Adsorption of Hexavalent Chromium from Wastewater Using Microcrystalline Cellulose

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In this study, microcrystalline cellulose (MCC) was utilised as an adsorbent for the removal of Cr(VI) from synthetic wastewater. FTIR spectroscopy confirmed the main characteristic infrared absorption bands of MCC. The MCC had a relatively low BET-specific surface area of 2.05 m\textsuperscript{2} g\textsuperscript{-1}. SEM revealed that the MCC had a short-fibre, rod-shaped morphology. XRD analysis confirmed the MCC semi-crystalline structure. Batch adsorption studies showed that the optimal conditions for the removal of Cr(VI) from the wastewater using the MCC were an initial Cr(VI) concentration of 10 mg L\textsuperscript{-1}, an adsorbent dosage of 20 g L\textsuperscript{-1} and a Cr(VI) solution pH of 1. The MCC required 96 h to reach equilibrium, and the equilibrium removal efficiency was 83 %. The point of zero charges of the MCC (pH 6.2) and occurrence of Cr(III) in solution during the adsorption process suggests that the Cr(VI) removal mechanism from the wastewater by the MCC was adsorption coupled by reduction. The Freundlich isotherm provided the best fit for the experimental kinetics data. The pseudo-second-order (PSO) model provided the best fit to the experimental equilibrium data. Compared to commercial adsorbents, the adsorption capacity of the MC was relatively low at 3.92 mg g\textsuperscript{-1}.

1. Introduction

Water pollution due to the introduction of contaminants into freshwater bodies contributes to the diminished availability and deteriorated quality of freshwater. Heavy metal pollution of freshwater bodies is a global problem that is attributed to the increase in urbanisation, industrialisation and anthropogenic activities (Akpor and Muchie, 2010). Hexavalent chromium, Cr(VI), is one of the priority heavy metal water pollutants. Exposure to Cr(VI) poses numerous hazards to human and plant health (Peng and Guo, 2020). Most conventional water treatment processes are not capable of effectively removing Cr(VI) present in water at trace concentration levels (<100 mg L\textsuperscript{-1}) and have several other disadvantages (Mohan and Pittman, 2006). As such, it is a challenge to conform to stringent regulations such as the maximum limit of 0.05 mg L\textsuperscript{-1} for Cr(VI) in drinking water recommended by the World Health Organization (WHO) (Kumar et al., 2020).

Adsorption has been studied as a suitable alternative remediation method for the removal of Cr(VI) present in water at trace concentrations (<100 mg L\textsuperscript{-1}) (Mohan and Pittman, 2006). Its feasibility in water treatment depends on the availability of inexpensive, highly selective and efficient adsorbents. Various materials have been studied as adsorbents for Cr(VI) (Tshemese et al., 2020). However, conventional adsorbents such as activated carbons, which are suitable for the effective and efficient removal of Cr(VI) present in water at trace concentration levels (<100 mg L\textsuperscript{-1}), are relatively expensive (González-López et al., 2021). Biosorbents are an attractive alternative as they are readily available and abundant in nature. They are also relatively inexpensive as they are mostly derived from naturally abundant waste biomass. Their major advantage is that they are biodegradable, and their disposal does not have an adverse effect on the environment (Michaliak et al., 2013). Several studies have demonstrated the effectiveness of plant-based biosorbents in the removal of Cr(VI) (Gupta et al., 2015). Microcrystalline cellulose (MCC) is purified, partially depolymerised cellulose (Ejikeme, 2008). The hydroxyl groups on cellulose materials can potentially interact effectively with pollutants such as heavy metals, enabling their removal from water. Cellulose-based materials are increasingly being considered for use as biosorbents due to their relatively low cost, biodegradability and abundance (Jamshaid et al., 2017). However, there have...
been a few studies on the use of pristine MCC as an adsorbent. In the studies reviewed, MCC was rarely used in its pristine form as an adsorbent for heavy metals (Garba et al., 2020).

The objective of this work was to determine the effectiveness of pristine MCC in the removal of Cr(VI), from wastewater. In the present work, batch adsorption studies on the removal of Cr(VI) from synthetic wastewater using MCC were conducted and reported upon.

2. Materials and methods

2.1 Materials

The MCC used in the study was grade Avicel 101 with a \( d_{50} \) particle size of 65 \( \mu \)m supplied by JRS Pharma industry, India. 1,5-Diphenylcarbazide (98.0 %) was supplied by Sigma Aldrich, South Africa. Potassium chromate (99.0 %), hydrochloric acid (37 %), ethanol (99.9 %), acetone (AR), and sodium hydroxide pellets (98 %) were supplied by Glassworld, South Africa. All the reagents were of analytical grade and were used as received. All solutions were prepared with deionised water.

2.2 Methods

Characterization of MCC

The Fourier Transform Infrared spectroscopy (FTIR) spectra of the MCC were recorded on a Perkin Elmer 100 FTIR Spectrophotometer equipped with an attenuated total reflectance (ATR) accessory in the range 4000-600 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\), using 64 scans. The morphology of the MCC was analysed using a ZEISS crossbeam 540 field emission gun scanning electron microscope. The specific surface area and pore characteristics of the MCC were evaluated with a Micromeritics TriStar II surface area and porosity analyser. The crystallinity of the MCC was analysed using a PANalytical X'Pert Pro powder X-ray diffractometer, using Cu-K\(\alpha\) radiation in the 2\(\theta\) range 0-90 °. The point of zero charges of the MCC was determined by the salt addition method, as described by Bakatula et al. (2018).

Batch adsorption experiments

A stock solution of 1,000 mg L\(^{-1}\) of Cr(VI) was prepared by dissolving 3.7344 g of \( K_2CrO_4 \) in 1 L of deionised water. Varying concentrations of the synthetic wastewater containing Cr(VI) (chromate solution) were then obtained by dilution of the stock solution with deionised water.

The adsorption performance of microcrystalline cellulose towards the removal of Cr(VI) from the synthetic wastewater was evaluated through batch adsorption experiments conducted at standard room temperature. The batch adsorption experiments were conducted in 250 mL glass bottles using 50 mL of the Cr(VI) solution. The bottles were agitated at 150 rpm using a mechanical shaker at room temperature for a predetermined period obtained from initial equilibrium results. Process parameters such as the MCC dosage, initial Cr(VI) concentrations, contact time, and solution pH were optimised by varying one variable at a time and fixing all other parameters. The MCC maximum adsorption capacity for Cr(VI) was determined through equilibrium isotherm studies. The effect of solution pH was investigated in the pH range 1-9, using a Cr(VI) concentration of 10 mg L\(^{-1}\) and the determined MCC optimum loading of 20 g L\(^{-1}\). The pH of the solution was adjusted by the addition of HCl or NaOH solution (0.01-5.0 mol L\(^{-1}\)) using a pH meter with a resolution of ±0.05 pH. Batch adsorption kinetics data were obtained by varying the contact time from 0 to 144 h with an initial Cr(VI) concentration of 10 mg L\(^{-1}\) and an adsorbent dosage of 20 g L\(^{-1}\). The changes in the concentration of Cr(VI) in the synthetic wastewater after adsorption were determined using the standard ultraviolet-visible (UV-Vis) spectrophotometric method described by Federation and Association (2005) using a WPA, Lightwave II, Labotec UV-Vis spectrophotometer at a wavelength of 540 nm.

The maximum amount of Cr(VI) adsorbed by the MCC for each run was determined using the following equation:

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

(1)

where \( q_e \) (mg g\(^{-1}\)) is the equilibrium adsorption capacity, \( C_0 \) (mg L\(^{-1}\)) is the initial concentration of Cr(VI), \( C_e \) (mg L\(^{-1}\)) is the equilibrium concentration of Cr(VI), \( V \) (L) is the volume of the Cr(VI) solution and \( W \) (g) is the mass of MCC added. The Cr(VI) removal efficiency \( R \) (%) was determined using Eq(2) below:

\[
R = \left( \frac{C_0 - C_e}{C_0} \right) \times 100
\]  

(2)

The total chromium concentration remaining in the solution after batch experiments was measured using a Perkin Elmer 1100 Atomic Absorption Spectrophotometer (AAS). To distinguish between Cr(VI) and Cr(III), the presence of Cr(VI) was determined using the UV-Vis spectrophotometric method described above. The amount
of Cr(III) in the supernatant was calculated as the difference between the total chromium determined by AAS and the Cr(VI) concentration determined by UV-Vis spectrophotometry. All experiments were performed in duplicates, and the results were averaged.

3. Results and discussions

3.1 Characterization of MCC

The FTIR spectrum of the MCC used in this study, presented in Figure 1a, shows the main characteristic infrared absorption bands of cellulose (Heinze et al., 2018). The XRD pattern of the MCC, also presented in Figure 1a, shows poorly resolved characteristic cellulose diffraction peaks at 2θ ca. 16 °, 26 ° and 40 ° confirming that the MCC was semi-crystalline (Terinte et al., 2011).

Figure 1: (a) FTIR spectra and XRD pattern and (b) SEM micrograph of microcrystalline cellulose

The SEM micrograph in Figure 1b shows that the MCC consisted of short fibre, rod-shaped morphology, similar to observations in previous studies. The BET surface area of the MCC (2.05 m² g⁻¹) was significantly lower compared to that of industrial adsorbents (Mohan and Pittman, 2006). The pore analysis of the MCC showed that the material was mesoporous.

3.2 Cr(VI) adsorption by microcrystalline cellulose

Figure 2a shows the Cr(VI) removal efficiency from the synthetic wastewater as a function of the MCC dosage at pH 1 and pH 7. Figure 2a shows that at both pH 1 and pH 7, the optimum adsorbent dosage was 20 g L⁻¹. Figure 2a also shows that at the optimum adsorbent dosage, the MCC had a Cr(V) removal efficiency of only 23 % with an initial solution of pH 7. With an initial solution of pH 1, the removal efficiency was above 90 %. To elucidate the observations in Figure 2a, the effect of the initial Cr(VI) solution pH on the removal of Cr(VI) from the aqueous solution was further studied by determining the point of zero charge (pHₚzc) of MCC. The point of zero charge indicates the pH where an adsorbent has zero charge as well as the pH values at which the adsorbent surface has negative or positive charges (Granados-Correa and Jiménez-Becerril, 2009). The point of zero charge of the MCC was ca. pH 6.2. This was slightly lower than the point of zero charge, which was obtained for cellulose by Silva et al. (2015). It was deduced from the point of zero charge of the MCC that for Cr(VI) solution pH values below ca. 6.2 the MCC had a positive surface charge, whereas for pH values above 6.2, the MCC surface had a negative charge. This suggests that at Cr(VI) solution pH values below 6.2, the removal of negatively charged Cr(VI) species from the aqueous solution was through electrostatic interaction. By varying the initial pH of the Cr(VI) solution used as synthetic wastewater, the highest Cr(VI) removal efficiency of 83 % was observed at pH 1.

The Cr(VI) adsorption process reached equilibrium at an MCC adsorbent contact time of 96 h, attaining a removal efficiency of 83 %. An adsorbent contact time of 120 h was used in subsequent adsorption experiments. An initial Cr(VI) concentration of 10 mg L⁻¹ resulted in the highest Cr(VI) removal efficiency of 89 %, although the equilibrium adsorption capacity at this concentration was minimal at 0.4 mg g⁻¹.
3.2.1 Cr(VI) removal mechanism from wastewater by MCC

At pH < 7, Cr(VI) exists as hydrogen chromate (HCrO$_4^-$) (Mohan and Pittman, 2006). It is postulated that at pH values below the point of zero charge (pH 6.2), hydronium ions in the aqueous solution protonated the hydroxyl groups on the MCC surface, resulting in highly positively charged MCC surfaces that interacted with the negatively charged HCrO$_4^-$ through electrostatic attraction, leading to high Cr(VI) removal efficiencies at low pH. However, if the interaction between Cr(VI) and MCC at low pH was only due to electrostatic interaction, it must be shown that Cr(VI) was not removed through reduction to Cr(III), i.e. there should be evidence that no Cr(III) existed in solution or on the adsorbent surface (Pakade et al., 2019).

To determine whether only electrostatic attraction was involved in the high removal efficiencies observed at low Cr(VI) solution pH, the presence of Cr(III) in the solution during the adsorption process was investigated. Figure 2b shows the evolution of Cr(III) in proportion to the Cr(VI) depletion, confirming that the reduction of Cr(VI) to Cr(III) was also involved in the adsorption process. Figure 2b also shows that the residual total Cr in the aqueous solution was 10 mg L$^{-1}$ after a contact time of 120 h, similar to the initial Cr(VI) concentration. This observation suggests, overall, no Cr was adsorbed onto the MCC surface. It is inferred that since at solution pH 1, the MCC surface was positively charged, as discussed previously, the MCC possibly electrostatically repelled the positively charged Cr(III) species back into the solution. The above inference fits the adsorption coupled reduction Cr(VI) removal mechanism for biosorbents suggested by Park et al. (2006).

3.2.2 Adsorption kinetics for the Cr(VI) removal by MCC

To investigate the adsorption kinetics of the Cr(VI) removal by MCC, the pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetics models in their linearised forms, Eq(3) and Eq(4)) were fit to the adsorption kinetics data. The parameters determined in fitting the models are given in Table 1.

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

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}
\]

Table 1: PFO and PSO kinetics model parameters for the removal Cr(VI) from synthetic wastewater by MCC

<table>
<thead>
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<th>Kinetics model</th>
<th>Parameter</th>
<th>Value</th>
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<tr>
<td>Pseudo first order</td>
<td>$k_1$ (min$^{-1}$)</td>
<td>0.000691</td>
</tr>
<tr>
<td></td>
<td>$q_e$ (mg g$^{-1}$)</td>
<td>0.479777</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9026</td>
</tr>
<tr>
<td>Pseudo second order</td>
<td>$q_e$ (mg g$^{-1}$)</td>
<td>0.4031</td>
</tr>
<tr>
<td></td>
<td>$k_2$ (g mg$^{-1}$ min$^{-1}$)</td>
<td>0.001791</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9549</td>
</tr>
<tr>
<td>Experimental value</td>
<td>$q_e$ (mg g$^{-1}$)</td>
<td>0.4038</td>
</tr>
</tbody>
</table>

In Eq(3) and Eq(4), $q_t$ and $q_e$ are the adsorption capacities at time $t$ (min), and at equilibrium (mg g$^{-1}$). $k_1$ is pseudo-first-order adsorption constant (min$^{-1}$), and $k_2$ is the pseudo-second-order rate constant (g mg$^{-1}$ min$^{-1}$).
Table 1 shows that the PSO model provided the best fit to the experimental kinetics data for the removal of the Cr(VI) from the synthetic wastewater by the MCC. The observations in this study agree with previous studies in which the PSO model provided good fits to describe the adsorption kinetics of metals such as Cr(VI) from aqueous solutions (Tran et al., 2017). A good fit of the experimental data to the PSO model is evidence that the adsorption mechanism was due to the chemisorption (Tran et al., 2017).

### 3.2.3 Adsorption isotherms for the Cr(VI) removal by MCC

The linearised forms of the Langmuir and Freundlich isotherms presented in Eq(5) and Eq(6) were fit to the adsorption equilibrium data in an attempt to describe the Cr(VI) adsorption characteristics of MCC.

$$
\frac{q_e}{C_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} \frac{C_e}{q_m}
$$

(eq 5)

$$
\log q_e = \log K_F + \frac{1}{n} \log C_e
$$

(eq 6)

In Eq(5) and Eq(6) \(C_0\) is the initial concentration of Cr(VI) (mg L\(^{-1}\)), \(C_e\) is the equilibrium concentration of Cr(VI) (mg L\(^{-1}\)), \(q_m\) is the Langmuir equilibrium adsorption constant (L mg\(^{-1}\)), \(q_e\) is the equilibrium adsorption capacity (mg g\(^{-1}\)), \(q_m\) is the maximum adsorption capacity (mg mg\(^{-1}\)), \(K_F\) is the Freundlich adsorption capacity constant (L\(^{1/n}\) mg\(^{1-1/n}\) g\(^{-1}\)) and \(1/n\) is the heterogeneity factor.

The parameters determined from fitting the two isotherms presented in Table 2 shows that compared to the Langmuir isotherm, the Freundlich isotherm provided the best fit to the experimental data for the Cr(VI) removal from the synthetic wastewater by the MCC. A good fit of the Freundlich isotherm to the experimental data suggests that there was a heterogeneous distribution of active adsorption sites on the MCC, and multilayer adsorption occurred (Al-Ghouti and Da’ana, 2020).

Table 2: Langmuir and Freundlich isotherm parameters for the adsorption of Cr(VI) by MCC

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>(q_m) (mg g(^{-1}))</td>
<td>3.9170</td>
</tr>
<tr>
<td></td>
<td>(K_L) (L mg(^{-1}))</td>
<td>0.0611</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.8948</td>
</tr>
<tr>
<td>Freundlich</td>
<td>(1/n)</td>
<td>0.5360</td>
</tr>
<tr>
<td></td>
<td>(K_F) (L(^{1/n}) mg(^{1-1/n}) g(^{-1}))</td>
<td>0.3819</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.9795</td>
</tr>
</tbody>
</table>

Table 2 also shows that the maximum monolayer adsorption capacity (3.12 mg g\(^{-1}\)) for Cr(VI) removal from synthetic wastewater by MCC obtained in this study was significantly low compared to those for commercial adsorbents (Garba et al., 2020). This was an indication that the MCC required modification and functionalisation to enhance its adsorption capacity.

### 4. Conclusions

Batch adsorption studies showed that the optimal conditions for the removal of Cr(VI) from synthetic wastewater using MCC as an adsorbent were an initial Cr(VI) concentration of 10 mg L\(^{-1}\), an adsorbent dosage of 20 g L\(^{-1}\) and a Cr(VI) solution pH of 1. The MCC required 96 h to reach equilibrium, and it attained an equilibrium removal efficiency of 83 %. Globally optimal parameters will need to be determined in future studies. Evidence of an adsorption coupled reduction Cr(VI) removal mechanism for the removal of Cr(VI) from solution by the MCC was established by indirect determination of the reduction of Cr(VI) bound to the MCC to Cr(III) during the adsorption process. The PSO model provided the best fit to the experimental kinetics data for the removal of the Cr(VI) from the synthetic wastewater by the MCC, showing that the adsorption of Cr(VI) by MCC was possibly through chemisorption. The Freundlich isotherm provided the best fit to the experimental data suggesting that there was a heterogeneous distribution of active adsorption sites on the MCC and multilayer adsorption occurred. The Cr(VI) adsorption capacity of the MCC was significantly lower at 3.92 mg g\(^{-1}\) in comparison to commercial adsorbents. This was attributed to the relatively low specific surface area of the MCC.

As the MCC contains hydroxyl groups, in future work, it will be modified and functionalised to enhance its adsorption properties through, for instance, the synthesis of composites or grafting of other polymers with various functionalities.
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