Stability and reusability of alginate-based adsorbents for repetitive lead (II) removal

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A R T I C L E   I N F O

Article history:
Received 19 September 2015
Received in revised form 11 November 2015
Accepted 21 November 2015
Available online 2 December 2015

Keywords:
Desorption
Stability
Lead
Reusability
Alginate
Halloysite nanotubes

A B S T R A C T

The aim of this work was to investigate the chemical and mechanical stability of the calcium-alginate and alginate-halloysite nanocomposite beads for repetitive Pb²⁺ removal from aqueous solution. A suitable eluent, i.e. HNO₃ or HCl at an appropriate concentration, was first determined to desorb Pb²⁺ from the beads. The beads were then reused for up to 10 consecutive adsorption–desorption cycles. The adsorption/desorption efficiency and the physicochemical–mechanical properties of the beads during the reuse were studied. HNO₃ at 0.10 M was found to be the most appropriate eluent with desorption efficiency >90%. The desorption process was rapid and can be completed within two hours. The beads remained intact during reuse but their size decreased after each cycle of reuse. The adsorption capacity of the beads remained high (i.e. approximately 183 mg/g) even after 10 consecutive reuse. Interestingly, the beads became more rigid after each cycle of reuse. Their Young’s modulus increased by 6-fold to 2.4 MPa at the tenth cycle of desorption. This study shows the long term reuse feasibility of the alginate-based beads for Pb²⁺ removal from aqueous solution.

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1. Introduction

Biopolymer-based beads made of alginate have been widely studied as adsorbents for removing toxic pollutants from aqueous solution because of the renewability and safety of alginate, the ease of preparation of the beads, the high adsorption capacity towards a wide range of pollutants, and the ease of separation and reuse of the beads. Recently, alginate-halloysite nanotubes (HNTs) nanocomposite beads have been studied as a potential adsorbent for treating aqueous solution containing methylene blue [1] and copper ions [2]. In our previous study, we use alginate-HNTs nanocomposite beads to remove Pb²⁺ from wastewater [3]. These beads not only outperformed conventional adsorbents such as zeolite [4] and ion exchange resins [5], but were also easily separated from the treated water by simple filtration, unlike carbon nanotubes or any other mobile nano-adsorbents which require energy intensive separation processes.

As adsorption is essentially a semi-batch process, eventually the adsorbents have to be regenerated via desorption or be replaced. A convenient and economical desorption method can prolong the life of the adsorbent and cut down the disposal frequency of the spent adsorbent, thus lowering the overall operation cost of the wastewater treatment process. Therefore, the desorption performance of an adsorbent and its mechanical or chemical stability during reuse is perhaps as important as the adsorption performance in practical application.

However, there are limited studies that report on the desorption performance of alginate-based beads and their physicochemical–mechanical properties during reuse. Indeed, a quick literature search in the database of Web of Science (WoS) revealed that the number of studies on adsorption by alginate outweighed the studies on desorption by 17 to 1. Liu et al. [1] and Wang et al. [2] have shown that the adsorption capacity of the alginate-HNTs
nanocomposite beads towards methylene blue and copper decreased by 10% and 35%, respectively, after desorption. However, these previous studies did not further examine the desorption behavior of the beads and the effects of repetitive adsorption/desorption process on the beads properties and stability.

The aim of this work is to address this gap by systematically assessing the effect of acid desorption of Pb$^{2+}$ on the adsorption/desorption performance and the physicochemical—mechanical properties of alginate-based beads during reuse. The selection of a potent desorbing agent is first addressed, followed by investigations on the effects of repeated adsorption/desorption cycle on the physicochemical—mechanical properties of the beads such as size, morphology, adsorption capacity, chemical stability, and mechanical strength. Such comprehensive study is needed to evaluate the feasibility of the alginate-based beads for practical application in treating water contaminated with heavy metals.

2. Materials and methods

2.1. Materials

Sodium alginate (Manugel GHB, FMC Biopolymer, UK) with a medium range molecular weight (~97 kDa) of 37% β-α-mannuronic acid residues (M) and 63% α-δ-guluronic acid residues (G) was used in this study. The viscosity of 2 w/v% alginate solution at 25 °C was 452 mPa s. Halloysite nanotubes (HNTs) were donated by Imerys Tableware, New Zealand. Calcium chloride dihydrate, sodium hydroxide, sulfuric acid (H$_2$SO$_4$), hydrochloric acid (HCl), nitric acid (HNO$_3$) and Pb$^{2+}$ standard solution for atomic absorption spectrophotometer (AAS) were purchased from Fisher Scientific, UK. Lead nitrate (Pb(NO$_3$)$_2$) was acquired from Sigma Aldrich, Germany and used for the preparation of 1000 mg/L Pb$^{2+}$ stock solution. All chemicals used in this study were of analytical grade and were used as received. All solutions were freshly prepared with ultrapure water before each experimental run.

2.2. Experimental methods

The procedures of desorption study are summarized in Fig. 1. Blank alginate beads and alginate-HNTs nanocomposite beads were used for desorption study and are abbreviated hereafter as blank beads and nanocomposite beads, respectively. Desorption study was divided into three stages which were screening of the desorbing acid, desorption kinetics, and reusability. Physicochemical—mechanical properties characterizations were performed throughout the entire experiment.

2.2.1. Fabrication of blank beads and nanocomposite beads

This procedure was carried out as described in our previous work [6]. Briefly, a homogeneous dispersion of 10 g/L HNTs was prepared by ultrasonication before mixed with 2 w/v% of alginate. Extrusion dripping method was then used to produce nanocomposite beads with calcium chloride as the curing agent. Identical procedures were used to prepare blank alginate beads without the HNTs.

2.2.2. Batch adsorption/desorption studies

Pb$^{2+}$ adsorption/desorption experiments were performed under ambient temperature (298 K) with 10 g of beads/L of wastewater (=10 g/L adsorbent dosage). Generally, the beads were removed from the solution by simple filtration and washed with ultrapure water to remove traces of Pb$^{2+}$ on the surface. Surface of the nanocomposite beads was blotted with filter paper before they were weighted. The solution was agitated by a shaker-incubator at 150 rpm. All experiments were performed in duplicate and repeated using blank beads. Altogether, ten successive cycles of adsorption and desorption of Pb$^{2+}$ were performed.

For adsorption, the beads were placed in 400 mL of 100 mg/L Pb$^{2+}$ aqueous solution. The solution was adjusted to pH 5 with either 0.1 M HCl or 0.1 M NaOH prior to adsorption. The adsorption process was carried out for 24 h.

For desorption, the beads were then added into 400 mL of an acid for 24 h. No pH adjustment was done to eliminate the effect of competing ions. Two different acids, i.e. HCl and HNO$_3$ were used to determine the maximum desorption efficiency of the beads. Each acid was prepared in concentrations of 0.01 M, 0.10 M, 0.50 M and 1.00 M. The beads were then subjected to mechanical and chemical stability tests to determine the best acid for desorption without significantly compromising the properties of the beads.

The chosen acid with 400 mL was used for desorption kinetics study by collecting 5 mL of the sample at preset time intervals up to 420 min. The samples withdrawn were replenished with liquid withdrawn from a parallel run under identical conditions to maintain the constant volume of the first beaker.

2.2.3. Data analysis

Unless specified otherwise, the calculation was done in dry weight basis. Results were reported as the mean ± range of variability of duplicate runs performed on different days with freshly prepared samples. Differences were assessed for significance using the unpaired t-tests as appropriate. The level of significance was set at α = 0.05.

2.2.3.1. Adsorption capacity. The amount of Pb$^{2+}$ adsorbed on the adsorbent was calculated using Equation (1).
\[ q_t = (C_i - C_f)v/m \]  

\[ q_t = \text{Amount of Pb}^{2+} \text{ adsorbed per gram of adsorbent (mg/g)} \]
\[ C_i = \text{Concentration of Pb}^{2+} \text{ in the solution at time } t \text{ (mg/L)} \]
\[ C_f = \text{Initial concentration of Pb}^{2+} \text{ in the solution (mg/L)} \]
\[ v = \text{Volume of Pb}^{2+} \text{ solution (L)} \]
\[ m = \text{Dry mass of the adsorbent before adsorption (g)} \]

1. Spectra were registered as the reflection spectra. A blank analysis window was used as reference.

2. Thermogravimetric analysis (TGA)

The beads were freeze-dried before undergoing TGA. Then the beads were heated from 100 to 800 °C at a rate of 10 °C/min under nitrogen atmosphere via thermogravimetric analyzer (Q50 TGA, TA Instruments, USA).

3. Mechanical strength post adsorption/desorption

The mechanical strength of the beads was characterized in terms of the Young’s modulus with the same procedures reported in our previous work [6]. Briefly, the beads were subjected to uniaxial compression by a texture analyzer (TAXTplus Texture Analyzer, Stable Micro Systems, UK) at a strain rate of 25 min⁻¹. The beads were compressed to 30% deformation. Five beads from each sample were compressed and the mean of results were reported.

4. Safety and disposal measures for Pb²⁺ containing solutions and specimens

Gloves must be worn during handling of Pb²⁺ containing solutions or specimens. The Pb²⁺ containing solutions were disposed in a waste bottle with proper labeling whereas Pb²⁺ loaded beads were placed in the special waste bin available in the laboratory after air drying. The collected waste was disposed in accordance with the law.

3. Results and discussion

3.1. Screening of the desorbing acid

The choice of desorbing agent will affect the desorption performance and the physicochemical—mechanical properties of the adsorbent. Commonly used desorbing agents include competing counter ions (salt solutions e.g. sodium chloride), proton exchangers (e.g. acids) and heavy metal chelator solutions (e.g. ethylenediaminetetraacetic) [9]. Among these, acid is the most suitable to desorb Pb²⁺ from both blank beads and nanocomposite.
beads because the alginate matrix is readily destabilized in the presence of Ca\(^{2+}\) complexes [10] or monovalent ions (exclusive of protons) [6], thus impeding reusability of the beads. Hence, acetic acid was used in this study because hydrogen ions can form intercalation hydrogen bonding with alginate to hold the structure of the alginate while also functioning as an ion exchanger.

Two inorganic acids (HNO\(_3\) and HCl) were chosen in this study due to their (i) potential to dissolve lead, (ii) properties are well established, (iii) relatively low cost, and (iv) ability to achieve desorption and regeneration in just one step. Another commonly encountered acid, H\(_2\)SO\(_4\), on the other hand, was ruled out in this study because the formation of insoluble lead sulfate (PbSO\(_4\)) within the beads would defeat the desorption process. The effect of acid type (HNO\(_3\) and HCl) was tested at different concentrations varying from 0.01 M to 1.00 M (for one adsorption/desorption cycle only) and the results are discussed from four aspects — desorption percentage, chemical interaction, mechanical properties, and macroscopic structure (see Figs. 2 and 3).

### 3.1. Desorption performance

The effectiveness of HNO\(_3\) and HCl to desorb Pb\(^{2+}\) are presented in Fig. 2A and B. HNO\(_3\) generally desorbed more compared to HCl. Furthermore, HNO\(_3\) had the highest desorption percentage of 96% for blank beads and 98% for nanocomposite beads. The desorbing power of 0.50 M HCl was also very promising (92% for blank beads and 96% for nanocomposite beads). The desorption percentage of the beads generally increased with acid concentration due to a larger driving force for ion exchange (chemical potential produced by activity difference between H\(^+\) in solution and H\(^+\) inside the beads). The desorption performance improved the most when the acid concentration increased from 0.01 M to 0.10 M. Further increase in the acid concentration resulted in no significant improvement.

### 3.1.2. Chemical interaction between acid and beads

The calcium-alginate matrix changed to alginic acid after acid desorption. Alginic acid is the protonated form of its more well-known salt equivalent alginate [11]. The formation of alginic acid after desorption by HNO\(_3\) was confirmed by the FTIR spectrum with a clear shift of the stretching band of the free carboxyl double bond (C=O) from 1633 before desorption to 1735 cm\(^{-1}\) after desorption (see Fig. 2C and D). The band shift is in agreement with Papa-georgiou et al. [12] and Fourrest and Volesky [13]. Another band shift is from 1419 to 1225 cm\(^{-1}\) which corresponds to the carbonyl C=O bond. The shifting of C=O and C=O bands reflected the successful displacement of Pb\(^{2+}\) by H\(^+\). Besides, the intensities of these two bands increased with the concentration of the acid used which means more ionic bonds were replaced by hydrogen bonds. Similar FTIR spectra were obtained for the blank beads and the nanocomposite beads desorbed by HCl.

### 3.1.3. Young’s modulus

In our previous study, we showed that the mechanical strength of alginate beads was significantly improved after the incorporation of HNTs [6]. The nanocomposite beads had an initial Young’s modulus of 475 kPa which was 10% higher than that of the blank beads. This is important to ensure the applicability and life span of the beads in packed adsorption systems. However, the beads became weaker after acid desorption. The Young’s modulus of the blank beads and nanocomposite beads decreased by at least 39% and 43% respectively after desorption by HNO\(_3\) (see Fig. 2E and F). The beads desorbed with HNO\(_3\) and HCl had no significant difference in their Young’s modulus. Draget et al. [14] also reported a 50% decrease of Young’s modulus when dialyzing calcium-crosslinked alginate gel to alginic acid gel by D-glucono delta-lactone. This is not unexpected as the protonated ends of alginic acid were linked via hydrogen bonds which were weaker than the initial ionic bonds with Pb\(^{2+}\). Further, mineral acids used in desorption might cause hydrolysis of the alginate polymer chains, resulting in less cross-linking per volume unit [11].

### 3.1.4. Macroscopic appearance (size and color)

Two changes in bead appearance were observed during acid desorption. Firstly, the beads shrunk in size (see Fig. 2G and H) regardless of the type of acid used. The size of the blank beads decreased significantly when the acid concentration was increased from 0.01 M to 0.10 M. Interestingly, the beads shrunk less at acid concentration higher than 0.10 M. The same trend was observed for the nanocomposite beads. At low acid concentration, the shrinkage occurred because H\(^+\) (0.012 Å) cations were much smaller than Pb\(^{2+}\) (1.19 Å), and the electrostatic repulsion between the protonated carboxylic groups was reduced [15], thus allowing the alginate polymeric chains to have a closer proximity to one another. However, at high acid concentrations (0.50 M and 1.00 M), the alginate polymer chains could be hydrolyzed, thus destroying the hydrogen bonding between the polymer chains. Hence, the beads shrunk less. Despite having the same trend, the blank beads shrunk 5% more compared to the nanocomposite beads regardless of the type and concentration of acid used. This result shows that HNTs, even at a low loading of 10 g/L, played a role in maintaining the size of the nanocomposite beads.

Secondly, the wet blank beads became more opaque after desorption (see Fig. 3C and E) compared to before desorption (see Fig. 3A). The denser alginate polymer chain network led to the enhanced light scattering which increased the bead opacity [16]. Interestingly, both the blank beads and nanocomposite beads desorbed by 0.50 M and 1.00 M of HCl turned into black color after freeze-drying (see Fig. 3D), but the beads desorbed by HNO\(_3\) remained whitish regardless of the acid concentration (see Fig. 3F). It is possible that HCl could cause damage to the beads, possibly via acid hydrolysis of alginate polymers [17]. On the other hand, it has been reported that the oxidizing properties of HNO\(_3\) have no effect on alginate structure [18]. Torres et al. [19] and Ibáñez and Umetzu [18] had shown that the alginate gel structure could disintegrate in the presence of HCl at pH 4 but remained intact in HNO\(_3\) at the same pH.

### 3.1.5. Selection of the desorbing acid

When choosing the type of desorbing acid and its concentration, one should consider the desorption performance of the acid and the damage the acid can cause to the beads. In this work, HNO\(_3\) was selected mainly because it generally delivered a greater desorption, albeit marginal compared to HCl. HNO\(_3\) also caused less damage to the beads. An acid concentration of 0.10 M was deemed reasonable since at this concentration, the desorption performance was comparable to when higher acid concentration was used. In addition, a lower acid concentration is less hazardous and less costly.

### 3.2. Desorption kinetics

The desorption of Pb\(^{2+}\) over time from the blank beads and nanocomposite beads by 0.10 M HNO\(_3\) is presented in Fig. 4. The desorption appeared to involve two phases. The first phase was rapid with more than 50% of Pb\(^{2+}\) desorbed within five minutes. This is because the significant departure from equilibrium provided a great driving force for ion exchange between the Pb\(^{2+}\) and H\(^+\). During the second phase, as much of the Pb\(^{2+}\) had already been desorbed, a chemical equilibrium was nearly established, thus slowing down the desorption process. The desorption was virtually complete within 2 h, and no changes in the Pb\(^{2+}\) concentration
were observed beyond 7 h.

The desorption process was faster than adsorption. For example, 50 mg/L of Pb$^{2+}$ were adsorbed in 30 min while the same was desorbed in only five to ten minutes. This is because during the ion exchange with Pb$^{2+}$, the smaller H$^+$ in desorption had higher mobility compared to Pb$^{2+}$ in adsorption. The short desorption time is desirable as it can minimize the regeneration time for the adsorption bed. In contrast, the study by Katsou et al. [20] indicated that desorption process was much slower than adsorption since desorption of Pb$^{2+}$ from zeolite required 840 min while only 240 min for adsorption. The reason was due to the ions that had been easily adsorbed were difficult to be desorbed.

A pseudo second order kinetics was fitted to the temporal profile of desorption. Both blank beads and nanocomposite beads show high values of coefficient of determination, R$^2$ 0.99 and 0.98 respectively, indicating the applicability of this model. The rate constant for desorption, $k_{des}$ for blank beads and nanocomposite beads were 0.0032 and 0.0035 L/mg-min respectively whereas the
concentration of Pb\(^{2+}\) desorbed at equilibrium, Pbe, were 88.83 and 84.78 mg/L. The parameters for the pseudo second order kinetics suggest that the blank beads and the nanocomposite beads had no significant difference in their desorption kinetics and equilibrium concentrations.

### 3.3. Reusability

The cost effectiveness of an adsorbent depends heavily on the number of adsorption–desorption cycles that it could endure while maintaining an acceptable performance. The potential for multiple reuses of the blank beads and nanocomposite beads was tested for ten identical cycles, with the results summarized in Fig. 5. The effect on adsorption capacity and desorption percentage is discussed first, followed by the effect on the physicochemical–mechanical properties (size, morphology, structure, composition, and Young’s modulus) of the beads.

#### 3.3.1. Adsorption capacity

Throughout ten cycles, the adsorption capacity of blank alginate beads was about 12% higher than that of the alginate-HNTs nanocomposite beads (see Fig. 5A). The adsorption capacity of the second cycle decreased by 6% and 11% for the blank beads and nanocomposite beads respectively. Statistical analysis showed that the adsorption capacity remained relatively constant afterward up to the tenth cycle (p-value > 0.05 which means the difference between the adsorption capacities with the mean from the second cycle onwards is not significant). Park and Chae [10], who performed 10 adsorption/desorption cycles for Pb\(^{2+}\) loaded blank alginate beads using 0.50 M HNO\(_3\) as the desorbing agent also observed the same trend. The study by An et al. [21], however, shows the adsorption capacity for copper increased instead by 10% at the second cycle after desorption by H\(_2\)SO\(_4\) and remained constant up to the tenth cycle. While the contradictory drop or rise in adsorption capacity suggest system or cation dependence, they nevertheless all showed that adsorption capacity was maintained beyond the second cycle.

#### 3.3.2. Desorption efficiency

The changes of desorption percentage with the number of cycles were statistically insignificant (p-values > 0.05). The desorption percentage remained at approximately 94% for both blank beads and nanocomposite beads for all ten cycles (see Fig. 5B). As expected from the incomplete desorption, a small amount of residual Pb\(^{2+}\) was detected by EDX (see Fig. 6J).

#### 3.3.3. Size

The beads shrunk after acid desorption (refer to section 3.1.4). The initial average diameters of the blank beads and the nanocomposite beads were 2.35 mm and 2.41 mm, respectively. The average diameter continued to decrease, fortunately only slightly, with each cycle of adsorption and desorption (see Fig. 5C), while the shape of the both types of beads remained spherical. After the tenth cycle, the diameters of the blank beads and nanocomposite beads were reduced to 1.25 mm (i.e. 47% reduction) and 1.42 mm (i.e. 41% reduction), respectively. A lesser size reduction in the latter indicates that nanocomposite beads are more resistant to the structural changes by hydrolytic effects as compared to blank beads.

#### 3.3.4. Microscopic imaging

A typical electron micrograph of the nanocomposite bead before and after an adsorption/desorption cycle is presented in Fig. 6. The comparison of Fig. 6A–H showed that acid desorption induced a discernible change in the surface and internal structure of the beads. The smooth surface became crumpled, rugged, and denser. Acid desorption increased concomitant intertwinement of polymer
which resulted in shrinkage and thus, rougher surface morphology. The first layer of alginate matrix polymer at the surface became thicker after adsorption/desorption compared to the original bead. The thicker layer consists of multiple layers of alginate matrix that were interconnected by fine strands. Acid desorption collapsed the original network structure and forced the alginate polymer chains to reorganize themselves.

On the other hand, HNTs retained their tubular shape after ten cycles (Fig. 6H). However, some of the tubes were damaged with spherical nanoparticles (30–50 nm in size) were found near the surface of remaining HNTs after desorption (see Fig. 6H) while none was observed before desorption (Fig. 6G). It is suspected that repetitive acid desorption caused the dissolution of HNTs, leading to the formation of amorphous spherical nanoparticles of SiO₂ both inside and outside the tubes [22,23]. This is further supported by the fact that the dissolution pH for aluminosilicate clay ranges between 2 and 3 [24] whereas an even lower pH = 1 was used in this study. SiO₂ nanoparticles tend to form small aggregates when present outside the tubes [22,23].

3.3.5. Elemental analysis

EDX analysis confirmed the elemental composition of the beads. Owning to the limited depth of EDX (a few microns), EDX result cannot reflect the full information of elemental distributions of an entire bead (size in the order of millimeters). Therefore scans of the surface (Fig. 6I) and zoom-in of the cross section of a bead (Fig. 6J) were done. Peaks of C (carbon) which are predominantly from the alginate matrix appeared in both spectra, while peaks of Al (aluminum) and Si (silicon) are from HNTs. The peaks of Pt (platinum) are due to the sputter coating during FESEM sample preparation. For desorbed beads, Pb²⁺ was still detected in the inner part of the bead (see Fig. 6J) but not from the outer surface (see Fig. 6I). The same Pb²⁺ distribution was observed in desorbed blank beads. Such a spatial distribution could be explained as it was much more difficult for H⁺ to diffuse deeper into the bead to ion exchange with Pb²⁺. No Ca²⁺ was detected however, confirming that calcium-alginate completely changed to alginic acid after ten cycles of adsorption/desorption.

3.3.6. Decomposition of the beads

TGA was done to examine the decomposition of the beads after repetitive adsorption/desorption. There are two observations from the TGA profiles (see Fig. 5D) as the number of cycles increases. First, the decomposition temperature shifted to a lower temperature. For example, the decomposition temperature for 50% mass loss decreased by 181 °C for blank beads and 446 °C for nanocomposite beads after the first adsorption/desorption cycle (see Table 1). The replacement of the ionic bonds (calcium-alginate) by the weaker hydrogen bonds (alginic acid) could be the main cause. Second, the percentage mass loss increased. For the blank alginate beads, calcium-alginate generated residues containing carbonaceous char, calcium carbonate, calcium hydroxide and calcium hydroxide whereas alginic acid generated carbonaceous char residue only [25]. The mass loss of blank beads further increased by 19% at the tenth cycle, likely due to the leakage of the more soluble alginate biopolymers from the bead over the cycles. The result is consistent with the finding by An et al. [21] who showed that 20% of the total organic carbon was released from the alginate beads after 10 cycles of desorption by 1 M H₂SO₄. Based on the stoichiometric equation for the formation of Ca-alginate beads (see equation (4)), the stoichiometric amount of Ca²⁺ required for the full gelation of alginate beads used in adsorption is 0.4 mmol. Half of the Ca²⁺ was released during adsorption of Pb²⁺, which means half of the adsorption sites were still available [3]. This is further affirmed by the EDX image which shows that the Ca²⁺ are concentrated at the

![Fig. 5. A) Adsorption capacity, B) desorption percentage, C) size, D) TGA profile, and E) Young's modulus of alginate beads and alginate-HNTs nanocomposite beads for ten consecutive cycles of adsorption/desorption by 0.10 M HNO₃ with a solid to liquid ratio of 10 g/L. The error bars, where present, depict maximum and minimum values.](image-url)
Therefore, the leakage of 20% of alginate has no effect on the adsorption capacity of the beads as the active sites were in excess.

Curiously, we believe that the HNTs also leaked out or damaged during repetitive adsorption/desorption based on two observations. Firstly, the residue mass of tenth cycle nanocomposite beads was 17% only which is less than the theoretical composition of HNTs within the nanocomposite beads (33%). Secondly, had the HNTs remained in the beads, the TGA mass loss percentage would decrease as the fraction of thermally degradable alginate dropped over the cycles. But the mass loss percentage became larger instead. These suggest that some HNTs could leak together with the alginate, but in different proportions. This hypothesis is not contradicted by the smaller size of the beads over the cycles.

3.3.7. Mechanical stability

As the beads underwent repeated cycles, there was a substantial increase in Young’s modulus (see Fig. 5E). However, this

<table>
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<th>Number of desorption cycle</th>
<th>50% Mass loss temperature (°C)</th>
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<tr>
<td>Blank alginate beads</td>
<td>441</td>
</tr>
<tr>
<td>Alginate-HNTs beads</td>
<td>741</td>
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<tr>
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Table 1

Mass loss percentage at 800 °C determined using TGA and the decomposition temperature of 50% mass loss of blank alginate beads and alginate-HNTs nanocomposite beads with 10 g/L HNTs loading after different number of adsorption/desorption cycles.

Fig. 6. FESEM-EDX images of alginate-HNTs nanocomposite beads prior to and post adsorption/desorption (the end of the 10th desorption). A, B, C, and D refer to the surface; while E, F, G and H refer to the cross-section. Red squares represent the regions of close-up views. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
contradicted the studies by Liu et al. [11], Jain et al. [26] and Wang et al. [2] who showed that blank beads swelled and disintegrated after the third cycle. This could be due to the type of acid and the high concentration of acid used in their works, i.e. 0.50 M—1.00 M HCl. As mentioned in section 3.1.4, this concentration range of HCl can destroy the structure of the beads and hence should be avoided. Whereas in our study, dilute HNO₃ (0.10 M) was used, and the reduced size of the beads post desorption resulted in higher density and a more compact structure, thus increasing the Young’s modulus. In addition, the residual Pb²⁺ ions in the beads post desorption could also contribute to the strength of the beads via the strong ionic bonds.

When the beads post desorption were subjected to subsequent Pb²⁺ adsorption, the Young’s modulus of the beads increased dramatically, especially from second cycle onwards. Interestingly, the blank beads became stronger than nanocomposite beads from fourth cycle onwards. This shows that HNTs might have obstructed the rearrangement of alginate polymer chains, thus resulted in larger and weaker nanocomposite beads. However, the mechanical strengths of the both types of beads post desorption were approximately similar but their strength was lower than that of the beads post adsorption. The difference in the strength post adsorption between both types of beads is not a major concern for applications because it is the lower strength post desorption that decides the usability of the beads in a packed bed. In this case, the strength of the beads post desorption were still higher than that of the freshly prepared beads (i.e. see Young’s modulus of beads at 0th cycle in Fig. 5E).

Altogether, a denser network of alginate after acid desorption and their subsequent crosslinking by Pb²⁺ synergistically contributed to the improved Young’s modulus of the alginate hydrogels to unprecedented levels (i.e. 11.4 MPa, see Young’s modulus of blank alginate beads at 10th adsorption cycle in Fig. 5E). From the perspective of industrial application, a higher Young’s modulus and a smaller size allow the packed height of the adsorbent bed to be refilled less frequently, to compensate for the slight loss in adsorption capacity beyond the first cycle, as well as to cater for a longer adsorption run. This can further reduce the wastewater treatment cost. As for the alginate-HNTs beads, they were found to have slightly lower post adsorption strength and adsorption capacity. However, their use is still justifiable because HNTs are significantly cheaper than alginate, thus the inclusion of HNTs in the alginate beads would lower the price of the adsorbent per unit mass.

4. Conclusion

This study represents the first ever comprehensive characterization of alginate-based beads post cyclic adsorption/desorption process. The desorption performance depends on the type and concentration of acid. Various physicochemical—mechanical characteristics revealed that both blank alginate and alginate-HNTs beads can be reused for at least ten cycles of Pb²⁺ adsorption without severe decrease in adsorption capacity or destruction of the bead structure. Interestingly, the mechanical strength improved over the cycles. These findings suggest that the alginate-based beads are feasible for long-term reuse for removing trace concentration of heavy metal from aqueous solution. To further explore the commercial opportunity of this adsorbent, a life cycle economic analysis is being pursued.

Acknowledgments

The authors would like to thank the Ministry of Higher Education Malaysia for supporting this research under the FRGS/1/2013/TK04/MUSM/02/1 scheme and the School of Engineering, Monash University Malaysia for providing the Ph.D. studentship to Christine Chiew.

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