Adsorption of Chromium (III) on Melamine: Kinetic, Isotherm, Thermodynamics and Mechanism Analysis

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Abstract. Melamine as single absorbance had been investigated in heavy metal ions removing and it showed good adsorption performance. This paper focused on the chromium (III) remove from wastewater by adsorption with melamine. The results showed that the melamine had a great adsorption surface area of 8.71 m²/g and high adsorption capacity (2843 mg/g) at removal efficiency of chromium (III) (98.63%) within 60 min at n (melamine)/n (chromium)=1.5 and reaction temperature at 90 ℃. The adsorption process was described by Langmuir isotherm and the kinetic process was fitted well with pseudo-second-order model. The adsorption process was a spontaneous, endothermic and physiosorption process according to the thermodynamic analyzing results. This study provided a good evidence for successful application of melamine in adsorptive removal of chromium (III) from wastewater.

1. Introduction

Nowadays, heavy metal pollutions had attracted much attention as it caused hazardous impact on environment and human life [1]. Various methods such as membrane filtration [2, 3], chemical precipitation [4], ion-exchange [5] and electrochemical method [6, 7] had been applied to remove heavy metal ions. Some existing methods were limited as unfavorable cost-effectiveness with large amount wastewater in industrial application. Adsorption was introduced as an alternative because of its simple operation without producing by-products, high efficiency and low input, especially when a suitable absorbance is available [8-13]. The design and fabrication of absorbance with advantageous properties are of great significance, including high adsorption rate, good reusability, large adsorption capacity, easy operation for absorbance collection and separation, and cost-effectiveness [11-18].

Metal-organic frameworks (MOFs) had attracted much more attention on adsorption because of their high porosity and specific surface areas [19]. MOFs as effective absorbance had showed great performance in removing heavy metal ions, like Pb (II) removal with Zn-MOF [20], Dy-MOF [21] and Fe-MOF-derived absorbance [22], Hg (II) removal with Ni-MOF [23], Cr (VI) removal with Ni-MOF [24] and Ag-MOF [25], Cd (II) removal with Ca-MOF [26], etc.

Melamine was used for vanadium ions adsorption in the wastewater and the results showed that it played good performance, the removal efficiency was nearly 100% and the adsorption capacity was about 1428.57 mg/g [27, 28].

Chromium was a high toxicity heavy metal ion and was classified as Group 1 (carcinogenic to humans). Some methods had been applied to remove chromium, such as precipitation, electro coagulation and so on. This paper focused on the adsorption performance of chromium on
The experiments are evaluated at different reaction temperatures, dosage of melamine, and reaction time.

2. Materials and Methods

2.1 Adsorption experiments

The chromium solution was prepared by dissolving a certain amount of chromium sulfate in distilled water. Batch adsorption experiments were conducted by adding melamine and chromium sulfate solution into a 250 mL beaker with a thermostatic mixing water bath pot at a stirring rate of 500 rpm. Various experimental parameters on chromium removal, such as reaction time, adsorbent dosage, and reaction temperature were investigated.

The concentration of Cr (III) in the filtrate was measured by ICP-OES. And the Cr (III) in the adsorbent phase at equilibrium (Qe, mg/g) and at reaction time t (Qt, mg/g) were calculated using Equation (1) and Equation (2) [28], and the removal efficiency of chromium (III) (η) was calculated using Equation (3).

\[
Q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)
\]

\[
Q_t = \frac{(C_0 - C_t) \times V}{m} \quad (2)
\]

\[
\eta = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (3)
\]

Where, \(C_0\), is the initial concentration of chromium (III), mg/L; \(C_e\), is the equilibrium concentration of chromium (III), mg/L; and \(C_t\), is the concentration of chromium (III) at different time t, mg/L; \(V\) is the volume of the chromium solution, L; and \(m\) is the mass of the melamine used in the experiment, g.

2.2 Kinetics, isotherm and thermodynamics models

Pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models were fitted in Equation (4) and (5) [29, 30] to analyze the experimental data.

\[
\ln(Qe - Qt) = \ln(Qe) - k_t \ln(t) \quad (4)
\]

\[
\frac{1}{Qt} = \frac{1}{k_t Qe^2} + \frac{1}{Qe} \quad (5)
\]

In this study, Langmuir isotherm and Freundlich’s isotherm models expressed as Equation (6) and (7) [31] were applied to analyze the experimental data.

Langmuir equation: \[
\frac{C_e}{Qe} = \frac{1}{Q_K} + \frac{C_e}{Q_L} \quad (6)
\]

Freundlich equation: \[
\ln Qe = \ln K_f + \frac{1}{n} \ln C_e \quad (7)
\]

3. Results

3.1 Physicochemical characterization of melamine

The results showed in Figure 1 indicated that melamine was the melamine showed a large specific surface area (8.71 m²/g) and adsorption pore volume (0.0040 mL/g). The pore size and pore volume distribution were summarized in Figure 2. The results indicated that melamine had narrow pore size distribution as the curve peak appeared at 10 nm.
3.2 Effect of operating conditions on chromium adsorption

3.2.1 Effect of dosage of melamine

Melamine as an absorbance was used to remove Cr (III) from the wastewater. The dosage of melamine had significant effect on the removal efficiency of chromium (III) during the process. The effect of dosage of melamine (molar ratio of melamine to chromium, $n(\text{C}_3\text{H}_6\text{N}_6)/n(\text{chromium})$) on the removal efficiency of Cr (III) was conducted as other conditions kept as constant: concentration of Cr (III) was 1000 mg/L, $t = 60$ min, and $T = 90$ °C. The results showed in Figure 3 indicated that the removal efficiency of Cr (III) was increased with the increasing of dosage of melamine. The removal efficiency of Cr (III) firstly increased linearly, which increased from 49.00% at $n(\text{C}_3\text{H}_6\text{N}_6)/n(\text{chromium})$ = 0.25 to 92.80% at $n(\text{C}_3\text{H}_6\text{N}_6)/n(\text{chromium})$ = 0.75, and then increased slowly, up to 98.63% at $n(\text{C}_3\text{H}_6\text{N}_6)/n(\text{chromium})$ = 1.50.

Figure 3 Effect of dosage of melamine on the removal efficiency of chromium
3.2.2 Effect of reaction temperature

The results showed in Figure 4 summarized the effect of reaction temperature and indicated that the removal efficiency of Cr (III) and adsorption capacity increased with the increasing of reaction temperature. High temperature was favorable for the adsorption process as the adsorption process of Cr (III) was endothermic. Other way, the diffusion rate of Cr (III) ions increased with the increase of temperature, which was beneficial for the contact of Cr (III) and melamine, and contributing to adsorb of Cr (III). The removal efficiency of Cr (III) was up to 98.63% at T = 90 ℃, and at the same time, the adsorption capacity of melamine was up to 2843 mg/g.

![Figure 4 Effect of reaction temperature on the removal efficiency of chromium](image)

3.2.3 Effect of reaction time

Figure 5 showed the effect of reaction time on the removal efficiency of Cr (III) and adsorption capacity of melamine at various reaction temperatures ranged from 45 ℃ to 90 ℃. The removal efficiency and adsorption capacity increased along with reaction time and reaction temperature. At the beginning of the adsorption process, the vacant sites on melamine was enough, the Cr (III) ions could easily react with the active sites and been adsorbed. With the increasing of reaction time, the adsorption rate decreased and the removal efficiency increased slowly as the adsorption sites of melamine reached its saturation. The removal efficiency of Cr (III) was up to 90.29% within 15 min and the adsorption capacity of 2268.55 mg/g, which indicated that the melamine was an effective absorbance.

![Figure 5 Effect of reaction time on the removal efficiency of chromium](image)
3.3 Kinetics Analysis

The experiments about adsorption of Cr (III) onto the melamine at different reaction temperatures ranged from 45 ℃ to 90 ℃ were studied. The correlation coefficients ($R^2$), $k_1$, $k_2$ and $Q_e$ values were detailed in Table 1 and Figure 6 (a-b). The $Q_e$ of PFO model was 867 mg/g at 90 ℃, while the $Q_e$ of PSO model was 3930 mg/g which was close to the experimental results discussed above. And the $R^2$ of the PSO model was 0.9995. It was concluded that the chromium (III) adsorption onto the melamine was followed PSO model.

Table 1 Correlation coefficients of PSO and PFO

| T   | $Q_e$  | $K_1$  | $R^2$ | $Q_e$  | $K_2$  | $R^2$ |
|-----|-------|--------|-------|-------|--------|-------|
| 45℃ | 525   | 0.0715 | 0.8246| 3610  | 2.46x10^{-4} | 0.9700|
| 60℃ | 253   | 0.0323 | 0.8358| 3878  | 4.97x10^{-4} | 0.9972|
| 75℃ | 718   | 0.0328 | 0.9592| 3837  | 1.68x10^{-4} | 0.9997|
| 90℃ | 867   | 0.0188 | 0.9965| 3930  | 1.43x10^{-4} | 0.9995|

3.4 Adsorption isotherms

Figure 7 and Figure 8 showed the Langmuir isotherms model and Freundlich isotherm model for chromium (III) adsorption at different reaction temperatures, respectively. The results were showed in Table 2. The $n$ of Cr (III) adsorption onto the melamine was 2.98, 7.76, 17.57 and 17.98 at 45 ℃, 60 ℃, 75 ℃ and 90 ℃, respectively, which indicated that Cr (III) was easily being adsorbed on melamine. The Langmuir isotherm model was more suitable for describing the adsorption of Cr (III) as the correlation coefficients ($R^2$) of Langmuir model was larger. Moreover, the $Q_0$ calculated from the Langmuir isotherm was 1591 mg/g, 2043 mg/g, 2336 mg/g and 2201 mg/g, which closed to the experimental data, and it was another evidence proved the adsorption of chromium (III) onto the melamine fitted well with the Langmuir isotherm model.
Figure 7 Langmuir isotherms for the adsorption of chromium with melamine: at different temperatures: a) 45°C;  b) 60°C; c) 75°C; d) 90°C

Figure 8 Freundlich isotherms for the adsorption of chromium with melamine at different temperatures: a) 45°C;  b) 60°C; c) 75°C; d) 90°C

| T     | Q0   | K_L  | R^2   | K_F  | n     | R^2   |
|-------|------|------|-------|------|-------|-------|
| 45°C  | 1591 | 0.0419 | 0.9700 | 12115 | 17.98 | 0.9700 |
| 60°C  | 2043 | 0.1414 | 0.9938 | 4161  | 17.57 | 0.9972 |
| 75°C  | 2336 | 0.0006 | 0.9984 | 3057  | 7.76  | 0.9997 |
| 90°C  | 2201 | 0.0006 | 0.9994 | 2983  | 2.98  | 0.9512 |

3.5 Thermodynamic analysis

Enthalpy change (\(\Delta H^0\)), Gibbs free energy change (\(\Delta G^0\)) and entropy change (\(\Delta S^0\)) expressed as Equation (8) and Equation (9) [32, 33] could provide an insight into the adsorption mechanism and behavior [34].

\[
\Delta G^0 = -RT\ln(K_L)
\]  
\[
\ln(K_L) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}
\]

The \(\Delta G^0\) value was calculated to -20.74 kJ/mol at 318 K and it was indicated that the adsorption of chromium (III) was thermodynamically favorable and spontaneous [30]. The value of \(\Delta S^0\) was calculated to 288 J/mol/K, which meant that the freedom degree increased at the C3N6H6@Cr interface.
during the reaction process. And the \( \triangle H^0 \) were calculated to be \(-71.36\) kJ/mol, which implied that the adsorption of chromium (III) onto the melamine was a physisorption process [35].

The entire above-mentioned thermodynamic parameters indicated that chromium (III) adsorption onto the melamine was favorable and melamine could be used as a high-efficiency absorbance to remove chromium (III) from wastewater.

4. Conclusions
This paper founded that melamine showed great adsorption performance of chromium (III). The removal efficiency of chromium (III) could up to be 98.63% and the adsorption capacity of melamine was up to 2843 mg/g at \( n(\text{melamine})/n(\text{Cr})=1.5 \), reaction temperature at 90 ℃, reaction time of 60 min. The adsorption process was fitted well with the pseudo-second-order model and Langmuir equilibrium isotherm model. And the main adsorption mechanisms for the adsorption of chromium (III)main was confirmed as electrostatic attraction and stacking interaction. The adsorption process was a spontaneous, endothermic and physisorption process according to the thermodynamic analyzing results.

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