Preparation and characterization of p-sulfonated calix [4] arene functionalized chitosan hydrogel beads and their preliminary adsorption study towards removal of lead (II) and zinc (II) ions

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INTRODUCTION

There is a major global concern on water quality. The rapid development in industrial and agricultural activities has contributed to the increase in wastes being released to the environment, thus deteriorating water quality. To overcome this problem, various techniques have been introduced to remove different types of pollutants such as heavy metal ions, dyes, nitrates and phosphates, and other hazardous and toxic chemicals from water (Reddy & Lee 2013; Akpor et al. 2014; Authman et al. 2015; Konczyk et al. 2016; Awad et al. 2017; Marbu & Benton 2018). Heavy metal ions are commonly found in industrial water effluents which tend to accumulate in both soil and water, posing threats to the living ecosystems as they can be easily transported and taken up (Akpour et al. 2014; Authman et al. 2015; Konczyk et al. 2016). The accumulation of these ions can damage or reduce the function of central nervous system or even cause kidney and liver damages (Akpour et al. 2014).

Several methods have been developed to remove heavy metal ions such as chemical coagulation, ion exchange, chemical oxidation/reduction, adsorption, bioremediation, reverse osmosis, membrane separation, electrochemical techniques, and ultrafiltration (Reddy & Lee 2013; Awad et al. 2017; Marbu & Benton 2018). Adsorption possesses several advantages over other methods such as simple, cost effective, high efficiency, easy recovery, reasonably high regeneration capacity, and it is sludge-free (Zhang et al. 2016). The underlying mechanism for adsorption is based on the favorable interaction between the target metal ion and active groups exist on the surface of adsorbent (Handayani et al. 2011). This can be achieved by utilizing chelating ligands or cavitands that has effective binding affinity toward the target metal ions (Konczyk et al. 2016; Zawierucha et al. 2016; Awad et al. 2017). To date, numerous materials have been studied in terms of effectiveness for metal adsorption. One of these materials is calixarene (Siswanta et al. 2016) which has a fairly unique molecular geometry with almost unlimited derivate possibilities (Siswanta et al. 2016). Calixarenes are present in three-dimensional structures where phenolic sub-units are bridged with methylene and forms a ring with an upper rim, central annulus, and lower rim (Figure 1) with several functional sites (McMahon et al. 2003). This enables the modification of their upper or lower rim in order to gain access to derivatives with functional groups selective to the targeted guest ions (Izatt et al. 1985; McMahon et al. 2003). Thus far, calixarenes have been utilized for extraction of various analytes, heavy metal, dyes, and oxyanions (Alahmadi et al. 2013).
Preparation of chitosan hydrogel beads

A schematic diagram representing the preparation of the calixarene functionalized chitosan hydrogel beads is as shown in Figure 2. In a typical preparation of chitosan hydrogel beads, 0.2 g of high molecular weight chitosan was dissolved in 12.5 µL of acetic acid and 20 mL deionized (DI) water. The chitosan solution was added drop-wise into 50% w/v sodium hydroxide solution using a 5 mL syringe and let aside for the beads to form. The hydrogel beads that were formed were filtered and washed with DI water.

Preparation of p-sulfonated calix[4]arene / chitosan (C4SCTS) hydrogel beads and p-sulfonated calix[4]arene / chitosan / graphene oxide (C4SCTSGO) hydrogel beads

Firstly, 0.1 g of p-sulfonated calix[4]arene was dissolved in DI water and diluted in 100 mL of volumetric flask. Next, chitosan solution was prepared by dissolving 0.2 g of chitosan in 12.5 µL of acetic acid and 10 mL DI water. To prepare p-sulfonated calix[4]arene / chitosan (C4SCTS) solution, 10 mL of p-sulfonated calix[4]arene stock solution was added into chitosan solution.

Meanwhile for the preparation of p-sulfonated calix[4]arene / chitosan containing graphene oxide, 1 mL of GO (1 mg / mL in water solution) was added into 10 mL of p-sulfonated calix[4]arene solution and then added into the chitosan solution. Calixarene modified mixture was then added drop-wise in 50% w/v sodium hydroxide solution using 5 mL syringe and let aside for the beads to form. The hydrogel beads that were formed were filtered and washed with DI water.

Preparation of heavy metal ion solution

This work involved two metal ions solutions which were Zn(II) and Pb(II) metal ion solutions. To prepare these solutions, 1.0 g of zinc chloride was dissolved in 30 mL of 5 M HCl and diluted with deionized water in 1000 mL volumetric flask, whereas 1.0 g of lead powder was dissolved in 30 mL 5 M nitric acid, and diluted with DI water in 1000 mL volumetric flask. Different concentrations of Zn(II) and Pb(II) metal ion solutions were prepared from the stock solutions, namely 1 ppm, 5 ppm, 10 ppm, 15 ppm, and 20 ppm.

Heavy metal ion adsorption test

To study the ability of the samples to adsorb heavy metal ions, the adsorption test was carried out using different concentrations of heavy metal ion solution, namely: 20 ppm, 15 ppm, 10 ppm, 5 ppm, and 1 ppm. 5 pieces of the hydrogel beads were added into 10 mL of heavy metal ion solution and stirred at 5 rpm for 30 minutes. Percent removal of heavy metal ions was calculated using the following equation:

\[
\text{Percent removal} = \left( \frac{C_i - C_f}{C_i} \right) \times 100\% \quad \text{Eq. 1}
\]

where \(C_i\) is the initial concentration of metal ion solution and \(C_f\) is the final concentration of metal ion solution. The filtrate solutions obtained in the adsorption process were analyzed using Atomic Absorption Spectrometer (AAS) where the initial and final concentration of heavy metal ion solution was investigated.

RESULTS AND DISCUSSION

Preparation of hydrogel beads

Hydrogel beads of pristine chitosan (CTS), p-sulfonated calix[4]arene functionalized chitosan (C4SCTS), and p-sulfonated calix[4]arene functionalized chitosan with addition of graphene oxide were successfully prepared. As shown in Figure 3 (a) and (b), both CTS and C4SCTS hydrogel beads are spherical (0.1 cm diameter) and white in color. Meanwhile, C4SCTSGO hydrogel beads appeared light brown.
functional groups or appear as small absorption peaks due to low concentration (Panchal et al. 2010). For instance, peaks attributed to vibrational mode of sulfonate group (νSO3) was reported to appear at ~1050 cm⁻¹ ~1200 cm⁻¹ which overlaps with the C-O stretching absorption peaks (Panchal et al. 2010). For the same reason, IR spectrum for C4SCTSGO also displays similar absorption peaks as CTS since it is dominant in the sample and in addition, the functional groups exist in GO are also similar as CTS (Ciplak et al., 2014).

Adsorption study of Pb(II) and Zn(II) using Atomic Absorption Spectroscopy (AAS)

The adsorbent’s heavy metal ions removal ability was tested by measuring the concentration of heavy metal ions left in the solution using a Thermo Scientific SOLAAR M series AAS. The adsorption behavior of Pb(II) and Zn(II) by the adsorbents at various initial concentrations (1 ppm, 5 ppm, 10 ppm, 15 ppm, and 20 ppm) are as summarized in Figure 5a and b. All operational parameters were kept constant (agitation speed: 100 rpm, pH: 5, contact time: 30 minutes). Based on the results obtained, increasing the initial concentrations of metal ions causes an increase in the adsorption capacity with the highest removal rate attained at 10 ppm. However, at higher than 10 ppm initial heavy metal ion concentration, the adsorption decreases with increase of Pb(II) and Zn(II) ions concentration. This could be due to less coordination ability of the adsorbent and sufficiently be removed from the solution. However, at concentrations higher than 10 ppm, the adsorbent presumably has reached the saturation limit causing limited active sites for metal binding. Therefore, more metal ions remaining in solution at higher concentration levels.

The highest percentage of Pb(II) ion removal was recorded at 98.83%, 90.65% and 60.58% by C4SCTS, C4SCTSGO and CTS hydrogel beads respectively (Fig. 4b). Meanwhile, for the removal of Zn(II) ion (Fig. 4b) the highest was recorded at 90.93%, 89.62% and 60.42% by C4SCTS, C4SCTSGO and CTS hydrogel beads respectively. For both cases, the removal of Pb(II) and Zn(II) ions are achieved at 10 ppm and decrease as the initial concentration increased. Result shows that C4SCTS hydrogel beads display the best adsorption performance followed by C4SCTSGO hydrogel beads and CTS. This strongly suggests that the presence of active functional groups of calixarene, such as sulfonate and hydroxyl groups play important role in the removal of the heavy metal ions. Interestingly, adsorbent containing GO shows lower adsorption performance, possibly due to the GO layers covering the functional groups of the calixarene molecules thus decreasing the number of available metal binding sites. Nevertheless, hydrogel beads containing GO are physically more robust compared to samples without GO. Results also show that the sorption efficiency for all adsorbents is higher for Pb(II) compared to Zn(II) metal ions.

CONCLUSION

An efficient adsorbent based on calixarene modified chitosan were successfully prepared using a facile technique. Results show that maximum removal of Pb(II) and Zn(II) by C4SCTS hydrogel beads was achieved at 10 ppm initial heavy metal ion concentration with 98.83% and 90.93% removal, respectively. This indicates that upon addition of p-sulfonated calix[4]arene into chitosan, the metal ion adsorption capacity of the hydrogel beads has dramatically increased. Meanwhile, the addition of graphene oxide did not contribute towards metal ion removal, however the stability of the hydrogel towards shrinkage was...
slightly improved in which the hydrogels without GO shrinks easier compared to the hydrogels with GO if left in open atmosphere for a prolonged period of time.

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