Investigating the uses of eggshell as a Low-Cost Adsorbent in Water Purification

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Abstract:

Eggshell is a waste product, with production of millions of tonnes per day all around the world. Most of the time, it is sent to the landfill with a high management cost. It contains 96% calcium carbonate, and thus is a promising material for adsorbing pollutants. This project aims to study the effectiveness of eggshell in removing phosphate ions, iron(III) ions and methylene blue dye. The effect of calcination on the adsorption capability of eggshell was investigated. pH studies and kinetic studies were also conducted to investigate the effect of pH and contact time on the adsorption process. In addition, characterisation of eggshell was conducted using Scanning Electron Microscope (SEM) and X-ray Diffractometer (XRD). Results show that calcined eggshell outperformed eggshell in the adsorption of methylene blue dye but not for phosphate and iron(III) ions. Both eggshell and calcined eggshell were effective in removing both phosphate and iron(III) ions, removing more than 95% of both. However, both eggshell and calcined eggshell are not as effective in removing dye, with calcined eggshell removing a mere 30% of the dye. Eggshell shows great promise to be a low-cost and eco-friendly adsorbent which can remove metal and phosphate ions from wastewater.

1. Introduction

The excessive amount of phosphate released by domestic and industrial wastewater into bodies results in eutrophication. Eutrophication is the process by which a body of water becomes rich in dissolved nutrients and minerals, markedly phosphate and nitrate compounds, and often grows shallow with a seasonal deficiency in dissolved oxygen. It is a major cause of the loss of natural lake ecosystems throughout the world. There is also great potential threat to the survival of large lake organisms through oxygen depletion and toxin accumulation, causing possible risks to human health, as well as marine life (Lalley *et al*., 2016; Carmichael, 2001).

To remove phosphate from water, many methods have been developed. The more common treatment processes to remove phosphate from water include ion exchange, chemical precipitation, biological treatment, and adsorption (Jiang & Wu, 2010; Long *et al*., 2011). However, although biological treatment and chemical precipitation have been widely used in the industry, both require high operational costs. Chemical precipitation results in the problem of sludge handling while biological treatment is slow and not effective due to variability in temperature of wastewater that would make the execution of this process inaccessible for wastewater treatment (Long *et al*., 2011). Among the current methods of removing phosphate, adsorption is by far the most versatile and widely used method due to the adsorbent's high removal capacity and the ease of operation at large scale (Carvalho *et a*l., 2011). The most commonly used adsorbent for water purification is currently activated carbon, however its use is restricted by its high cost (Carvalho et al., 2011). Based on previous study (Quakouak & Youcef, 2016), activated carbon, which is used commercially for the removal of phosphates, can only absorb a maximum of around 50% of phosphates from solutions. Hence there is a need to explore low-cost and effective adsorbents in place of commercial activated carbon.

Eggs are among the most nutritious food consumed. In 2017, approximately 80 million metric tonnes of eggs were produced worldwide, up from 37.4 million metric tonnes in 1990 (Statista, 2019). Although eggs serve as delicious meals, their shells, which are not consumed, are disposed and wasted. The costs associated with eggshell disposal (mainly on landfill sites) are significant and expected to continue increasing as landfill taxes increase (Smirnova, Kalnina & Locs, 2017). Occasionally, waste eggshell is put to good use as fertilizers due to its high nutrition contents such as calcium, magnesium and phosphorus (Tacon, 1982). According to Carvalho, Araujo, & Castro (2011), eggshells can effectively adsorb certain heavy metal ions and organic compounds, due to its porous nature and the structure of eggshell and eggshell membrane (ESM). Eggshell is made up of 94% calcium carbonate ($CaCO_3$), 1% magnesium carbonate, 1% calcium phosphate and approximately 4% organic matter (Carvalho et al., 2011). Calcium carbonate is also an effective phosphate binder (Yanamadala, 2005), thus it can potentially remove phosphate, and prevent eutrophication in water bodies.

This study aims to investigate eggshell's effectiveness as a low-cost adsorbent in removing methylene blue dye, phosphate and iron (III) ions. Additionally, the effects of different experimental conditions such as pH value and contact time on adsorption would be investigated.

2. Objectives and Hypothesis

2.1 Objectives

- Investigate the effectiveness of eggshell and calcined eggshell (CES) in adsorbing phosphate, iron (III) ions and methylene blue dye
- Investigate the effect of pH and contact time on the adsorption by eggshell and CES

2.2 Hypothesis

This study hypothesized that

- calcined eggshell (CES) will be more effective than eggshell in removing all 3 pollutants.
- pH and contact time will affect adsorption of pollutants

3. Materials and Methods

3.1 Materials

Sodium di-hydrogen phosphate and iron(III) nitrate were procured from GCE Chemicals while methylene blue was procured from Unichem. Phosphate and Iron (III) Reagent Powder Pillows were obtained from Hach Company.

3.2 Preparation of eggshell and Calcined eggshell

Eggs of the same batch were bought from a supermarket. Eggshell was collected, washed with deionised water, dried and blended. Calcined eggshell (CES) was obtained by calcining the eggshell powder in a furnace at 450 °C for 40 minutes under atmospheric conditions.

Figure 1. Washing eggshell with deionised water

Figure 2. Blending eggshell into powder

Figure 3. Calcining eggshell in a furnace

3.3 Evaluating effectiveness of eggshell/ calcined eggshell in removing methylene blue dye, iron (III) ions and phosphate

0.2g of eggshell/ calcined eggshell was added to 20ml of 50 ppm of respective pollutants solution and stirred for 24 hours. Subsequently, the mixtures were centrifuged and the supernatants were collected. The supernatants were diluted 20-fold before being analysed for the remaining concentration of pollutants. A colorimeter (HACH DR890) was used for the analysis of phosphate and iron(III) ions while a UV-Visible Spectrophotometer (Shimadzu UV 1800) was used for the analysis of methylene blue dye at 665 nm. A control with no eggshell was included in the set up for every pollutant.

The following formula was used to calculate the percentage of dye removed:

$$R(\%) = 100 \times \frac{C_o - C_e}{C_o}$$

Where
R (%) is the percentage of pollutant removed
C_e is the final concentration of dye/ppm
C_o is the initial concentration of dye/ppm

Figure 4. Stirring of set-up with methylene blue dye

3.4 Effect of pH on adsorption

pH was varied from pH 2 to 10 for phosphate solution and from pH 2 to 5.3 for iron(III) ion solution using 1 mol dm^{-3} HCl or NaOH. As iron(III) ions precipitate out as iron (III) hydroxide at a pH greater than 5.3, the maximum pH used was 5.3. The adsorption was carried out as previously described in section 3.3.

3.5 Kinetic studies

Adsorption was carried out with a total duration of 100 min for phosphate adsorption. At every 20 min interval, sample was withdrawn and analysed for the concentration of remaining pollutants. The percentage adsorption of each pollutant was plotted against time to determine and compare the rate of adsorption.

4. Results and Discussion

4.1 Characterisation of Eggshell by EDS and SEM

Eggshell was characterised using the Energy Dispersive Spectroscopy (EDS) and Scanning Electron Microscopy (SEM). The EDS spectrum (figure 5) reveal the presence of carbon, oxygen and calcium, all of which are elements present in calcium carbonate.

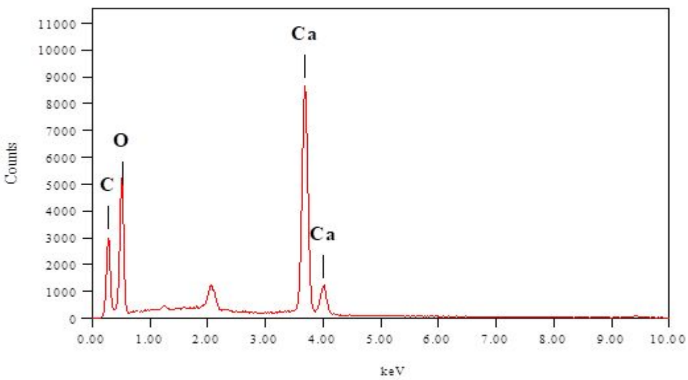

Figure 5. EDS of eggshell powder

The SEM images of both eggshell and calcined eggshell powder reveal that both eggshell and calcined eggshell are porous, which agree with past studies (Pramanpol & Nitayapat, 2006).

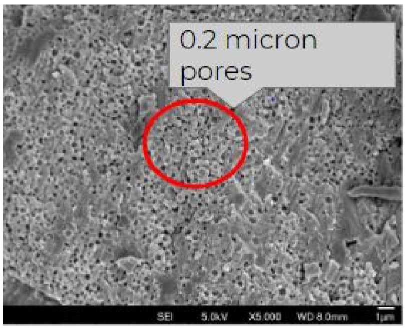

Figure 6. SEM image of eggshell powder

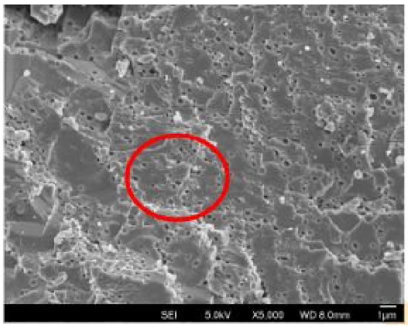

Figure 7. SEM image of calcined eggshell powder

4.2 Characterisation of eggshell by X Ray Diffraction

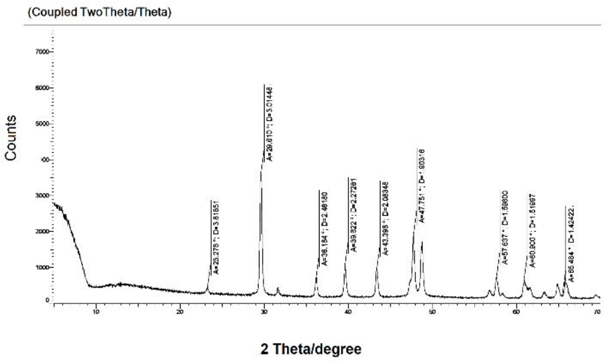

Figure 8. XRD pattern of eggshell powder

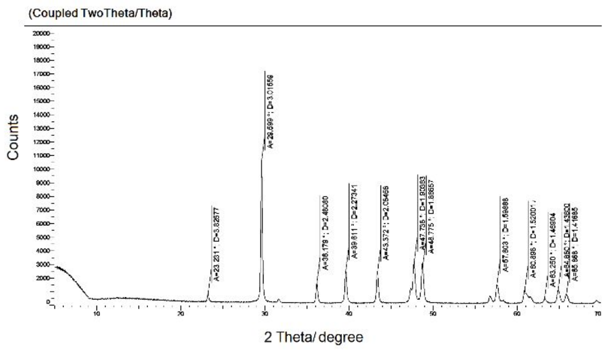

Figure 9. XRD pattern of calcined eggshell powder

XRD pattern of eggshell powder (figure 8) is similar to that of calcined eggshell powder (figure 9). The two theta peaks at 29.6°, 36.2°, 39.6°, 47.8° and 57.6° are characteristic of calcium carbonate (Choudhary, Koppala, & Swamiappan, 2015).

4.3 Removal of pollutants by Eggshell and Calcined Eggshell

4.3.1 Phosphate and iron(III) ions

Figure 10 shows the percentage of phosphate and iron(III) ions removed by eggshell and calcined eggshell. As seen from the Figure 10, both eggshell and calcined eggshell removed more than 90% of phosphate present. Using the Mann-Whitney U-Test, a p-value of 0.02 was obtained, hence, we reject the null hypothesis that there's no difference between the means and conclude that a significant difference does exist between the adsorption capabilities of eggshell and calcined eggshell in removing phosphate. Similarly, iron(III) ions were effectively removed by eggshell and calcined eggshell. The p-value of 0.754 suggests that there is no significant difference between the adsorption capabilities of eggshell and calcined eggshell in removing iron(III) ions.

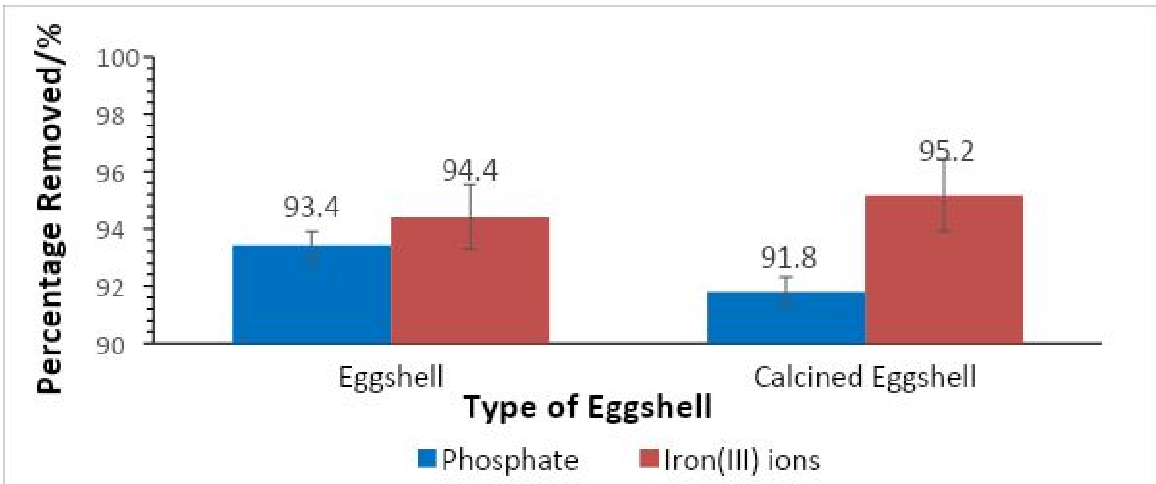

Figure 10. Percentage of phosphate and iron(III) ions removed by eggshell and calcined eggshell powder

Eggshell contains calcium carbonate which reacts chemically with the phosphate ion, producing both hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ and carbonated-substituted hydroxyapatite $Ca_{10-x}(PO_4)_{6-x}(CO_3)_x(OH)_{2-x-2y}(CO_3)_y$ (Minh, Tran, Nzihou & Sharrock., 2013).

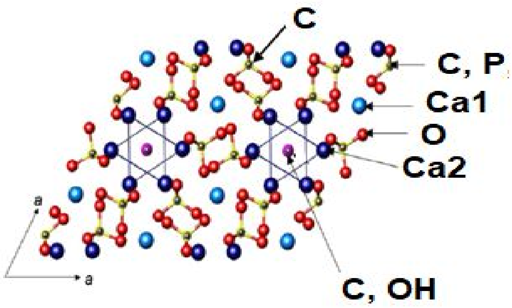

Figure 11. Lattice structure of hydroxyapatite

As for the removal of iron (III) ions, the main mechanism involved was proposed to be ion exchange. Fe^{3+} ions replace Ca^{2+} ions in the calcium carbonate lattice structure, producing iron(III) carbonate as a precipitate.

4.3.2 Methylene blue dye

As seen from Figure 12, both eggshell and calcined eggshell did not perform as well for the adsorption of methylene blue dye, even though calcined eggshell performed significantly better (p value of Mann Whitney Test = 0.013). Upon calcination, organic matter such as the membrane in eggshell has been converted to graphitic carbon, which aids in the adsorption of methylene blue dye.

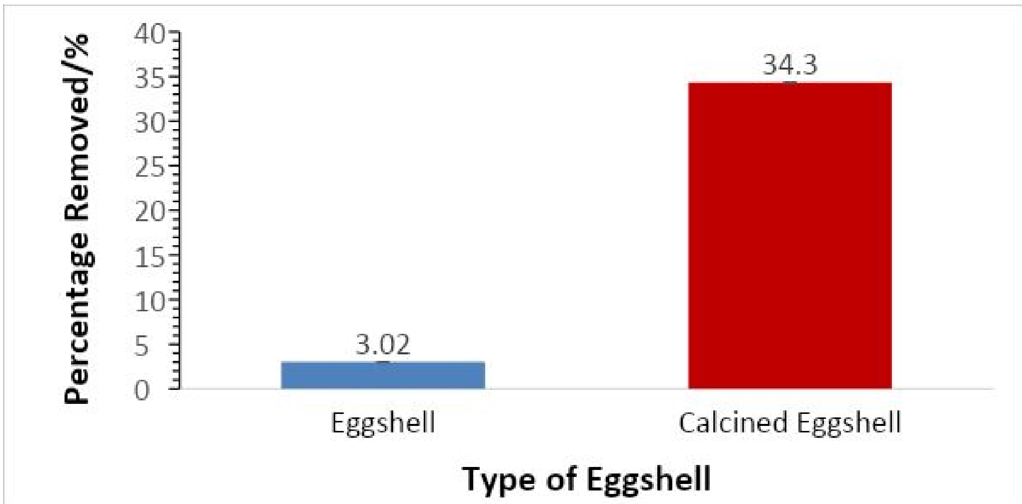

Figure 12. Percentage of methylene blue removed by eggshell and calcined eggshell powder

The mechanism involved in the adsorption of methylene blue dye by the graphitic carbon of calcined eggshell is proposed to occur via pi-pi interactions between the aromatic rings of the dye and carbon in eggshell as well as electrostatic interaction between the positively charged nitrogen in methylene blue and the negatively charged groups in carbon (Figure 13).

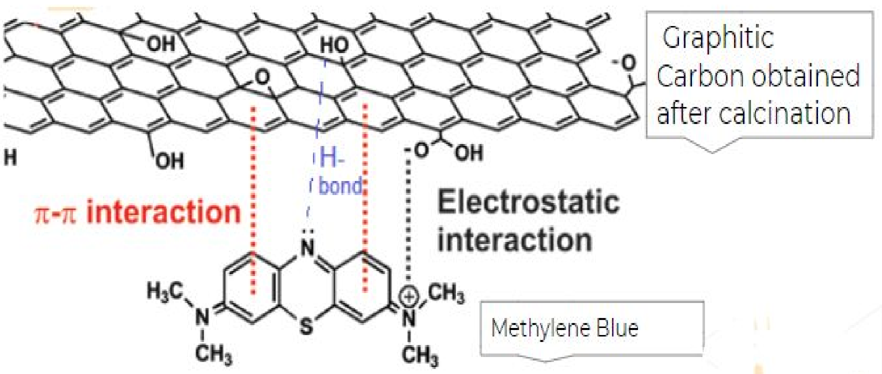

Figure 13. Proposed mechanism of how methylene blue is adsorbed by calcined eggshell powder

4.4 Effect of pH on the removal of phosphate and iron(III) ions

pH studies were conducted for phosphate and iron(III) ions solution. The range of pH values for the phosphate solution pH studies was 2, 4, 6, 8 and 10. As any pH beyond 5.3 would result in the precipitation of iron(III) hydroxide, the pH values for the iron (III) solution were 2, 2.5, 4 and 5.3.

Figures 14 and 15 show the effect of pH on adsorption of phosphate and iron(III) ions respectively. For phosphate, the percentage of phosphate removed by eggshell and calcined eggshell generally showed a downward trend as pH increases. The reason for this trend is due to the higher concentration of OH^- ions in solutions of higher pH, which compete with phosphate ions in the process of precipitation of hydroxyapatite, leading to less effective phosphate removal.

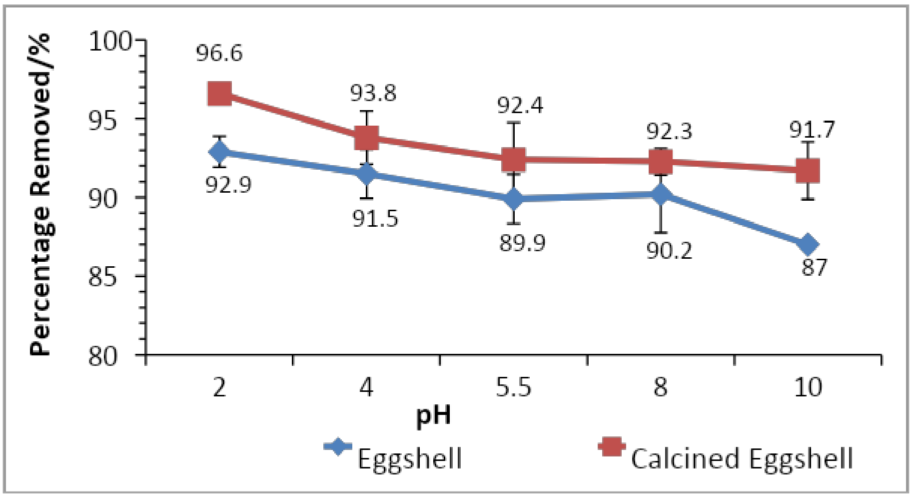

Figure 14. Effect of pH on phosphate removal

Figure 15 shows the effect of pH on removal of iron(III) ion. It is evident that adsorption is more effective with higher pH, up to pH 4. However, there is a dip in the percentage removed between pH 4 and 5, with pH 4 being the optimum pH for iron (III) ion removal. At lower pH, concentration of H^+ ions is high, leading to competitive adsorption by the H^+ ions. However, above pH 4, OH^- ions begin to bind with iron (III) ions, forming iron (III) hydroxide precipitate as observed in Figure 16.

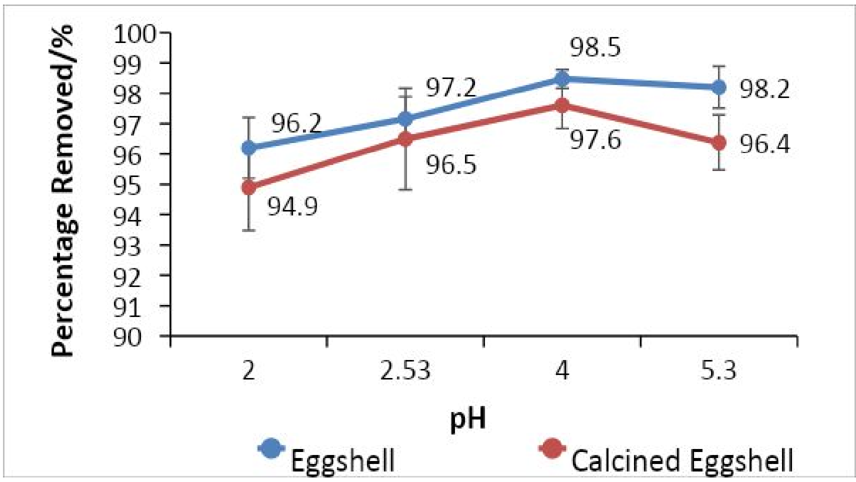

Figure 15. Effect of pH on iron(III) ion removal

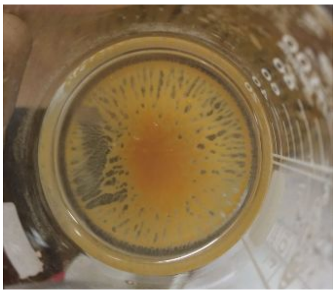

Figure 16. Iron (III) hydroxide precipitate observed

4.5 Kinetic studies

Figure 17 shows the effect of contact time on the removal of phosphate by eggshell and calcined eggshell. For both eggshell and calcined eggshell, the removal rate was slow initially but increases sharply after 40 minutes. For calcined eggshell, equilibrium was reached within 60 minutes while eggshell took 80 minutes to reach equilibrium. Rate of removal of phosphate by calcined eggshell was slightly greater than that by eggshell, likely because in addition to calcium carbonate, calcined eggshell contains graphitic carbon which provides additional binding sites for the adsorption of phosphate. On the other hand, Figure 18 presents the data of the effect of contact time on the removal of iron (III) ions by eggshell and calcined eggshell. The removal rate was extremely high at 97.1% for eggshell even with only 20 minutes of contact time. Calcined eggshell performed comparably with eggshell.

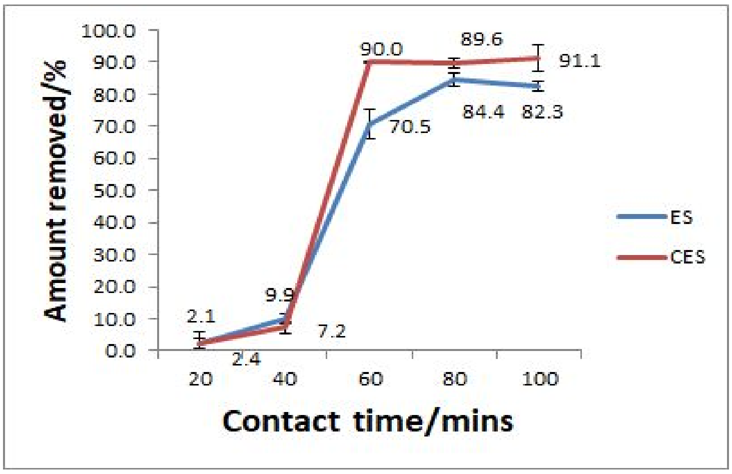

Figure 17. Effect of contact time on the removal of phosphate by eggshell and calcined eggshell

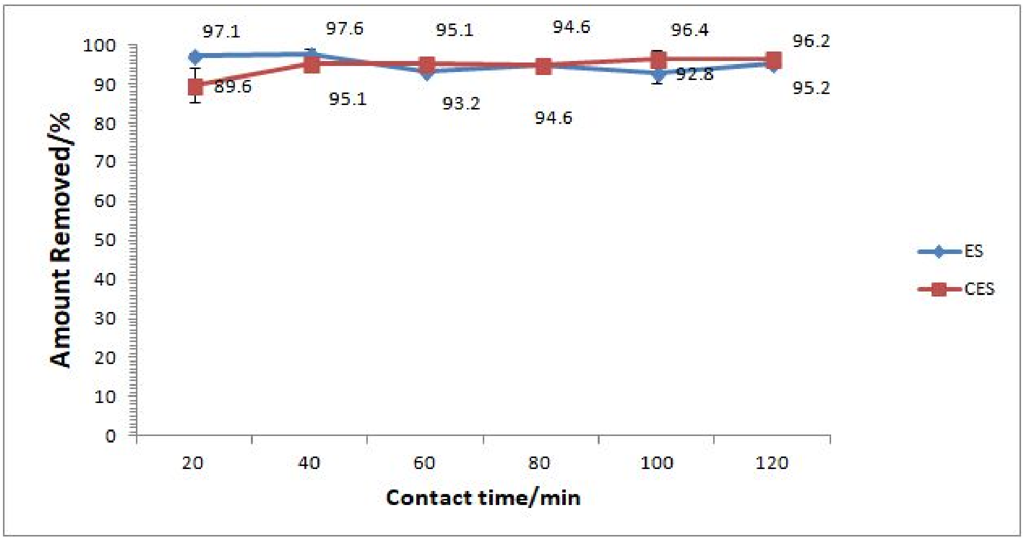

Figure 18. Effect of contact time on the removal of Iron (III) by eggshell and calcined eggshell

5. Conclusion and Recommendations for future work

5.1 Conclusion

SEM, EDS and XRD data reveal that eggshell contains calcium carbonate and has a porous nature. These characteristics allow it to remove phosphate and iron(III) ions effectively. Both eggshell and calcined eggshell were found to be effective in removing both phosphate and iron(III) ions, with more than 90% removal. Furthermore, there was a significant difference in eggshell and calcined eggshell's capabilities in removing phosphate, with eggshell performing better. However, there was no significant difference in their capabilities in removing iron(III) ions. Both eggshell and calcined eggshell were not very effective in removing methylene blue, although calcined eggshell was significantly more effective. The optimal pHs for phosphate and iron(III) ion removal were determined to be at pH 2 and 4 respectively. Calcined eggshell removes phosphate at a faster rate than eggshell, reaching equilibrium within 60 minutes, whereas eggshell took 80 minutes to reach equilibrium. In contrast, the rate of adsorption of iron(III) ions is more rapid, with equilibrium being reached in less than 40 minutes for both eggshell and calcined eggshell. The use of eggshell to remove phosphate and iron(III) ions is effective and yet does not require energy intensive pretreatment, hence they have great potential to be used as low cost adsorbents in water treatment to remove phosphate and iron(III) ions.

5.2 Future work

In future, kinetic studies on the removal of iron (III) ions will be conducted and compared with that of phosphate.

The effect of initial concentration on the removal of phosphate and iron(III) ions could also be carried out to determine the maximum adsorption capacity of the pollutants.

A prototype using eggshell as the filtration media (figure 19) will also be constructed and tested for its ability to remove phosphate and iron(III) ions from water. The first layer is eggshell which removes phosphate and iron(III) ions while the second layer is sand to filter out sediments. Such a device can be used domestically to treat water polluted with metal ions and phosphate ions.

Figure 19. Filter containing eggshell for water purification

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