Green and Facile Synthesis of Magnetic Hydroxyapatite Polymeric Hydrogel Composite for Water Purification

Ang Jayden (4i3), Lu Zihan (4i2), Ang Yong Heng (4O3)

Group 1-06

Abstract

This project investigated the removal of heavy metal ions and organic dyes using magnetic hydroxyapatite polymeric hydrogel composite for water purification. The experiment involved cross-linking commercially available cellulose with chitosan and then coating it on hydroxyapatite synthesised from eggshells, as well as magnetite synthesised via co-precipitation, to form the composite. The composite was then investigated on its properties in removing copper(II) and zinc ions, as well as methylene blue. In summary, the composite was as effective as commercial activated carbon in removing all pollutants tested with more than 90% percentage removal. The maximum adsorption capacity of the composite for methylene blue was also found to be relatively high at 53.8mg/g. Furthermore, the composite's magnetic properties allow it to be reusable while remaining effective with more than 85% removal even after 5 cycles.

1. Introduction

This project aims to synthesize magnetic hydroxyapatite polymeric hydrogel composite via green and facile means for water purification. Recently, there has been increasing concern about water pollution in the world, which is expected to worsen in the coming decades with water scarcity occurring globally (Shannon et al., 2008). Rapid industrialization over recent years has resulted in rampant discharge of pollutants containing heavy metal ions and organic dyes (Alo, 2019). Metals are introduced in aquatic systems due to the weathering of soils and rocks, volcanic eruptions and a variety of human activities involving the mining, processing or use of substances that contain metal pollutants. Thus, when a high amount of metal ions are being released into the water and subsequently be consumed, toxic amounts of heavy metals enter the body and accumulate in their tissues. The resulting poisoning can cause serious damage, such as serious health problems and water-borne diseases like cholera and kidney

damage (Akram & Fazal, 2018). Dyes on the other hand are highly toxic and pose a strong tendency toward eutrophication (Bianco Prevot et al., 2001).

To solve this problem, other techniques of removing heavy metal ions and organic dyes have been employed, but are either expensive, energy-demanding, include chemical coagulation (Geçgel et al., 2013) or require advanced oxidation processes (Silva et al., 2013). Thus, there is an urgent need for highly efficient and cost-effective adsorbents for water purification.

Hydroxyapatite, with chemical formula $Ca_{10}(PO_4)_6(OH)_2$ has received much attention as an effective adsorbent, as it has demonstrated high efficiency to remove metal pollutants from wastewater through an ion-exchange mechanism, in which the Ca^{2+} ions in hydroxyapatite is replaced with the heavy metal ion. 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. Furthermore, due to its biocompatibility, osteoconductivity, biodegradability and synthetic nanostructures (calcium and phosphorus combined hydroxide), hydroxyapatite has an affinity for polymers (Cawthray et al., 2015). However, it was found to be ineffective in adsorbing dyes (Azis et al., 2015).

By extracting the hydroxyapatite from eggshells, food wastage problems can be solved, as around 250,000 tonnes of eggshells waste are dumped annually worldwide (Nitin et al., 2012).

On the other hand, cellulose and chitosan are the two most abundant biopolymers available on earth and are environmentally friendly (Shen et al., 2016). Cellulose, when used as a blending polymer, can provide strong mechanical strength and improve the chemical stabilities of the hydrogel composite, whereas chitosan can prevent particle agglomeration, which can serve as an effective coating to stabilize the composite (Liu et al., 2012). By making use of the abundant amine ($–NH_2$) and hydroxyl (–OH) functional groups of cellulose and chitosan, the swelling and absorbent characteristics of hydrogels will be enhanced due to strong hydrogen bonding, thus enhancing the adsorption capacity of the composite for heavy metal ions and especially organic dyes which hydroxyapatite is found to be ineffective in (Azis et al., 2015).

Magnetising the cellulose-hydrogel polymer with magnetite renders the separation of the hydrogel from treated wastewater quick and efficient.

2. Objectives and Hypothesis

2.1. Objectives

- To investigate whether the Magnetic Hydroxyapatite Polymeric Hydrogel is able to remove both heavy metal ions and organic dyes from wastewater
- To compare the composite's adsorption capacity for the pollutants against its individual constituents, as well as against commercial activated carbon
- To investigate the maximum adsorption capacity of the composite
- To investigate the reusability of the composite

2.2. Hypotheses

- The Magnetic Hydroxyapatite Polymeric Hydrogel Composite can be synthesised
- The composite will have a greater adsorption capacity for pollutants as compared to its individual constituents
- The adsorption capacity for the pollutants of the composite will be comparable to that of activated carbon
- The composite will sustain its effectiveness in pollutant removal for at least 5 cycles

3. Materials and Methods

3.1. Synthesis of Hydroxyapatite (Ca-HAP) from eggshells

With stirring, 5 g of eggshells was added to 48.5 cm^3 of 2 mol dm^{-3} HNO_3. The reactants were mixed for 1 h before being filtered into a volumetric flask and the volume made up to 100 cm^3 using deionised water. The synthesis of $Ca(NO_3)_2$ occurs via the following reaction:

$$CaCO_3 + 2HNO_3 \rightarrow Ca(NO_3)_2 + CO_2 + H_2O$$

50 cm^3 of 0.400 mol dm^{-3} diammonium hydrogen phosphate was added dropwise into 50 cm^3 of the synthesised $Ca(NO_3)_2$ solution. The pH was adjusted to 10 with the addition of aqueous ammonia (14 wt%). Calcium hydroxyapatite was formed as a white precipitate. The precipitation reaction is shown below. The Ca/P molar ratio was kept at 1.67 corresponding to the stoichiometry of Ca-HAP.

$$10Ca(NO_3)_2 + 6(NH_4)_2HPO_4 + 20NH_3 \rightarrow Ca_{10}(PO_4)_6(OH)_2\ (s) + 12NH_4NO_3 + 8HNO_3$$

The reaction mixture was stirred and heated at 70 ℃ for 45 min. The suspension was subjected to ageing without heating for 24 h. The obtained calcium hydroxyapatite precipitate was filtered and washed with deionised water until pH neutral, before being dried at 100 ℃ until constant mass and calcined at 800 ℃ for 2 h.

3.2. Synthesis of magnetite via co-precipitation

Iron (II) and Iron (III) salts were mixed in a molar ratio of 1:2 in DI water. 3.87 g of iron(II) sulfate and 7.97 g of iron(III) chloride were dissolved in 50 cm^3 of deionized water and heated to 80 °C and stirred for 30 min. 20 cm^3 of aqueous ammonia (14 wt%) was then added slowly to adjust the pH of the solution to 10. To provide the capping agent to prevent agglutination, 6.34 g of trisodium citrate was added to stabilize the magnetite. The magnetite powder obtained was then separated by vacuum filtration, and was subsequently dried. The chemical reaction for the co-precipitation of magnetite is shown below:

$$Fe^{2+} + 2Fe^{3+} + 8NH_3 \bullet H_2O \rightarrow Fe_3O_4\ (s) + 8NH_4^+ + 4H_2O$$

3.3. Synthesis of Magnetic Hydroxyapatite Polymeric Hydrogel Composite

2 g of hydroxyapatite was added into 20 cm^3 10 % acetic acid and 80 cm^3 of DI water in a beaker. The contents in the beaker were then mixed on a hot plate stirrer at 70 ^{0}C at 200 rpm until the contents fully dissolved. 2 g of cellulose and chitosan powder was then added into the solution and the mixing was continued at 70 ^{0}C at 200 rpm on the stirrer until it fully dissolved, forming the stock solution. 2 g of magnetite was then added. The blended solution was then dropped into 1.00 mol dm^{-3} NaOH solution to form hydrogel beads. The hydrogel beads were allowed to stay in the NaOH solution with slow stirring for another 48 h. After 48 h, the hydrogel beads were washed with DI water until pH 7. They were then stored for further use in DI water.

3.4. Adsorption studies

The percentage of pollutants removed is calculated using the following formula:

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

3.4.1. Removal of heavy metal ions

50 ppm of Cu^{2+} and Zn^{2+} ions solutions were prepared. To 20 cm^3 of each metal ion solution, 0.1 g of adsorbent was added in a beaker with a magnetic stirrer to stir for 24 h at 200 rpm. 5 replicates were conducted for each test. Afterwhich, the solution was centrifuged to obtain the supernatant, which was measured using a colorimeter (HACH DR/890) to determine the final concentration of pollutant. 5 replicates were conducted for each adsorbent.

3.4.2. Removal of organic dyes

50 ppm of Methylene Blue dye solution was prepared. To 20 cm^3 of the dye, 0.1 g of adsorbent was added in a beaker with a magnetic stirrer to stir for 24 h at 200 rpm. Afterwhich, the solution was centrifuged to obtain the supernatant, which was measured using the UV-Vis spectrophotometer (Shimadzu UV-1800) to determine the final concentration of pollutant. 5 replicates were conducted for each adsorbent.

3.5. Isotherm studies

Adsorption was carried out with 10-100 mg/L pollutant, and the equilibrium concentration data was fitted into the linearised Langmuir and Freundlich isotherm models (**Appendix, Pg 15**). The adsorption capacity, q_e, was determined via the following formula:

$$q_e = \frac{(C_i - C_e) \times V}{1000 \times m}$$

where C_i = initial concentration of pollutant in mg/L;
C_f = final concentration of pollutant in mg/L;
V = volume of solution in dm^3;
m = mass of composite in g

3.6. Regeneration of composite and reusability tests

Adsorption and regeneration of the pollutants was repeated for 5 cycles. After each adsorption cycle, the composite is separated via magnetic separation and washed with 1.0 mol dm^{-3} NaOH, followed by deionized water until pH 7. 1.0 mol dm^{-3} HCl was then added to regenerate the hydrogel.

4. Results and Discussion

4.1. Characterisation by Fourier-transform infrared spectroscopy (FTIR)

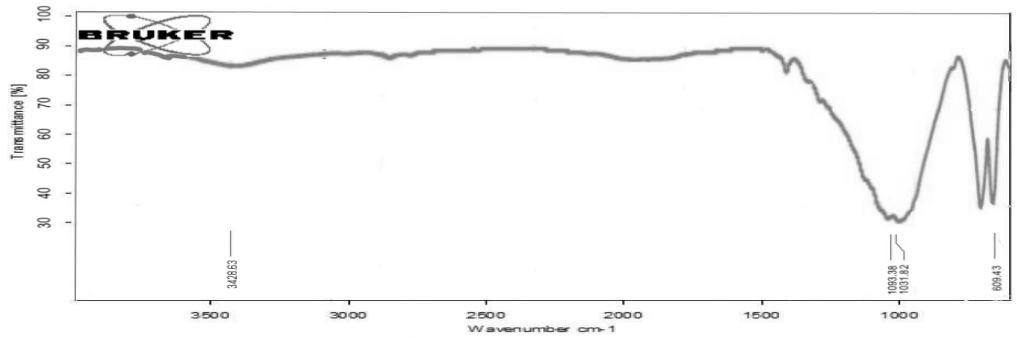


Fig. 1: FTIR spectrum of magnetic hydroxyapatite polymeric hydrogel composite

In Figure 1, the peak at 3428 cm^{-1} can be attributed to stretching vibrations of -OH groups of chitosan, which is characteristic of -OH groups subject to intermolecular hydrogen bonds. The characteristic bands in the range of 1093–1031 cm^{-1} and at 609 cm^{-1} can be associated with the stretching and bending vibrations of the PO_4^{3-} group in hydroxyapatite. The broadening of the band around 1050 cm^{-1} shows the presence of the cellulose and chitosan polymers and its interaction with phosphate groups (Ragab et al., 2019).

4.2. Batch Adsorption Studies

Activated carbon, hydroxyapatite, and the composite without hydroxyapatite (magnetic cellulose-chitosan hydrogel) are the controls for this experiment.

4.2.1. Adsorption of Copper (II) and Zinc ions

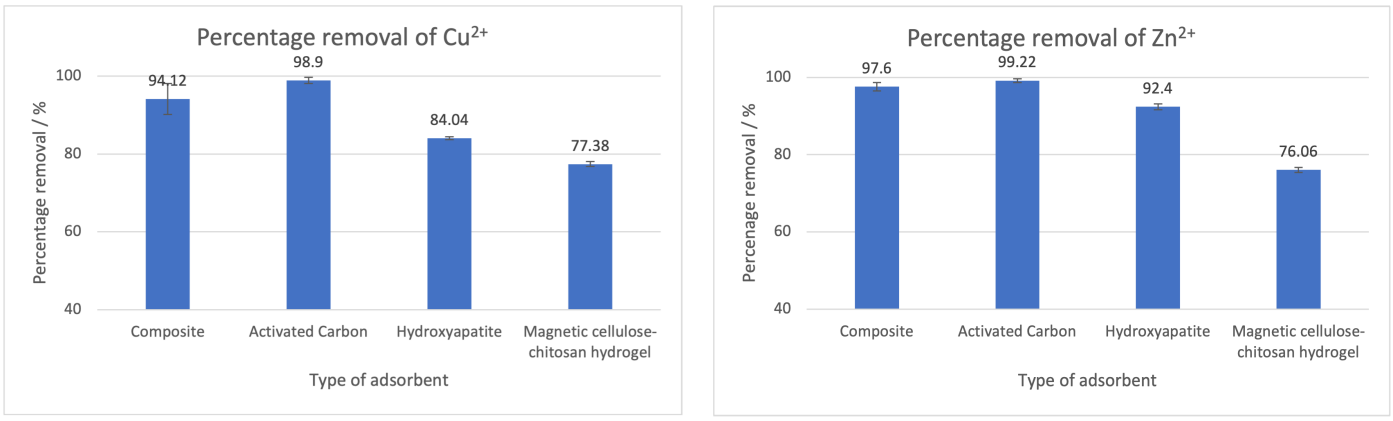


Fig. 2: Removal of Cu^{2+} and Zn^{2+} respectively by different adsorbents

Figure 2 shows that the composite yields a higher percentage removal of Cu^{2+} and Zn^{2+} ions, at 97.6% and 94.1% respectively, than its individual constituents. Its percentage removals were comparable to that of commercial activated carbon. The percentage removal of the heavy metal ions were analysed via the Mann-Whitney U Test.

Table 1: Mann-Whitney U Test on heavy metal ions

Metal ion tested	Sample comparison	p-value	Conclusion
Copper (II) ion	Composite against activated carbon	0.290 (>0.05)	Insignificant difference
	Composite against magnetic cellulose-chitosan hydrogel	0.015 (<0.05)	Significant difference
	Composite against hydroxyapatite	0.039 (<0.05)	Significant difference
Zinc ion	Composite against activated carbon	0.138 (>0.05)	Insignificant difference
	Composite against magnetic cellulose-chitosan hydrogel	0.007 (<0.05)	Significant difference
	Composite against hydroxyapatite	0.015 (<0.05)	Significant difference

Table 1 shows that the composite is more effective at removing both Cu^{2+} and Zn^{2+} ions compared to its constituent components. The composite is also shown to be comparable to commercial activated carbon at removing both Cu^{2+} ions (p-value 0.290) and Zn^{2+} ions (p-value 0.138).

4.2.1.1. Hydroxyapatite adsorption mechanism

The adsorption possibly took place through an ionic exchange reaction, surface complexation with phosphate and through calcium and hydroxyl (–OH) groups. The Ca^{2+} ion in hydroxyapatite is replaced with the heavy metal ion, thus removing it from wastewater. The chemical reactions for the ion-exchange mechanism are shown in equations:

$$Ca_{10}(PO_4)_6(OH)_2 + 14H^+ \rightleftharpoons 10Ca^{2+} + 6H_2PO_4^- + 2H_2O$$

$$10M^{2+} + 6H_2PO_4^- + 2H_2O \rightleftharpoons 14H^+ + M_{10}(PO_4)_6(OH)_2 \text{ , M denotes } Cu^{2+}/Zn^{2+}$$

4.2.1.2. Cellulose-chitosan hydrogel adsorption mechanism

The dissolved pollutant ions possibly penetrated easily into cellulose or chitosan hydrogels and established bonds with the $–NH_2$ and/or –OH groups through three different kinds of interactions, either through chelation between the lone pair electrons of N and/or O and the metal ions (**Appendix, Pg 14**), through the crystallization of the metal ions with the complexed metals as nucleation sites, or through ion exchange between the protonated amino groups and various anions allows hydrogel to easily adsorb the Cu^{2+} and Zn^{2+} ions (Liu et al., 2012).

4.2.2. Adsorption of Methylene Blue dye

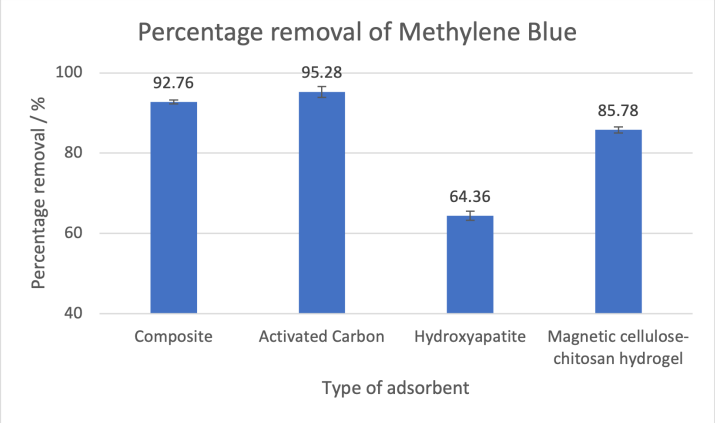


Fig. 3: Removal of Methylene Blue by different adsorbents

Figure 3 shows that the composite yields a higher percentage removal of methylene blue than its individual constituents at 92.8%. Its percentage removal was also close to that of commercial activated carbon. The percentage removal of the organic dye was analysed via the Mann-Whitney U Test.

Table 2: Mann-Whitney U Test on organic dyes

Organic Dyes	Sample Comparison	p-value	Conclusion
Methylene Blue	Composite against activated carbon	0.294 (>0.05)	Insignificant difference
	Composite against magnetic cellulose-chitosan hydrogel	0.012 (<0.05)	Significant difference
	Composite against hydroxyapatite	0.011 (<0.05)	Significant difference

Table 2 shows that the composite is more effective at removing methylene blue compared to its constituent components, especially against hydroxyapatite significantly (p-value 0.011). The composite is also shown to be comparable to activated carbon at removing methylene blue (p-value 0.294).

4.2.2.1. Hydroxyapatite adsorption mechanism

The strong H-bonding interaction between the P-OH group of hydroxyapatite nanocomposite and the nitrogen atom of the methylene blue molecules may possibly contribute to the adsorption of methylene blue dye molecules (**Appendix, Pg 14**). However, the low number of hydroxyl groups on the surface of hydroxyapatite slows down the binding process, thus explaining hydroxyapatite's low affinity for methylene blue adsorption (Cui et al., 2015).

4.2.2.2. Cellulose-chitosan hydrogel adsorption mechanism

Methylene blue adsorption occurred possibly due to an adsorption transport mechanism into swollen polymer networks. The higher water content and porous structure networks allows for solute diffusion through the hydrogel structure. When dipped into an aqueous media, it absorbs water, resulting in considerable changes of its polymer structure, allowing the dye molecules to easily penetrate into our hydrogel and establish bonds with the $–NH_2$ and/or –OH groups (Paulino et al., 2006).

4.3. Isotherm Studies

The maximum adsorption capacity of the composite was derived from the Langmuir isotherm model (**Appendix, Pg 16-18**) on Cu^{2+}, Zn^{2+}, and methylene blue.

Table 3: Maximum adsorption capacity, q_{max} (mg/g) of composite on the respective pollutants

Pollutant	Maximum adsorption capacity, q_{max} (mg/g)
Copper (II) ions	16.5
Zinc ions	13.4
Methylene Blue	53.8

Table 3 shows that while the maximum adsorption capacity for Cu^{2+} and Zn^{2+} of the composite is not ideal, the maximum adsorption capacity for methylene blue is relatively high (q_{max}=53.8).

4.4. Reusability test

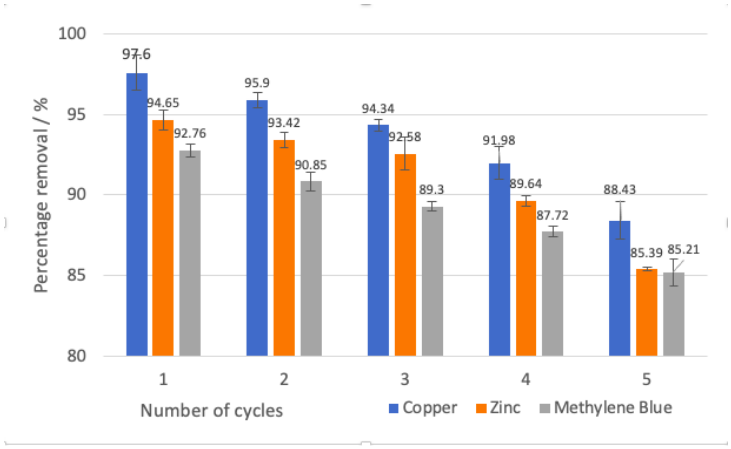


Fig. 4: Reusability of composite on Cu^{2+}, Zn^{2+} and methylene blue

Figure 4 shows that the composite has the ability to remain effective in removing the pollutants even when reused for multiple times, with a percentage removal greater than 85% for each cycle.

5. Conclusion

Magnetised hydroxyapatite polymeric hydrogel composite was successfully synthesized, and is more effective than its individual constituents in the removal of Cu^{2+}, Zn^{2+}, and methylene blue dyes from wastewater, with at least 90% of each pollutant removed. The performance of the composite is also comparable to that of activated carbon used in commercial water treatment, thus justifying its synthesis due to its lower cost of synthesis and easier process. The maximum adsorption capacity of the composite was found to be 16.5, 13.4 and 53.8 mg/g for Cu^{2+}, Zn^{2+} and methylene blue respectively. The composite can also be reused and regenerated while still remaining consistent in efficacy, with at least 85% of pollutant removed across 5 cycles. The Magnetised hydroxyapatite polymeric hydrogel composite is a promising adsorbent which can be used for water treatment to remove metal ions and methylene blue dye.

For the applications of the composite, it can be used to purify wastewater in third world countries where such pollutants are found in large concentrations, and can be used for recycling of ions by using the composite to adsorb and desorb the ions attracted.

6. Future Work

In future, more work can be done by getting more data on characterisation of the composite, such as through Scanning Electron Microscope (SEM), Energy Dispersive Spectrometry (EDS), and X-Ray diffraction (XRD). More work can also be done by expanding the scope of pollutants tested, as well as investigating the effect of pH on the adsorption capacity of the composite. Mixing the heavy metal ions and organic dyes together to simulate real-life competitive adsorption situations, where various types of pollutants are found in wastewater can also be considered.

References

Akram, S., & Fazal, R. U. (2018). Hardness in Drinking-Water, its sources, its effects on humans and its Household Treatment. Journal of Chemistry and Applications, 4(1), 01–04. https://doi.org/10.13188/2380-5021.1000009

Alo, B. T. (2019, March 2). List of water pollutants. Sciencing. https://sciencing.com/list-water-pollutants-6309497.html.

Azis, Y., Jamarun, N., Arief, S., & Nur, H. (2015). Facile synthesis of HYDROXYAPATITE particles FROM Cockle Shells (anadaragranosa) by Hydrothermal Method. Oriental Journal of Chemistry, 31(2), 1099–1105. https://doi.org/10.13005/ojc/310261

Bianco Prevot, A., Baiocchi, C., Brussino, M. C., Pramauro, E., Savarino, P., Augugliaro, V., Marcì, G., & Palmisano, L. (2001). Photocatalytic degradation of Acid Blue 80 in aqueous solutions Containing TiO2Suspensions. Environmental Science & Technology, 35(5), 971–976. https://doi.org/10.1021/es000162v

Cawthray, J. F., Creagh, A. L., Haynes, C. A., & Orvig, C. (2015). ChemInform abstract: Ion exchange IN Hydroxyapatite With lanthanides. ChemInform, 46(17). https://doi.org/10.1002/chin.201517280

Cui, L., Wang, Y., Hu, L., Gao, L., Du, B., & Wei, Q. (2015). Mechanism of pb(ii) and methylene blue adsorption onto magnetic carbonate hydroxyapatite/graphene oxide. RSC Advances, 5(13), 9759–9770. https://doi.org/10.1039/c4ra13009j

Geçgel, Ü., Özcan, G., & Gürpınar, G. Ç. (2013). Removal of methylene blue from aqueous solution by activated Carbon prepared from PEA Shells (Pisum sativum). Journal of Chemistry, 2013, 1–9. https://doi.org/10.1155/2013/614083

Liu, Z., Wang, H., Liu, C., Jiang, Y., Yu, G., Mu, X., & Wang, X. (2012). Magnetic cellulose–chitosan hydrogels prepared from ionic liquids as reusable adsorbent for removal of heavy metal ions. Chemical Communications, 48(59), 7350. https://doi.org/10.1039/c2cc17795a

Paulino, A. T., Guilherme, M. R., Reis, A. V., Campese, G. M., Muniz, E. C., & Nozaki, J. (2006). Removal of methylene blue dye from an aqueous media using superabsorbent hydrogel supported on modified polysaccharide. Journal of Colloid and Interface Science, 301(1), 55–62. https://doi.org/10.1016/j.jcis.2006.04.036

Ragab, A., Ahmed, I., & Bader, D. (2019). The removal of brilliant green dye from aqueous solution using nano hydroxyapatite/chitosan composite as a sorbent. Molecules, 24(5), 847. https://doi.org/10.3390/molecules24050847

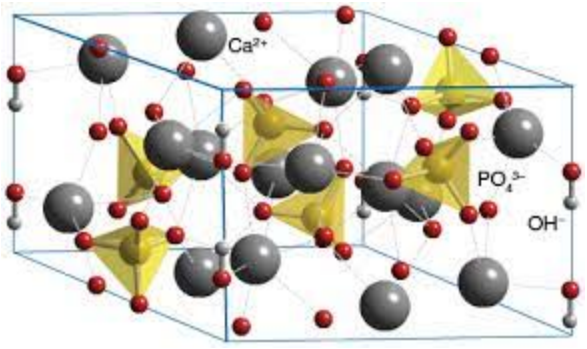
Shannon, M. A., Bohn, P. W., Elimelech, M., Georgiadis, J. G., Mariñas, B. J., & Mayes, A. M. (2008). Science and technology for water purification in the coming decades. Nature, 452(7185), 301–310. https://doi.org/10.1038/nature06599

Shen, X., Shamshina, J. L., Berton, P., Gurau, G., & Rogers, R. D. (2016). ChemInform abstract: Hydrogels based on cellulose and Chitin: Fabrication, properties, and applications. ChemInform, 47(9). https://doi.org/10.1002/chin.201609274

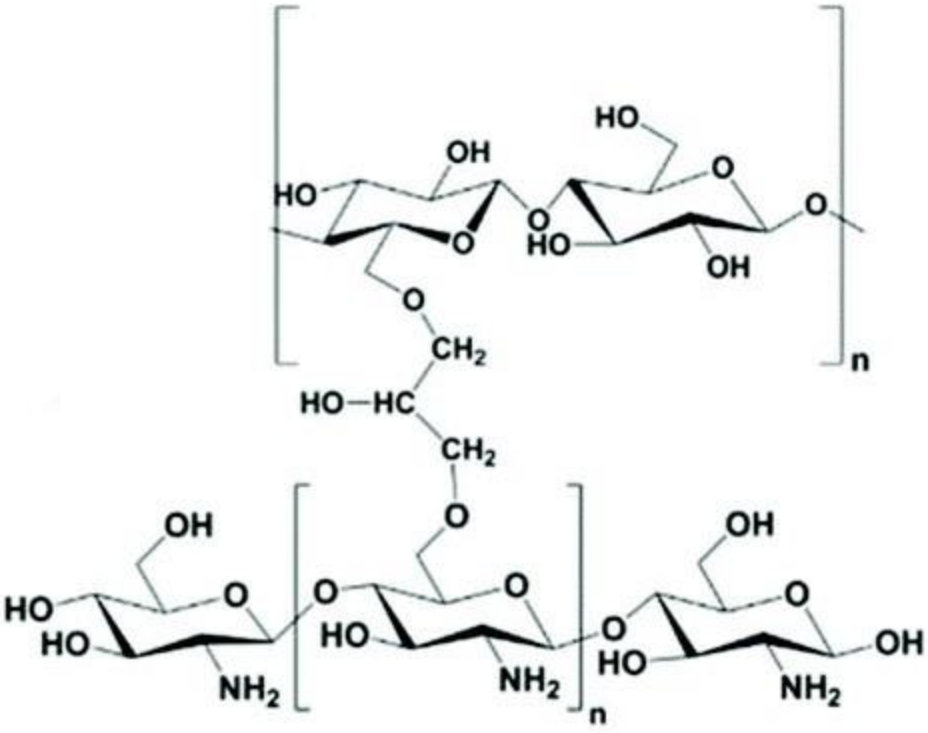
Silva, C. R., Gomes, T. F., Andrade, G. C., Monteiro, S. H., Dias, A. C., Zagatto, E. A., & Tornisielo, V. L. (2013). Banana peel as an Adsorbent for removing Atrazine and AMETRYNE from Waters. Journal of Agricultural and Food Chemistry, 61(10), 2358–2363. https://doi.org/10.1021/jf304742h

Appendix

Structure of hydroxyapatite in the composite

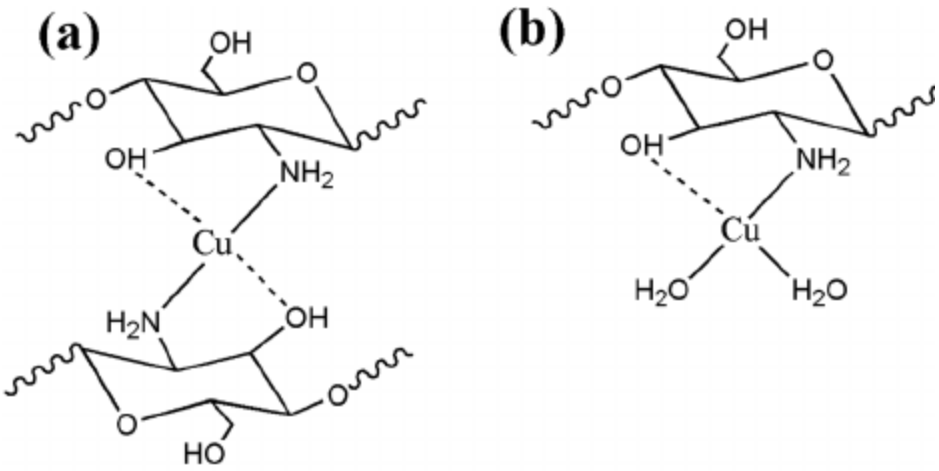


Structure of cellulose-chitosan in the composite

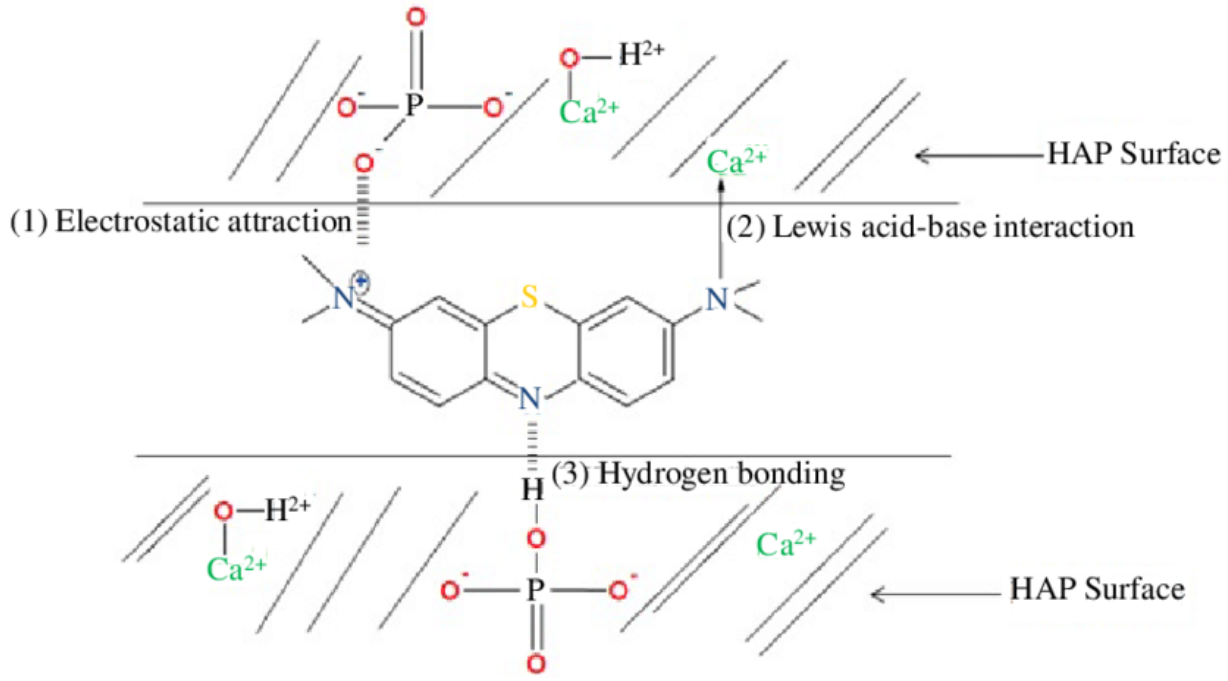


The $-NH_2$ and the –OH are the main groups in the polymers.

Heavy metal ions forming metal-chelate with cellulose-chitosan in the composite



Hydrogen bonding between the P-OH group of hydroxyapatite and the nitrogen atom of methylene blue



Equilibrium adsorption isotherm studies on the composite

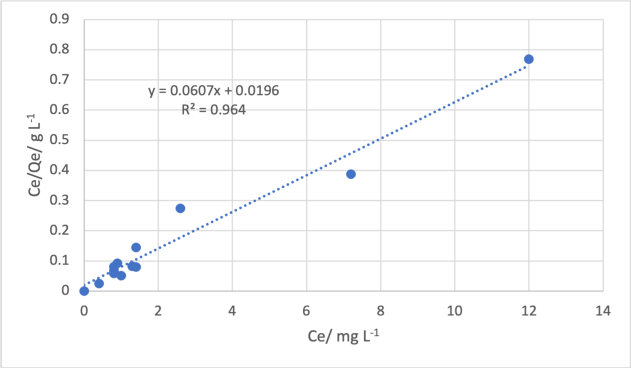
The equilibrium concentration data was fitted into the Langmuir and Freundlich linearised adsorption isotherm models as shown in the following equations:

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}} \quad (1)$$

$$lnq_e = \frac{1}{n} lnC_e + lnK_F \quad (2)$$

Where C_e represents the equilibrium concentration of pollutant (mg/L), q_e represents the adsorption capacity (mg/g), Q_{max} represents the maximum adsorption capacity (mg/g), b is the Langmuir constant indicating sorption intensity, K_F is a constant related to sorption capacity and n corresponds to sorption capacity.

The Langmuir adsorption model assumes that the adsorbate is absorbed over a uniform adsorbent surface at a constant temperature. On the other hand, the Fruendlich isotherm assumes that the adsorption is multilayer and occurs through a heterogeneous surface. If the equilibrium concentration data fits the Langmuir isotherm model, adsorption can be deduced to be monolayer. By plotting the graph of C_e/q_e against C_e, the maximum adsorption capacity, q_{max}, can be obtained through the inverse of its gradient. If the data fits the Freundlich isotherm, however, adsorption can be inferred to be multilayer, occurring on a heterogeneous surface.



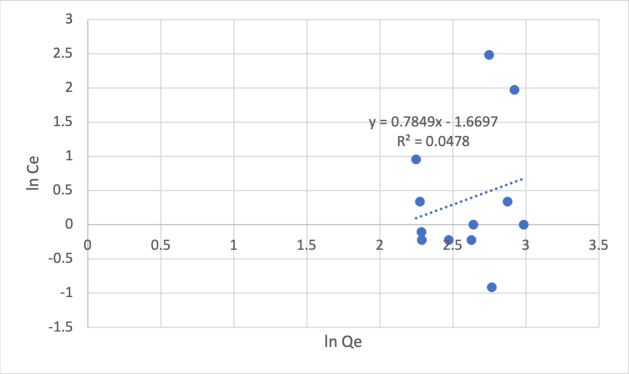


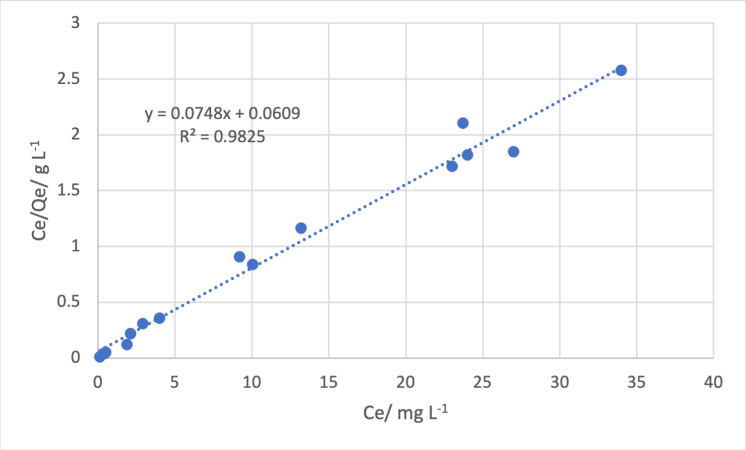
Fig. 5: Langmuir isotherm for Cu^{2+}

Fig. 6: Freundlich isotherm for Cu^{2+}

Table 4: Isotherm parameters for the adsorption of Cu^{2+}

Pollutant	Langmuir		Freundlich
	Q_{max} (mg/g)	R^2	R^2
Cu^{2+}	16.5	0.964	0.0478

Figure 5 shows the linearised Langmuir plot, of which its gradient was inversed to find the maximum adsorption capacity, q_{max}, and tabulated in table 4. Figure 6 shows the linearised Freundlich plot. By comparing the correlation coefficients, R^2, it was found that the adsorption of the composite fits the Langmuir model better. Thus, maximum adsorption capacity on Cu^{2+} ions was determined to be 16.5mg/g.



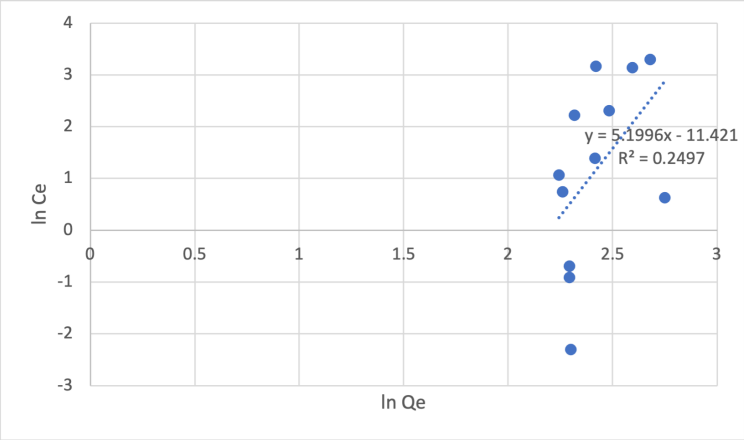


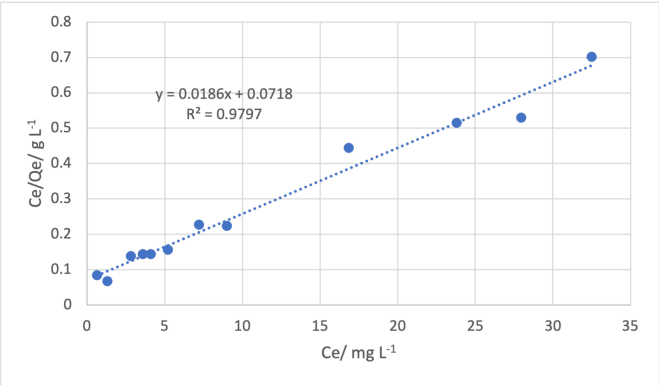
Fig. 7: Langmuir isotherm for Zn^{2+}

Fig. 8: Freundlich isotherm for Zn^{2+}

Table 5: Isotherm parameters for the adsorption of Zn^{2+}

Pollutant	Langmuir		Freundlich
	Q_{max} (mg/g)	R^2	R^2
Zn^{2+}	13.4	0.9825	0.2497

Figure 7 shows the linearised Langmuir plot, of which its gradient was inversed to find the maximum adsorption capacity, q_{max}, and tabulated in table 5. Figure 8 shows the linearised Freundlich plot. By comparing the correlation coefficients, R^2, it was found that the adsorption of the composite fits the Langmuir model better. Thus, maximum adsorption capacity on Zn^{2+} ions was determined to be 13.4mg/g.



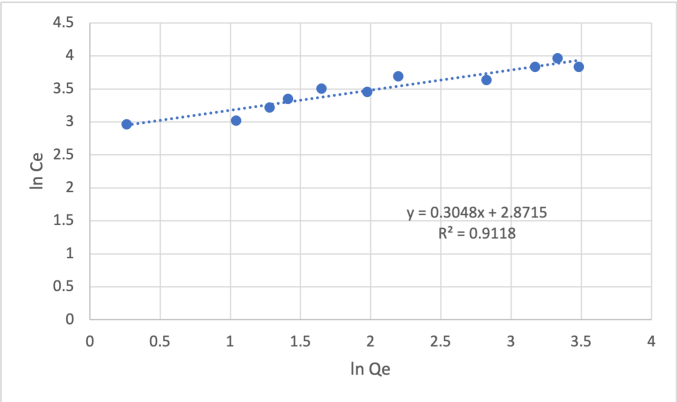


Fig 9: Langmuir isotherm for methylene blue

Fig 10: Freundlich isotherm for methylene blue

Table 6: Isotherm parameters for the adsorption of methylene blue

Pollutant	Langmuir		Freundlich
	Q_{max} (mg/g)	R^2	R^2
Methylene blue	53.8	0.9797	0.9118

Figure 9 shows the linearised Langmuir plot, of which its gradient was inversed to find the maximum adsorption capacity, q_{max}, and tabulated in table 6. Figure 10 shows the linearised Freundlich plot. By comparing the correlation coefficients, R^2, it was found that the adsorption of the composite fits the Langmuir model better. Thus, maximum adsorption capacity on methylene blue was determined to be 53.8mg/g.