, 1560 cm$^{-1}$, 1454 cm$^{-1}$, 1434 cm$^{-1}$, 1164 cm$^{-1}$, 1066 cm$^{-1}$, and 806 cm$^{-1}$ for Ni(II) loaded adsorbent. There were new bands at 1735 cm$^{-1}$ (C=O stretching), 1454 cm$^{-1}$ (CH$_2$ bending) and 1164 cm$^{-1}$ in the spectrum of CMC-g-PAA adsorbent that were related to the stretching vibration and symmetrical stretching of –COO group [20].

3.5. SEM image

SEM images of carboxymethyl cellulose adsorbent before adsorption, after adsorption and after desorption are shown in Figure 5.

![SEM micrograph of CMC-g-PAA hydrogel adsorbent: (a) before adsorption; (b) after adsorption; (c) after desorption.](image)

The SEM micrograph of hydrogel adsorbent in Figure 5 (a) showed fractured and rough surface morphology that provided better adsorption sites. It can be observed that the surface of the adsorbent after adsorption (b) changed, and their visible pores of the adsorbent had disappeared or had been filled up. Also, it can be seen that the surface of adsorbent was back to become fractured and rough again after desorption process in three times [20].

4. Conclusion

The Freundlich isotherm model was represented by $K_F$ and $n$ empirical constants as characteristics of the system; $K_F$ represent the adsorption capacity and $n$ was indicating the intensity of adsorption. The Freundlich model was the best-fit isotherm for adsorption of Ni(II) to CMC-g-PAA hydrogel adsorbent with the correlation coefficient of Freundlich isotherm ($R^2$) was 0.999 and the magnitude of the exponent $1/n$ gave an indication of the favorability or adsorption capacity of the solid adsorbent for the Ni(II) adsorbate. Values $n > 1$ represented favorable adsorption conditions.

The Langmuir isotherm model indicated the intercept $1/(q_{max}K_L)$ and slope $(1/q_{max})$ of $C_e/q_e$ versus $C_e$. The adsorption constant of Langmuir isotherm model parameters are $q_{max}$ and $K_L$. $q_{max}$ is related to adsorption capacity and $K_L$ is related to rate of adsorption. The Langmuir isotherm was a good fitting model for CMC-g-PAA hydrogel adsorbent with correlation coefficient ($R^2$) of 0.935.

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