

Green Synthesis of Hydroxyapatite for the Removal of Cationic and Anionic Pollutants

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Abstract

Rapid industrialization over recent years has resulted in rampant discharge of pollutants containing pollutants such as copper(II), lead(II), and fluoride ions into water bodies. These ions pollute the water, posing a threat to those consuming water. Activated carbon is commonly used for water purification, however, its synthesis requires toxic chemicals. Calcium hydroxyapatite (Ca-HAP), has been gaining attention as a viable adsorbent in the removal of these ions. However, the current synthesis method of Ca-HAP from waste eggshells requires 2 rounds of calcination, which is energy intensive, rendering it expensive to synthesize. A cheaper and less energy intensive method involving the acid digestion of eggshells to form $\text{Ca}(\text{NO}_3)_2$ and single round of calcination has been studied and investigated. The effectiveness of the Ca-HAP synthesized by both methods in removing copper(II), lead(II) and fluoride ions was investigated and compared with commercial activated carbon. The Ca-HAP synthesized by both methods was found to be comparable to commercial activated carbon in terms of copper(II) and lead(II) ions adsorption. They also outperform activated carbon in adsorbing fluoride ions. The optimal pH for fluoride adsorption was found to be pH 4. Ca-HAP synthesized by the method proposed in this study is less energy intensive and resulted in a higher percentage yield than the conventional method, rendering the production of Ca-HAP cheaper. Ca-HAP has great potential to be used as an eco-friendly adsorbent in wastewater treatment to remove metal ions and fluoride ions

1. Introduction

Rapid industrialisation over the past couple of years has led to water pollution becoming a pertinent issue. Untreated wastes from industries and farms are often discharged directly into the environment, causing adverse impacts on both the environment and human (Mayor, 2017). One common harmful pollutant is heavy metal ions, such as lead (II) ions and copper (II) ions. Lead (II) ions can leach from polyvinyl chloride (PVC) pipes and lead piping (Zhang, Wilson, & Ge, 2015), while the major sources of contamination of copper in wastewater are electroplating, paints and dyes, petroleum refining, fertilizers, mining and metallurgy, and pesticides (Varma & Misra, 2016). A recent example of heavy metal ion pollution would be the 2014 Flint water crisis where lead from the aging pipes leached into the water supply, leading to extremely elevated levels of the heavy metal neurotoxin and exposing over 100,000 residents to elevated lead levels (Campbell, Greenberg, Mankikar & Ross, 2016). Lead poisoning has serious health implications, notably its teratogenic effect. Lead

poisoning also causes the inhibition of the synthesis of haemoglobin, dysfunctions in the kidney and joints (Verma & Dwivedi, 2013), while copper poisoning could cause one to experience nausea, vomiting, stomach cramps, or diarrhea. High intakes of copper can cause liver and kidney damage and even death (Varma & Misra, 2016).

Another common water pollutant would be fluoride ions. Fluoride from aluminium melting, glass manufacturing, phosphate fertilizer and brick manufacturing may leach out and potentially enter water supply if not carefully treated (Sankhla & Kumar, 2018). Fluoride concentrations in groundwater of some places in the world exceed the acceptable value; for example, in some area of Northeast China the fluoride concentration is about 4mg/l, exceeding the international WHO guideline of 1.5 mg/l (Korir et al., 2009). Fluoride poisoning mainly causes dental and skeletal fluorosis. However, the toxicity of fluoride cannot be undermined as high fluoride concentration in take could ultimately result in death (Dey & Giri, 2015).

Current methods of wastewater purification commonly utilize carbon-based adsorbents, which are known to be good organic pollutant adsorbents due to its ability to form pi-pi interactions with organic adsorbents. However, carbon-based adsorbents are less effective in removing inorganic pollutants although it is capable of adsorbing heavy metal ions onto its surface via ion exchange mechanism (Tumin, Chuah, Zawani, Rashid & 2008). Furthermore, carbon-based adsorbents have poor adsorption capabilities for anions as the surface hydroxyl group, -COH, has to form covalent bonds with H⁺ ions before being able to bind with the anions (Araga, Soni, & Sharma, 2017). As such, carbon-based adsorbents perform poorly on inorganic pollutants.

Calcium hydroxyapatite (Ca-HAP) is a main component of human bones and teeth (Sari & Yusuf, 2018). It has a chemical formula of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. Ca-HAP has received a great deal of attention as a good adsorbent. It is highly stable under reducing and oxidizing conditions and possesses various favourable surface characteristics, such as surface functional groups, acidity and basicity, surface charge, hydrophilicity and porosity. The performance of Ca-HAP for the removal of toxic metal ions from an aqueous solution has also been widely demonstrated at laboratory scale. Ca-HAP has strong affinity for the fixation of different metal ions including cadmium, zinc, strontium, mercury, and cobalt (Minh et al., 2018).

A variety of synthesis techniques of Ca-HAP have been developed such as sol-gel procedure, precipitation, hydrothermal and solid-state reactions (Sari & Yusuf, 2018). This study proposes the use of eggshells as the precursor for the synthesis of Ca-HAP. Eggshells represent a significant waste and they are commonly disposed of in landfills or incinerated. Such activities are highly undesirable to the environment. The use of eggshells to synthesise Ca-HAP is more environmentally friendly and inexpensive. Furthermore, it could also help

solve food wastage problems, with close to 250,000 tonnes of eggshells waste being produced annually worldwide (Verma, Kumar, & Bansal, 2012).

However, the conventional method of using eggshells to synthesize Ca-HAP requires double calcination steps which are costly and energy intensive.

Objectives and hypothesis

This study aims to synthesise Ca-HAP from eggshells using two reaction routes. The first method is a conventional method which involves double calcination, where eggshells was first calcined to form calcium oxide, followed by reaction with diammonium hydrogenphosphate and a second round of calcination (Sari & Yusuf, 2018). The second method is the improvised method proposed by this study. It involves only one calcination step, which lowers the energy consumption. It involves the conversion of eggshells to calcium nitrate by reaction with nitric acid, followed by reaction with diammonium hydrogenphosphate and calcination. The yield and morphology of Ca-HAP synthesised by the two methods were compared. The effectiveness of Ca-HAP synthesized by the two methods in removing cationic pollutants (copper(II) ions and lead(II) ions), and an anionic pollutant (fluoride ion) was evaluated and compared with commercial activated carbon, a commonly used adsorbent. The effect of pH on the adsorption of fluoride ions by Ca-HAP was also studied.

This study hypothesized that Ca-HAP can be synthesized from eggshells via the two methods – single calcination and double calcination. The removal of metal and fluoride ions by Ca-HAP synthesized from both methods would be comparable to commercial activated carbon. Changes in pH will affect the adsorption of fluoride by Ca-HAP.

2. Materials and methods

2.1 Materials

Eggshells were obtained from the school canteen. Diammonium hydrogenphosphate was procured from Hanawa. Nitric acid was purchased from Scharlau. 25% (w/w) aqueous ammonia, lead(II) nitrate and copper(II) sulfate from GCE Laboratory chemicals. Activated carbon was purchased from Unichem. Caesium fluoride was purchased from Sigma Aldrich.

2.2 Methods

2.2.1 Synthesis of Ca-HAP Via Double Calcination Method

The double calcination method was carried out as reported by Sari and Yusuf (2018). Eggshells were washed with deionised water, dried and blended into powder. The blended eggshells was then calcined at 800°C for 3h to obtain calcium oxide. The reaction is shown in equation 1.



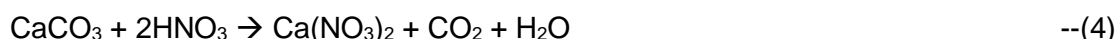
2g of calcined eggshells (CaO) was mixed with 50ml of deionised water. Then, 50 ml of 0.428 M diammonium hydrogenphosphate solution was added dropwise to the mixture. The mixture was subsequently stirred for 45 minutes while being heated at 75°C. The pH of the mixture was adjusted to 10 by adding 25% (w/w) aqueous ammonia. The mixture was then subjected to 24 hours of ageing without heating. The mixture was then filtered and the precipitate of Ca-HAP was retrieved and washed with deionised water until pH was neutral. The precipitate of Ca-HAP was dried in an oven until constant mass before being calcined at 800°C for 3h. The following reactions occurred:



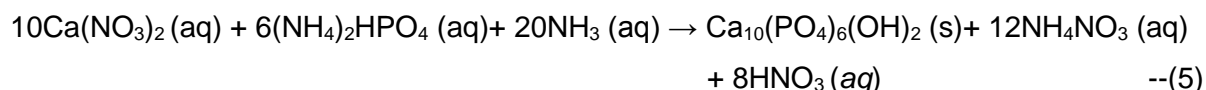
2.2.2 Synthesis of CaHAP via single calcination method

This method was self-improvised to reduce the frequency of calcination. The percentage of calcium carbonate in eggshells was determined by reacting 0.6 g of eggshell with 10.0 cm³ of 1.00 mol dm⁻³ hydrochloric acid. The resulting mixture was filtered into a 100 ml volumetric flask and the volume made up to 100 ml mark using deionised water. 10.0 cm³ of aliquots of the resulting solution was titrated with 0.100 mol dm⁻³ NaOH using methyl orange as an indicator. The titration was repeated until consistent readings were obtained. The titre obtained from the titration was used to calculate the percentage of calcium carbonate in eggshells which in turned was used to determine the volume and concentration of nitric acid required for the conversion of eggshell to calcium nitrate. The percentage of calcium carbonate in eggshell was determined to be 97.5%

With stirring, 5g of eggshells was added to 48.5cm³ of 2M HNO₃. The reactants were mixed for 1 hour before being filtered into a volumetric flask and the volume made up to 100 ml using deionised water. The synthesis of Ca(NO₃)₂ occurs via the following reaction:



50ml of 0.400 M diammonium hydrogenphosphate was added dropwise into 50 ml of the synthesised Ca(NO₃)₂ solution. The pH was adjusted to 10 with the addition of 25% (w/w) aqueous ammonia. Ca-HAP was formed as a white precipitate. The precipitation reaction is shown in equation 5. The Ca/P molar ratio was kept at 1.67 corresponding to the stoichiometry of Ca-HAP.



The reaction mixture was stirred and heated at 100°C for 1h. The suspension was subjected to ageing without heating for 24h. The obtained Ca-HAP precipitate was filtered and

washed with deionised water until pH neutral, before being dried at 100°C until constant mass and calcined at 800°C for 2h.

2.2.3 Characterisation of Ca-HAP

The Ca-HAP synthesized was characterised using a X-Ray Diffraction (XRD). The size and morphology of the Ca-HAP were determined using a Scanning Electron Microscope (SEM).

2.2.4 Adsorption studies

2.2.4.1 Adsorption of heavy metal ions and fluoride ions

0.1g of Ca-HAP was added to 20ml of solution containing 50mg/L of metal ions or fluoride in a beaker. A control containing the same volume and concentration of pollutant but without any Ca-HAP was included. 5 replicates were conducted for each type of Ca-HAP. The mixture was stirred with a magnetic stirrer for 24h. The concentrations of metal ion or fluoride ion left were then measured using a colorimeter (HACH DR 890) for copper(II) ions and fluoride ions and an Atomic Absorption Spectrophotometer (AA 6300 Shimadzu) for lead(II) ions. The percentage of metal ion/fluoride removed was calculated using the following formula:

$$\text{Percentage removed} = \frac{\text{Initial concentration} - \text{Final concentration}}{\text{Initial concentration}} \times 100\%$$

2.2.4.2 Effect of pH on adsorption of fluoride ions by Ca-HAP

The pH of fluoride solution was adjusted to pH 2, 4, 6, 8, 10. Adjustment of pH was accomplished using 1 M hydrochloric acid or sodium hydroxide. Adsorption studies as described in section 2.2.4.1 were conducted.

3. Results and discussions

3.1 Characterization of calcium hydroxyapatite (Ca-HAP)

3.1.1 By Scanning Electron Microscope (SEM)

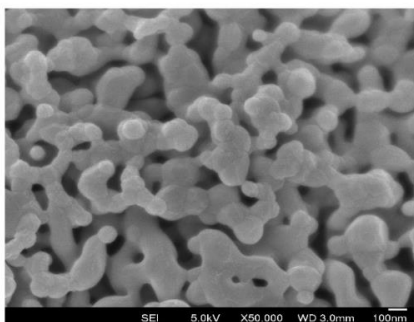


Figure 1: SEM image of Ca-HAP synthesized using “double calcination” method at 50000x magnification

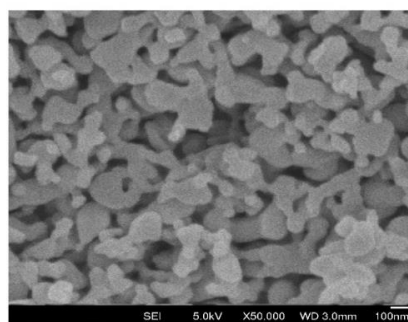


Figure 2: SEM image of Ca-HAP synthesized using “single calcination” method at 50000x magnification

Figures 1 and 2 reveal that the Ca-HAPs synthesized by both methods consist of particles of similar globular shapes and structures and are more than 100nm.

3.1.2 By Energy Dispersive Spectrometry (EDS)

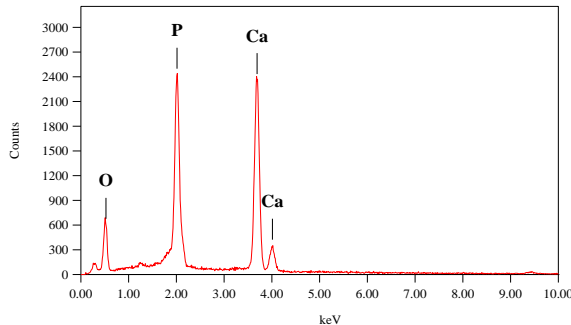


Figure 3. EDS spectrum of Ca-HAP synthesized using “double calcination” method

Figure 3 shows the presence of calcium, oxygen and phosphorous, which is in good agreement with the composition of Ca-HAP. EDS spectrum of Ca-HAP synthesized by “single calcination” method shows similar peaks.

3.1.3 By X-Ray diffraction (XRD)

The reflection patterns of Ca-HAP synthesized match the XRD pattern of hydroxyapatite reported in literature. The two theta peaks at 26.1°, 31.9°, 40.0° and 46.8° are characteristic of hydroxyapatite (Ariffin, Yatim, & Hamzah, 2017). XRD of Ca-HAP synthesized using the single calcination method was not available due to closure of external analytical laboratory during the circuit breaker period.

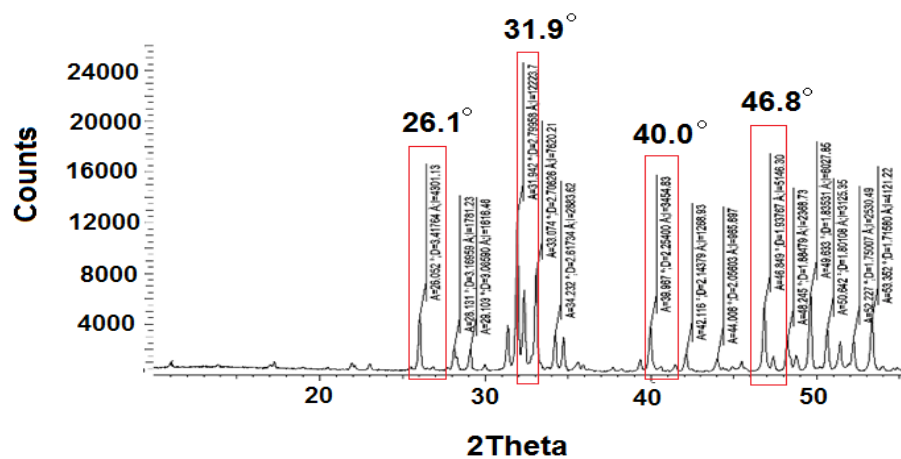


Figure 4. XRD pattern of Ca-HAP synthesized using “double calcination” method

3.2 Batch Adsorption Studies of Ca-HAP

3.2.1 Adsorption of heavy metal ions (Copper (II) ions and Lead (II) ions)

Figure 5 shows that Ca-HAP synthesized from both single calcination and double calcination methods are comparable with commercial activated carbon in the removal of lead(II) ions but are slightly less effective than commercial activated carbon in the removal of copper(II) ions. Copper (II) ions and lead (II) ions are likely adsorbed via an ion-exchange

mechanism. The chemical reactions for the ion-exchange mechanism are shown in equations 6 and 7:

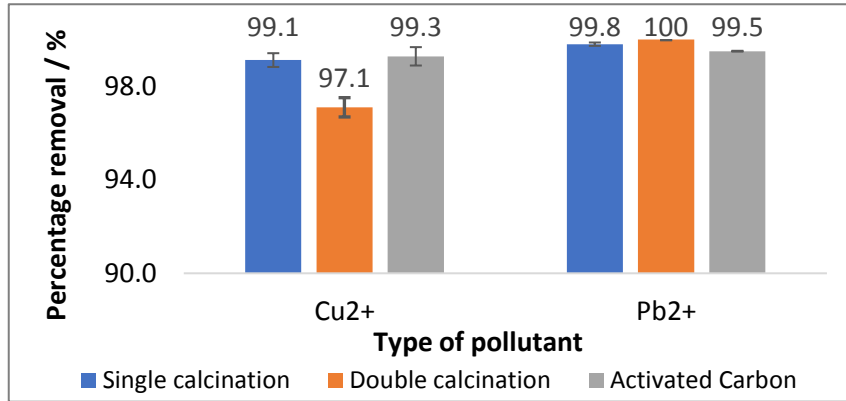
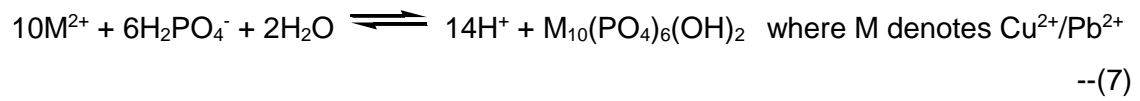
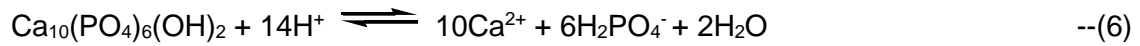


Figure 5. Adsorption of metal ions by Ca-HAP

On the other hand, activated carbon contains functional groups such as hydroxyl and carboxyl groups which possess lone pair of electrons on the oxygen atoms and are able to form dative bonds with the electron deficient heavy metal ions (Huang et al., 2011).

3.2.2 Adsorption of fluoride ions

Figure 6 shows that Ca-HAPs synthesized by both methods are a lot more effective than activated carbon. The difference is statistically significant as Mann-Whitney U tests between each type of HAP and activated carbon yield a p-value of 0.019, which is less than 0.05.

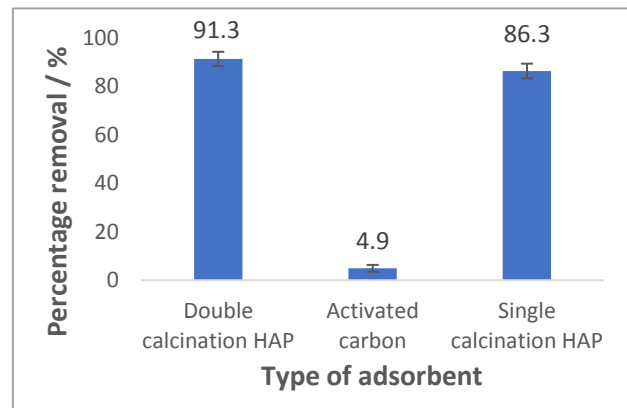


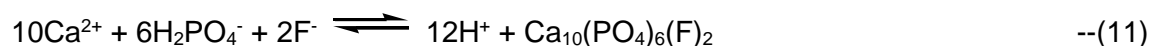
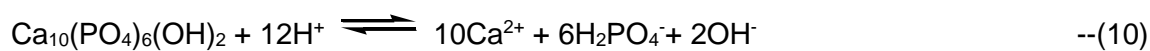
Figure 6. Comparison of the adsorption of fluoride ions by Ca-HAP with activated carbon

Activated carbon removes fluoride ions through the reaction between protonated surface hydroxyl group of activated carbon and fluoride ions (Araga, Soni, & Sharma, 2017), as shown in equation 8 and 9.



As protonation of hydroxyl groups is involved, activated carbon is only effective in removing fluoride ions at pH less than 3 (Li et al., 2001).

The adsorption of fluoride ions on the Ca-HAP surface likely occurs through electrostatic attraction between Ca-HAP surface charges and fluoride ions (Nayak, Samant, Patel, & Misra, 2017). Fluoride ions are also adsorbed through ion-exchange mechanism, in which the OH⁻ ions in Ca-HAP is replaced with fluoride ions to form fluorapatite (Ca₁₀(PO₄)₆(F)₂) (Nayak, Samant, Patel, & Misra, 2017). The chemical reactions for the ion-exchange mechanism are shown in equation 10 and 11.



In addition, Ca-HAP contains surface hydroxyl groups which protonate to form OH₂⁺, hence attracting fluoride ions through ion pair formation (F⁻⋯OH₂⁺). Fluoride ions can also be adsorbed onto the surface of Ca-HAP through hydrogen bond formation (Nayak, Samant, Patel, & Misra, 2017).

As such, F⁻ ions can be absorbed by Ca-HAP by both chemisorption, which is the ion-exchange mechanism, and physisorption, which is the ion pair formation and hydrogen bonds. In contrast, activated carbon could only remove fluoride through one mode. This explains why Ca-HAP is many times more effective than activated carbon in the removal of fluoride ions.

3.3 Effect of pH on adsorption of fluoride ions by Ca-HAP

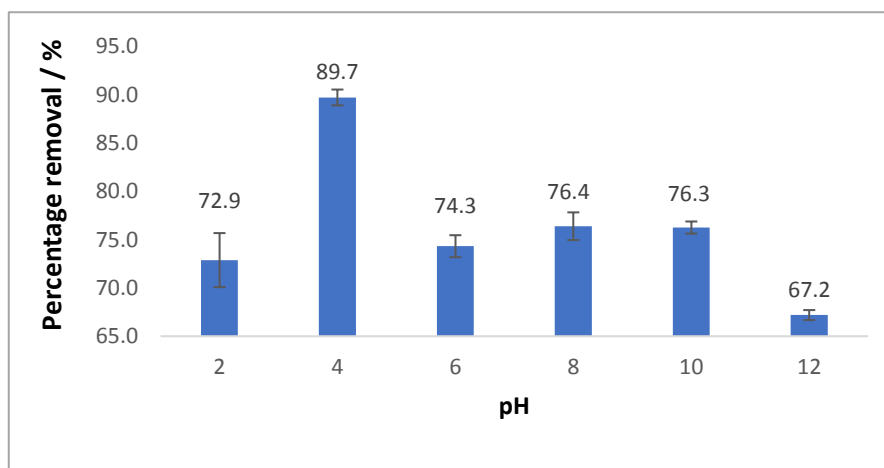
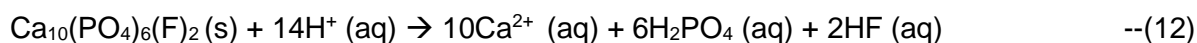


Figure 7. Effect of pH on adsorption of fluoride ions by Ca-HAP

Based on figure 7, there is a major increase in percentage removal between pH 2 to pH4. This could be attributed to the desorption of fluoride ions from fluorapatite formed when Ca-HAP adsorbs fluoride ions, which occurs via the following reaction:



At low pH, the high concentration of H⁺ ions favours the dissociation of fluorapatite, which would lead to a decrease in the percentage removal of fluoride ions.

Similarly, there was a major drop in percentage removal between pH 10 and 12. At pH 12, the high concentration of hydroxide ions compete with fluoride ions for adsorption sites, resulting in fewer adsorption sites available for adsorption of fluoride ions and in turn leads to a lower percentage of fluoride ion removed.

3.4 Comparison between single calcination and double calcination methods

Table 1: Comparison between single calcination and double calcination method

	Single calcination	Double calcination
Duration of calcination	2h	5h
Percentage yield/%	76.4	72.2
Cost/kg	\$30.98	\$68.11

CaHAPs synthesized by both the single calcination and double calcination methods are comparable in terms of their effectiveness in removing copper(II), lead(II) and fluoride ions. Other aspects were also compared, as shown in table 1.

Cost is calculated based on electrical consumption and the amount and cost of chemicals required to synthesize 1 kg of Ca-HAP. The breakdown of cost for synthesis of Ca-HAP from each method is shown in appendix (Pg 13). Evidently, single calcination is the recommended method to synthesise Ca-HAP as it is less energy intensive, less expensive and results in a higher percentage yield.

4 Conclusion and Future Work

Ca-HAP has been successfully synthesized through 2 methods involving either single calcination or double calcination. In the single calcination method, non-calcined eggshell was converted to calcium nitrate before reacting with diammonium hydrogenphosphate through precipitation. The resulting precipitate was then calcined once to form Ca-HAP. In the double calcination method, eggshell was first calcined and reacted with diammonium hydrogenphosphate to form a precipitate which underwent another round of calcination. The Ca-HAPs synthesized by both methods are globular in shape and larger than 100nm. Single calcination is the recommended method to synthesise Ca-HAP due to its lower cost and energy consumption, and slightly higher percentage yield. The adsorption capability of Ca-HAPs synthesized by both methods are slightly less effective than activated carbon in removing copper(II) ions but are comparable to activated carbon in the removal of lead(II) ions. The Ca-HAPs synthesized by both methods are able to remove at least 95% of both copper(II)

and lead(II) ions. Ca-HAPs synthesized by both methods are also about 15 times more effective than activated carbon in removing fluoride ions. The optimum pH for the removal of fluoride ions is determined to be pH 4. Ca-HAP is a promising adsorbent which can be used in wastewater treatment to remove metal ions and fluoride.

In future, the effect of pH can be investigated on heavy metal ions to gain a deeper understanding of the adsorption mechanism of these heavy metal ions by Ca-HAP. Maximum adsorption capacity of all 3 pollutants can also be determined through isotherm studies.

For application purposes, Ca-HAP can be incorporated in sand filters (Figure 8) to improve its ability to remove metal ions and fluoride ions. These filters can be distributed to individuals from lower income families in less developed countries who lack safe access to clean drinking water to purify water before consuming it.

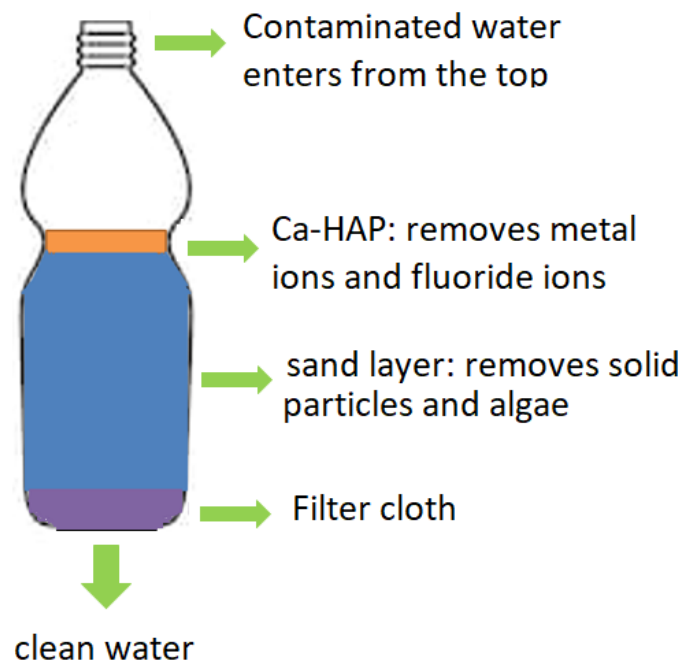


Figure 8. Filter containing Ca-HAP

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Appendix: Breakdown of cost of synthesis of Ca-HAP

Table 2. Cost of synthesis of 1 kg of Ca-HAP using double calcination method

Item	Cost / \$
Calcination	66.11
Chemicals	2.10
Total cost/kg	68.11

Table 3. Cost of synthesis of 1 kg of Ca-HAP using single calcination method

Item	Cost / \$
Calcination	26.45
Chemicals	4.53
Total cost/kg	30.98

Cost of calcination is calculated by taking into account the power of the furnace, the duration of calcination and the tariff as stipulated by Sembcorp Power.