Impact of Cross-linking Agents on the Performance of Alginate-Cellulose Nanocrystals Adsorbent Beads

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Research Article

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Abstract
A detailed investigation on the adsorption of methylene blue (MB) to sodium alginate/cellulose nanocrystal (ALG-CNC) composite hydrogel beads was conducted. The impact of physical cross-linking and calcium ions on the binding of MB onto the beads and the swelling/shrinkage of bead during the adsorption process in batch vessel and continuous fixed bed operations was examined. Changes in the bulk calcium ion concentrations during the batch adsorption experiments on the binding of MB to the beads were monitored when the beads were subjected to different pretreatments. The calcium ions reduced the adsorption capacity by charge screening instead of competitive adsorption, and the removal of calcium ions contributed to an initial shrinkage of the adsorbent during binding tests in the packed column.

1 Introduction
Hydrogels are multifunctional materials that have been used in many applications from tissue engineering, drug delivery [1], and ewater treatment [2],[3]. By convention, hydrogels are water-swollen polymer networks held together by physical cross-links or covalent bonds [4]. Depending on the polymer, type of cross-linking and degree of cross-linking, hydrogels can be rigid and tough materials or soft and stretchable. Sodium alginate is a water-soluble polysaccharide derived from brown seaweed, consisting of repeating mannuronate (M) and guluronate (G) units [5]. This polymer can easily form a polymer network when a divalent cation such as Ca$^{2+}$ is introduced through ionotropic gelation through the dropwise addition of alginate into a bath of Ca$^{2+}$ ions. Divalent cations can coordinate with the repeating G units on the alginate chains and bridge the adjacent alginate polymer chainss to form an egg-box structure, resulting in a physically cross-linked network [6].

Due to the ease of formation of calcium alginate hydrogels as well as the abundance of available carboxylate groups, these hydrogels have been exploited for use as adsorbents for various waterborne contaminants. In one study, Aravindhan et al. used calcium alginate beads to remove basic black dye from water [7] and reported a maximum adsorption capacity of 78 mg/g at 30°C. Additional experiments by Papageorgiou et al. examined the capacity of calcium alginate beads to remove Cd$^{2+}$, Cu$^{2+}$ and Pb$^{2+}$ from aqueous solutions [2]. They observed that alginates with higher M/G ratios displayed higher capacities to remove these three metal ions, where the maximum adsorption capacities for Cd$^{2+}$, Cu$^{2+}$ and Pb$^{2+}$ were determined as 1.16, 1.40 and 1.81 mmol/g, respectively. The adsorption performance of calcium alginate hydrogels could be further enhanced by mixing various types of nanoparticles with a suspension of alginate prior to ionotrophic gelation. In some instances, this step was shown to also improve the mechanical properties of the hydrogels [8],[9].

Negatively charged cellulose nanocrystals (CNCs) have been used together with sodium alginate to prepare Ca$^{2+}$ cross-linked hydrogels for the removal of methylene blue dye [9]. CNC enhanced the ability of the hydrogels to capture MB through their large surface area (~ 250 m$^2$/g) and abundant surface
sulfate ester groups, allowing them to work better and it displayed a theoretical adsorption capacity of 256 mg/g. When the hydrogels were used in a continuous packed column, an unexpected overshoot in the MB effluent breakthrough curve was observed, as well as expansion and shrinkage of the adsorbent during operation [10]. While the previous study examined the impact of the MB adsorption on adsorbent expansion and shrinkage, there was no investigation into whether the cross-linking by the Ca\(^{2+}\) ions could affect this process or if they are responsible for the MB profile overshoot observed in the breakthrough curve.

In this study, CNC-ALG beads were prepared for the adsorption of MB dye, and the impact of Ca\(^{2+}\) ions on this process was closely monitored. As Ca\(^{2+}\) ions have the potential to screen electrostatic interactions, the CNC-ALG was subjected to various pretreatments to remove unbound Ca\(^{2+}\) prior to MB adsorption in both batch and continuous systems to understand the effects of Ca\(^{2+}\) on the adsorption process. In addition, the effect of bead shrinkage and expansion with Ca\(^{2+}\) concentration was closely monitored in the column operation in order to understand how the calcium concentration in the beads would vary over time, and if any competitive adsorption occurred between Ca\(^{2+}\) and MB on the adsorbent surface.

# 2 Materials And Methods

## 2.1 Materials

Cellulose nanocrystals (CNCs, spray dried) were supplied by CelluForce Inc. Sodium alginate (ALG, PROTANOL GP 3350) and methylene blue hydrate (MB) were purchased from FMC Corporation and Sigma Aldrich, respectively. Calcium chloride (CaCl\(_2\)) was purchased from Fisher Scientific, while MilliQ water was produced onsite using a MilliPore system (> 18 MΩ/cm). Perspex tubings of 2.54 cm outer diameter and 2.22 cm inner diameter were purchased from P&A Plastics Inc, Hamilton, Ontario.

## 2.2 Preparation of Adsorbent

The procedure for preparing the adsorbent was reported previously [9]. CNC-ALG beads were prepared by mixing equal volumes of 4 wt% CNC and 1 wt% ALG solutions using a IKA-WERK Ultra-turrax homogenizer at 20,000 rpm for 5 minutes and dispensing them through a hypodermic needle into an aqueous CaCl\(_2\) gelation bath. For batch experiments, the ALG-CNC beads were produced by dispensing solution through a 22 G needle tip at a flow rate of 5 mL/min into a 2 wt% CaCl\(_2\) gelation bath, where they were kept immersed for 15 minutes to initiate the cross-linking process. Following this, the beads were rinsed with MilliQ water, and placed in a 14,000 MW cutoff dialysis tubings kept in deionized water for 3 days before subsequent adsorption experiments. For column experiments, the CNC-ALG solution was dispensed through multiple 22 G needles at a flow rate of 12.5 mL/min into a 2 wt% CaCl\(_2\) solution that was cycled through the fixed bed vessel to randomly pack the beads. The hydrogel beads were formed upon contact with the gelation bath and allowed to crosslink for 15 minutes at neutral pH and 25°C. The
beads were subjected to varying pretreatments, including rinsing with deionized water as well as rinsing or soaking in stagnant 2 wt% CaCl₂ solution.

2.3 Characterization of adsorbent

The porosity of the beads was determined using a gravimetric method similar to that reported by Zhao et al. [11] using the following expression:

$$\varepsilon_p = \frac{(W_w - W_d)/\rho_w}{W_d/\rho_m + (W_w - W_d)/\rho_w}$$  \hspace{1cm} (1)

where $\varepsilon_p$ is the bead porosity, $W_w$ (kg) and $W_d$ (kg) are the weight of the hydrogel in the wet and dry state, respectively, $\rho_w$ is the density of water (1000 kg/m³) and $\rho_m$ is the density of the dry hydrogel matrix (1600 kg/m³). The radius of the adsorbent particles ($R_p$) was determined using a caliper to be $1.00 \pm 0.07$ mm.

2.4 Batch adsorption experiments

Experiments were conducted as described previously [9]. CNC-ALG adsorbent (375 mg dry basis) was immersed in MB dye solutions (25 mL) having concentrations of 345.2, 2078, 3066, and 4292 mg/L and agitated for 180 minutes to allow equilibrium to be reached. Eq. (2) was used to determine the dye uptake onto the adsorbent:

$$q_e = \frac{(C_0 - C_e) V_L}{m}$$

where $C_0$ and $C_e$ are the initial and equilibrium dye concentrations respectively (mg/L), $V_L$ is the volume of dye solution (L), $m$ is the mass of adsorbent used (g) and $q_e$ is the mass of dye adsorbed per mass of adsorbent (mg/g). The Langmuir isotherm as given in Eq. (3) was used to describe the adsorption process:

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

where $K_L$ is the Langmuir constant (L/mg) and $q_m$ is the theoretical maximum loading (adsorption capacity) of the adsorbent (mg/g). $K_L$ and $q_m$ were determined using non-linear regression analysis embedded in Microsoft Excel's SOLVER function. All adsorption experiments conducted were reproducible to within 10% of their original value.

2.5 Fixed bed column adsorption experiments

Fixed bed adsorption experiments were conducted in a 2.22 cm inner diameter perspex column that can accommodate approximately 11 adsorbent particles across its diameter (this satisfies the requirement of
fitting at least 10 adsorbent particles along the diameter of the column to limit fluid channeling along the bed walls [12]). Water was introduced at the bottom of the column using a Watson-Marlow peristaltic pump 101U/R, and a stainless-steel mesh was placed 2.54 cm above the fluid inlet to promote proper flow distribution at the column inlet and support the adsorbent particles. A UV-Vis spectrophotometer fitted with a flow-cell was used to provide real-time measurements of the MB concentration in the column effluent. All the experiments were conducted at room temperature (25 ± 2 °C) and neutral pH. Breakthrough curves were obtained by plotting $C_b$ (mg/L) versus $t$ (min).

### 2.6 Calcium Elution Experiments

The concentration of CaCl$_2$ leaving the beads was monitored in batch and column experiments using an ion selective electrode (ISE). For batch experiments, Ca$^{2+}$ was measured by immersing the ISE into the batch vessel for the duration of the experiment. For column experiments, Ca$^{2+}$ was measured by immersing the electrodes in a beaker serving as a continuous stirred vessel fed by the effluent from the column, while an outflow emptied the vessel at the same flowrate to maintain a constant volume. To calculate the actual concentration of Ca$^{2+}$ leaving the column (i.e. the input to the measurement vessel), the following equation was used:

$$C_0 = \frac{dC}{dt} \frac{V}{Q} + C'$$

where $C$ is the concentration of Ca$^{2+}$ measured by the ISE in the measuring vessel, $V$ is the volume of the measuring vessel (mL), $Q$ is the flowrate through the vessel (and conversely the column), and $C_0$ is the concentration of Ca$^{2+}$ leaving the column and entering the measuring vessel. $dC/dt$ was determined by central difference approximation:

$$\frac{dC_i}{dt} = \frac{C_{i+1} - C_{i-1}}{2\Delta t} + O(\Delta t)^2$$

where $C_{i+1}$ and $C_{i-1}$ represent the measured concentrations measured after and before $C_i$, respectively (mg/L), $\Delta t$ is the time measurement interval (s), and $O(\Delta t)^2$ represents the associated residual error.

### 2.7 Instrumentation

#### 2.7.1 UV-Vis Spectrophotometry

The concentration of MB was determined using a Cary 100 UV-Vis spectrophotometer for the batch adsorption experiments, and a calibration curve was obtained by measuring the absorbance at $\lambda = 664$ nm to determine the initial and final concentrations of the batch system using the Beer-Lambert law. This was used for samples diluted in the range of 0.1–5 mg/L. Similarly, a Cary 300 UV-Vis spectrophotometer was used for the continuous experiments, where the effluent from the column was pumped to a quartz
flow-cell with a path length of 1 cm. The calibration curve was determined by measuring absorbance at \( \lambda = 664 \text{ nm} \) as this was found to vary linearly with concentration within the range of 0.1–5 mg/L MB.

### 2.7.2 Ion selective electrode

The concentration of CaCl\(_2\) diffusing from the beads was monitored in both the batch and column experiments. An ORION calcium ion selective electrode and Metrohm AgCl reference electrode were immersed in the solution and the Ca\(^{2+}\) concentration was monitored via a Metrohm Potentiometric Titrator. A calibration curve was used to convert the measured signal to Ca\(^{2+}\) concentration.

# 3 Results And Discussion

### 3.1 Influence of CaCl\(_2\) on MB uptake: Batch studies

As shown in our previous studies, CNC-ALG beads could remove MB in solution with an adsorption capacity of 256 mg/g[9]. The adsorption was found to occur on the carboxylate groups of the sodium alginate and sulfate ester groups of the CNCs [13], as the % dye removal was found to decrease with increasing NaCl concentrations, which screened the electrostatic interactions between these groups and MB. The effect of the solution ionic strength on the electrostatic interaction is well-documented, especially in adsorbate/adsorbent systems that rely on such attractive forces for adsorption [14]. Although calcium chloride plays an important role as cross-linkers for preparing the beads, free calcium ions could influence the binding of MB to the adsorbent by increasing solution ionic strength. The adsorption of Cu\(^{2+}\) ions onto calcium alginate beads by An et al. [3], where the calcium ions could screen the electrostatic interaction. The presence of residual calcium chloride on the adsorbent during the packed bed operation was believed to be responsible for the overshoot observed in the concentration profile in the early stages of column adsorption process [10]. We further examined this phenomenon by studying the displacement of Ca\(^{2+}\) ions by MB via the ion exchange during the binding process. The initial experiment involved monitoring the release of Ca\(^{2+}\) from CNC-ALG beads in both pure water and a MB solution. Figure 1 shows the concentration of Ca\(^{2+}\) released when rinsed adsorbent was placed into 50 mL of MilliQ water and 250 mg/L MB respectively. In both cases, an identical trend was observed, where the Ca\(^{2+}\) diffused from the adsorbent to the bulk solution, approaching an equilibrium after 1600 seconds. This is likely a combination of unbound and bound calcium ions diffusing into the bulk solution along with chloride counterions, and in both cases, the concentration plateaued at approximately the same value. Thus, it could be concluded that MB did not directly displace Ca\(^{2+}\) in the CNC-ALG adsorbent, rather that Ca\(^{2+}\) and Cl\(^{-}\) counterions diffused into the bulk solution driven by the concentration gradient.

Following this observation, it was necessary to investigate whether the presence of Ca\(^{2+}\) ions leaching into the bulk solution would impact the uptake of MB to the beads. Figure 2 shows equilibrium adsorption experiments conducted using two different adsorbent pretreatments: (1) dialyzing the beads against deionized water for 2 days (blue dots) or (2) rinsing the beads with 10 mL of deionized water twice
(orange dots) and draining the wash water prior to the adsorption experiments. The equilibrium parameters determined for the dialysis and rinsing were; $q_m = 401.8$ mg/g and $K_L = 7.9$ m$^3$/kg and $q_m = 298$ mg/g and $K_L = 1.7$ m$^3$/kg, respectively. It was hypothesized that 2 days of dialysis would be sufficient to remove all free calcium from the alginate bead, while the 2 times rinsing was sufficient to remove loosely bound calcium ions not incorporated as crosslinker during the bead formation process. The lower dye adsorption resulting from the latter pretreatment was due to calcium leaching from the beads during the adsorption experiment that subsequently participated in charge screening, inhibiting the diffusion and adsorption of the MB onto the adsorbent. Free Ca$^{2+}$ ions in the adsorbent could have a detrimental effect on the adsorption capacity in a closed system, as they would remain in the bulk solution and induce charge screening for the duration of the adsorption experiment. However, a continuous system such as a fixed bed column might not be impacted as severely by this phenomenon as the free Ca$^{2+}$ would be transported out of the system by the continuous stream of wastewater travelling through the system. Therefore, it is necessary to investigate the effect of Ca$^{2+}$ ions on MB during column adsorption in order to confirm this hypothesis.

### 3.2 Influence of CaCl$_2$ on MB uptake: Column studies

Two studies were designed to investigate the effect of Ca$^{2+}$ ions on the uptake of MB on the adsorbent during the beginning stages of the column experiments: (i) use of adsorbent without pre-wash, and (ii) use of absorbent washed with 250 mL MilliQ water for 1200 seconds (20 min wash). Figure 3 shows the discharge concentration of Ca$^{2+}$ ions and MB as a function of time for both adsorbents (i) and (ii), using a short column containing only 1.25 g adsorbent. In case (i) (hollow blue and hollow red curves), a 20 mg/L solution of MB was pumped through the column, and unbound Ca$^{2+}$ ions were liberated from the adsorbent/column resulting in a steady decrease in the concentration, with a corresponding overshoot in the MB concentration profile (similar to previous results [10]). In case (ii) (solid blue and solid red curves), MilliQ water was pumped through the column for 1200 seconds to remove excess/unbound Ca$^{2+}$ from the adsorbent, after which a solution of 20 mg/L MB was flowed through the column. The trend observed for Ca$^{2+}$ concentration was nearly identical to case (i); however, the MB concentration profile was markedly different. No overshoot was observed, instead the MB concentration did not display breakthrough until 1500 sec and then increased to 4 mg/L. Due to the small amounts of adsorbent used in these two cases, the mass transfer zone did not fully form within the column and caused an early breakthrough. In case (i), the MB concentration appeared to also plateau at 4 mg/L, occurring after the concentration of Ca$^{2+}$ ion leaving the column became negligible. Thus, we concluded that the presence of unbound Ca$^{2+}$ ions in the column have a dramatic impact on MB removal at the initial stage due to charge screening. Based on case (ii), it appeared that 250 mL of MilliQ water (equivalent to 4.6 bed volumes for the 1.25 g of adsorbent) was sufficient to remove unbound Ca$^{2+}$ that would have interfered in MB uptake once the solution was pumped through the column. In addition to these findings, comparison of the results from studies in case (i) and (ii) indicated that the presence of MB in the
incoming solution did not displace the Ca\(^{2+}\) ions, which is in agreement with the batch studies as described in the previous section.

### 3.3 Influence of CaCl\(_2\) on Bed Height

Similar to previous studies, the swelling and shrinkage of the hydrogel adsorbent occurring during the MB adsorption was investigated. Figure 4 shows the concentration of MB eluting from the column over time as well as the height of the packing material (experimental operating parameters \(C_0 = 111\) mg/L, \(Q = 0.492\) L/hr, and \(m = 6.25\) g). The adsorbent in this case undergo a similar pretreatment to Case (ii), where it was washed with MilliQ water for 30 minutes prior to contacting with MB solution. During the initial 500 minutes, the packing height increased by almost 10% due to expansion of the adsorbent beads and subsequently decreased until 2750 minutes corresponding to 50% breakthrough before leveling off thereafter. Since the changes in the bed height could be influenced by MB adsorption, we investigated the role of Ca\(^{2+}\) on adsorbent swelling/shrinkage.

In this investigation, three scenarios were postulated to study the effect of adsorbent pretreatment on the packing height and MB concentration leaving the column during the initial stages of adsorption. The following three pretreatments prior to contact with MB were conducted: (1) Soaking the adsorbent in 2 wt% CaCl\(_2\) solution for 30 minutes, (2) cycling a 2 wt% solution of CaCl\(_2\) solution through the adsorbent for 30 minutes to expand the bed, and (3) washing the adsorbent with 250 mL MilliQ water for 30 minutes. Figure 5 shows the breakthrough curve and bed height for cases (1) & (2). In case (1), the soaking of the adsorbent in stagnant CaCl\(_2\) did not affect the bed height and the size of the adsorbent hydrogel particles. This indicated that the adsorbent achieved a fast equilibrium with the CaCl\(_2\) cross-linking solution when initially prepared and did not uptake more Ca\(^{2+}\) ions when left to soak in the solution beyond 15 minutes. In Case (2), pumping 2 wt% CaCl\(_2\) through the adsorbent at 0.492 L/hr for 30 minutes prior to adsorption did not change the bed height, suggesting no change in the adsorbent size and packing density. This further confirmed that a flow rate of 0.492 L/hr for column experiments did not cause the adsorbent packing to expand, thus any changes in size could be attributed to exposure to MB solution or MilliQ water. However, a visible change in packing height was observed only after pumping of the MB solution through the column commenced. In case (1), an overshoot in the MB concentration and a corresponding reduction in the Ca\(^{2+}\) ions leaving the column were observed (this trend was identical to case (i) Fig. 3). The packing height also increased, suggesting that the adsorbent beads expanded. Since the flowrate (0.492 L/hr) was below the fluidization velocity, the bed expansion was not caused by fluid dynamics but by changes in adsorbent size. The behaviour observed in Case (2) was similar to Case (1), where a larger overshoot in MB concentration was observed in Case (2). This larger overshoot was due to a higher charge screening of the adsorbent by the higher CaCl\(_2\) concentration in the column resulting from the pretreatment step. As in Case (1), the bed height increased and followed an identical trend in terms of rate of height increase and final height. The bed height appeared to plateau after 5500 seconds,
which coincided with the Ca\(^{2+}\) and MB concentrations approaching a steady state. It can be concluded that exposing the adsorbent to either stagnant or flowing CaCl\(_2\) did not influence its initial packing height.

Figure 6 shows the trends in bed height, MB and calcium concentration for Case (2) and (3). The effect of pre-washing with water for 30 minutes (Case (3)) was very noticeable. Over the first 30 minutes of Case (3) (prior to introduction of MB), the bed height decreased due to the shrinkage of the adsorbent. Davidovich-Pinhas et al. investigated the swelling and shrinkage (syneresis) of calcium cross-linked alginate tablets prepared with differing concentrations of calcium and found that alginate cross-linked with 25 mM Ca\(^{2+}\) or higher led to a reduction in the mass when placed in water. This was attributed to water exudation, resulting in a reduction of volume of the cross-linked alginate tablets [15]. The adsorbent bed appeared to stop shrinking after 1200 seconds, at which point it remained at a constant level of 95% of its starting height. With the introduction of MB into the column (at 1800 s), the adsorbent began to swell, but it did not reach the same bed height observed in Cases (1) and (2) (+ 20%). It however achieved +12% of the initial height, which is very close to the bed height expansion observed in run 2 (Fig. 4), which experienced a 9% increase when exposed to the incoming MB solution and shrank 2% initially from the same water pretreatment.

The results observed in case (3) (Fig. 6) could be used to elucidate what occurred in Fig. 4 since they underwent the same pretreatment process and similar operating conditions. Figure 7 shows the proposed mechanism for the role of washing pretreatment and MB exposure on the expansion/shrinkage of the adsorbent. In stage (1), water washing the adsorbent caused unbound Ca\(^{2+}\) and Cl\(^{-}\) ions to leave the adsorbent, reducing the net repulsion inside the hydrogels and causing them to shrink. In stage (2), the hydrogel possessed an abundance of unshielded negatively charged sulfate ester and carboxylic acid groups which facilitated the transport of MB molecules into the hydrogel, causing it to swell due to osmotic pressure [10]. After stage (1) in Case (3) (Fig. 6b), the Ca\(^{2+}\) concentration in solution decreased to a negligible concentration once the bed had expanded to the maximum height. Therefore, this same trend should be expected in columns with more packing, such as the experiment in Fig. 4. Since the adsorbent had already lost most of its calcium in the initial stages of operation, the bed shrinkage observed during later times must be caused by the high concentrations of adsorbed MB and not the loss of Ca\(^{2+}\) ions. After the adsorbent has swelled to its maximum size, stage (3) occurred and the hydrogel interior experienced charge shielding from the adsorbed dye, resulting in the expulsion of water and the gradual shrinkage of the hydrogel matrix. Stage (4) occurred when the adsorbent approached its maximum capacity and could not adsorb more dye, so that its size remained constant. Hence, it appeared that both the external Ca\(^{2+}\) concentrations and the amount of MB adsorbed influenced the size of the adsorbent beads, with the MB having a larger effect over the course of the adsorbent usage.

4 Conclusions

The impact of calcium ions on the adsorption of MB onto CNC-ALG beads in both batch and continuous fixed bed modes was investigated. Batch experiments indicated that the MB did not displace Ca\(^{2+}\) as it
was adsorbed onto the hydrogel, however, that high Ca$^{2+}$ concentration in the final adsorbent during adsorption experiments showed lower degrees of adsorption due to electrostatic charge screening. In continuous column experiments, high concentrations of Ca$^{2+}$ were directly responsible for the overshoot in MB concentration observed at the beginning, and washing pretreatment of the adsorbent prevented this overshoot of the concentration profile. The size change of the adsorbent during column experiments was also influenced by the presence of Ca$^{2+}$ in the hydrogel, as an initial water rinse resulted in the shrinkage of the beads due to the loss of Ca$^{2+}$ ions reducing the net repulsion between the alginate chains. The expansion of the bed was further attributed to the adsorption of MB that led to adsorbent shrinkage due to the loss of water, resulting in a 40% loss in the packed bed volume. The findings from these studies offer valuable insights in the designing of absorbent and packed bed columns containing CNC-ALG adsorbent to remove cationic molecules such as MB in wastewater treatment process.

**Declarations**

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**Ethics approval and consent to participate**

The authors confirm that the research was conducted in accordance to the ethical standard, and all the authors are eligible to participate in the research and publication of the data and results.

**Consent for publication**

All the authors consent to the submission and publication of the content in this paper.

**Availability of data and materials**

The data are available on request.

**Competing interests**

We declare that the authors have no competing interests.

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**Authors’ contributions**

Nathan Grishkewich: experimental planning, data acquiring and analysis, writing manuscript draft.
Nishil Mohammed: data acquiring and analysis

Kam Chiu Tam: Securing funding, supervision of project, editing of manuscript

References


Figures

Figure 1

Release of Ca\(^{2+}\) ions in batch mode in 50 mL of MilliQ water (red) and 250 mg/L MB solution (blue)
Figure 2

Batch experiments showing the effect of Ca\(^{2+}\) removal via dialysis (Blue dots) vs. rapid wash (Orange dots) on MB uptake
Figure 3

Ca$^{2+}$ and MB concentration in effluent from column after different adsorbent pre-treatments, operating at an initial MB concentration of 20 mg/L and 1.25 g of adsorbent
Figure 4

Breakthrough curve and variations of height of packing material with time (run parameters $C_0 = 111$ mg/L, $Q = 0.492$ L/hr, $m = 6.25$ g)

Figure 5
MB concentration and bed height (left) and Ca\(^{2+}\) concentration and bed height (right) for pretreatments involving 30 minutes of CaCl\(_2\) cycling through the adsorbent and 30 minutes of adsorbent soaking in CaCl\(_2\) with \(C_0 = 20\) mg/L, \(Q = 0.492\) L/hr and \(m = 1.25\) g

**Figure 6**

MB concentration and bed height (left) and Ca\(^{2+}\) concentration and bed height (right) for pretreatment involving 30 minutes of adsorbent soaking in CaCl\(_2\) and 30 minutes of washing adsorbent with water with \(C_0 = 20\) mg/L, \(Q = 0.492\) L/hr \(m = 1.25\) g (the dashed line indicates the 30 minutes mark when MB solution was introduced in water washing case).
Figure 7

Mechanism of bead swelling/shrinkage corresponding to bed height changes during column operation