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Article

Developing porous copper/aluminium-chitosan biosorbent hydrogel beads for the removal of phosphate from wastewater

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ABSTRACT

Excess phosphorus is one of the principal causes of eutrophication, which causes severe ecological imbalance and harm to human health. In this study, several chitosan (CS)/copper and aluminum (CNT, ACH) hydrogel beads were created and tested for phosphorus removal. Further Microcrystalline cellulose and Cellulose Nano Fiber were also used to create stable CS/CNT - ACH hydrogel beads. The optimized CNT/CS settings with 0.2 mg CNT demonstrated outstanding removal efficacy. It effectively removed phosphate from an aqueous solution with a pH range of 4.5-5.5 using a completely mixed batch of 0.01M sodium dihydrogen phosphate, with 80% phosphate absorption achieved after 48 hours of contact time. The measured maximum adsorption capacity at pH 5.5 solution was 11.39 mg per 0.0206g of the beads (10 beads). The FTIR study revealed that all three varieties of synthesized beads have a healthy microstructure. Furthermore, the findings of the kinetic study indicated a low absorption rate at 15ºC and a moderate absorption rate at 45ºC. The adsorbent efficiently removed phosphate during 12 hours of contact time, according to a batch adsorption study, using 20 beads weighing 0.0412g. Electrostatic attraction and ion exchange can both be responsible for phosphate absorption. Furthermore, 10 of the 21 control MCC and CNF beads could remove more than 60% phosphate after 48 hours of contact time with identical solute distributions. This adsorbent might be deployed to effectively treat phosphorus-contaminated water to prevent eutrophication.

1. Introduction

Regardless of the fact that water covers 71% of the earth's crust, we humans manage to endanger the natural equilibrium of water bodies across the world by releasing wastewater. For a multitude of reasons, the Earth's limited supply of fresh water, which accounts for around 2.5% of total water content, must be safeguarded. According to the UN, approximately 80% of wastewater created by all urban housing projects, big-scale production chains, and even small-scale manufacturing enterprises, among other things, is released into natural water bodies untreated. This research focuses on the chemical component phosphate, which becomes contaminated in natural water bodies by wastewater discharge due to its widespread use in everyday goods. To design a long-term sustainable engineering solution for removing this chemical from a regulated wastewater sample. Phosphorous is a nonmetal element having a valency of 5+. When fluorapatite, often known as phosphate rock, is exposed to acid, it creates phosphoric acid. Orthophosphate, polyphosphates, and organically bound phosphates are the three types of phosphates. The natural phosphate cycle is critical for animal and plant health, and its imbalance arises when it is released in bulk quantities after human ingestion. All of these kinds are extra phosphate deposits that disrupt the normal chemical equilibrium. Phosphorous contributes significantly to water pollution, with negative impacts ranging from eutrophication, ocean acidification, and algae overgrowth to suffocating of some aquatic animal species, shortening their life span. Organically bound phosphates are primarily discharged in conjunction with waste solids or organic waste [1]. Phosphorous has a noteworthy impact on human health degradation, ranging from dehydration and diarrhoea to renal disease and endothelial dysfunction [2]. The significance of creating technology for chemical removal from effluent wastewater has long been explored and acknowledged. There have been several ways based on its scientific foundation. Physical removal methods such as adsorption and magnetic field use, chemical removal methods such as precipitation with lime or aluminium chromate, biological removal methods such as biomass adsorption and reagent use, physical-chemical removal methods, and even chemical-biological removal methods have all been studied and put into practice. This study focuses on the physio-chemical removal approach, specifically the inclusion of Hydrogel in anion removal. Over the last few decades, researchers have created various hypotheses, proposed numerous chemical compositions, and even succeeded in many situations with phosphate removal using the physio-chemical removal approach. The first limitation of present techniques appears with phosphate removal utilizing metal-impregnated hydrogels. Phosphate anion has a valency of 3, and there haven't been many viable methods for eliminating it at a high percentage. The second limitation is that the effects of additive variations on phosphate absorption are not clearly examined. The majority of investigations use one kind of bead and one set type of additive (metal or non-metal). This makes guessing the absorption levels of a few distinct types of beads prepared for a substantial sort of anion elimination difficult. Hydrogel beads prepared in this study are simple structures of the biopolymer 'Chitosan' integrated with cationic ions such as Copper and Aluminium, which can conceive a gel bead-like structure after several experimental steps, with a hollow sponge-like middle sector with hydrophilic abilities due to its surface having water permeable qualities. Existing approaches do not generate significant outcomes when adding hydrogel beads in phosphate removal. The research gap is addressed by attempting to synthesize and characterize various types of hydrogel bead structures incorporating copper and aluminium, on their absorbance and ability to absorb targeted anions in a controlled experimentation series, with the hope of also monitoring the beads' response to stimuli changes.

2. Literature review

2.1 Phosphate in water

Water is the 'universal solvent' due to its ability to dissolve more substances than any other liquid on earth. Phosphates occur in many ways, leading to adverse effects on mankind as well as flora and fauna. Depending on its contamination action, they can be listed into three different methods of contamination. 'Point source' pollution through phosphates is the way that they end up in natural water bodies in bulk loads without any objection, decay time, or treatment. Oil refinery effluents, wastewater from process industries such as dye and acid manufacture, chemical dumping by big-scale laboratories and supply networks, and medical waste from any institution of medicine are the finest examples. Phosphate contamination is caused by the late addition of phosphate-rich effluents to water bodies that do not originate from a single source or site. Excess fertilizer or weedicides used in agriculture, mine explosions that contaminate ground waterways, and landslides or volcanoes that are natural risks with a large release of phosphates that wash away to water over time are instances of pollution. Transboundary pollution is described as contamination that begins in one country but travels to another country's water sources. Oil spillage on ocean or river water, chemical deposits (medicine/cosmetics) from accidents on ships/boats traveling by water, and chemical manufacturing fumes carried away by winds or rain are the greatest examples. As previously established, all of these pollution strategies have negative effects on plant and animal species irrespective of water ecosystems. Phosphorus is a limiting nutrient needed for all plant development, including aquatic plants and algae. Excess concentrations can induce algal blooms, especially in rivers and lakes. A lake with a concentration of less than 0.010 mg/L is considered oligotrophic, whereas one with a concentration between 0.010 and 0.020 mg/L is considered mesotrophy, and concentrations greater than 0.020 mg/L are classified as eutrophic [3]. The acceptable phosphate levels in Malaysia are 0.1 mg/L and 0.2 mg/L, according to the National Water Quality Standards, Malaysia. These two concentrations are divided into two water classes, and samples with 0.1 mg/L phosphorous content fall into water CLASS IIA/IIB. The samples with a phosphorus value of 0.2 mg/l fall into the water CLASS III. To be clear, CLASS IIA/IIB water is appropriate for water supply after simple treatment, for delicate aquatic species, and for recreational body contact. After considerable treatment, CLASS III water is appropriate for water supply, common species of fish, and cattle drinking.

2.2 Existing methods of phosphate removal

2.2.1 Ion exchange

This method is applied in small-scale industries, municipal drinking water treatment units, and even in-home water softeners. Ion exchange requires passing the water through a specialized ion exchange resin in a closed vessel. The surface of the resin involves active sites, which help remove the constituent of interest in exchange for other feasible, less effective ions. Once all the active sites of the resin are used, the resin must be restored or regenerated, and since the used resin is a strong anion resin, NaCl can be used for restoration purposes. An example of this application is if a water flow with 5 mg/L phosphate ions is introduced to the ion exchanger, the treated water would contain less than 2 mg/L of phosphate in the system [4].

2.2.2 Magnetic field method

Here, phosphates are bound to a reagent in the insoluble compound. Once the magnetic field is activated with magnetic material addition to the water system, it isolates the phosphate-containing sediment.

2.2.3 Electric coagulation method

Here, electrodes are used to isolate the phosphates inside the water system. Electrodes of 2 types can be used, iron-aluminium or steel. This method ensures an easier extraction of phosphates too.

2.2.4 Chemical removal methods

A) Adding aluminium chromate to wastewater in the presence of an alkali generates the following reactions,

$$\mathrm{Al_2(CrO_4)_3} + 6\mathrm{HCO_3}^- \rightarrow 2\mathrm{Al(OH)_3} + 3\mathrm{CrO_4}^{2-} + 6\mathrm{CO_2} \quad (1)$$

$$\mathrm{Al_2(CrO_4)_3.14H_2O + 2PO_4{}^{3-} \rightarrow 2AlPO_4 \downarrow +3CrO_4{}^{2-} + 14H_2O} \quad (2)$$

These reactions will fight for the aluminium ions dispersed after the addition of aluminium chromate. The aluminium hydroxide flakes attract the aluminium phosphate particles and colloid particles of solid impurities.

B) Adding 3 valent iron salts as a coagulant

$$\mathrm{FCl_3 + PO_4{}^{3-} \rightarrow FePO_4 + 3Cl^-} \quad (3)$$

In here the ferric phosphate particles sediment. Any excess of ferric ions will produce iron hydroxide. Iron hydroxide will attract ferric phosphate particles and other particles and sediment itself.

C) Adding calcium hydroxide as a coagulant

$$\mathrm{Ca(OH)_2 + HCO_3{}^- \rightarrow CaCO_2 \downarrow + H_2O + OH^-} \quad (4)$$

$$5Ca + 4OH^- + 3HPO_4 \rightarrow Ca_5OH(PO_4) \downarrow +3H_2O \quad (5)$$

In here lime readily reacts with any bicarbonate ions in the water complex. In addition, it also reacts with phosphates. The orthophosphates are precipitated with the help of calcium ions and produce oxyapatite. When the pH value of the water body increases, the solubility of calcium oxyapatite decreases, and the removal of phosphate increases (pH > 9.5 is the ideal).

Biological methods are said to give the best removal percentage of phosphorous from water complexes. There are different approaches with different efficiencies in the matter, varying the effective removal percentages from 20% - 50%. This percentage can be enhanced up to 95% with the current technological maturity. Such biological treatment approaches are Phostrip, A/O (Anaerobic–Oxic), and EASC (Extended Anaerobic Sludge Contact process). However, there are several biological – chemical applications as well [5]. They all pose higher quality compared to chemical treatment and biological treatment separately. They each differ from each other by reagent source and reagent composition.

2.2.5 Hydrogel beads

Hydrogel beads are cross-linked polymers that have hydrophilic traits, and once immersed in aqueous solutions, they swell by attracting water inside the 3D structure. The component must account for at least 10% of the total weight of the material to be called a hydrogel [6]. Many alternative theories have been developed over the years to assist in predicting the structural result of hydrogels, which gives us the gel's elasticity value, porosity, and pore size of the hydrogel network. All these theories consider enthalpy, entropy, and other thermodynamic factors in order to establish the structure and pore sizes of hydrogels, and computer modeling methods may then be utilized to accurately create the hydrogel intended. Hydrogels are classified as those made from natural polymers, those made from synthetic polymers, and those made by modifying natural polymers with synthetic linkers (semi-synthetic hydrogels) [7]. As a result, hydrogels can undergo structural transformations in response to a stimulus, which can be chemical or physical. Chemically prepared gels rely on covalent bonding to introduce the integrity required to form a gel structure [8].

The gels can be cationic, anionic, or neutral depending on the ionic charges on the bonded groups. By stacking various hydrogel layers that each react to a particular stimulus, shape-changing hydrogels may be constructed [9]. Hydrogels may also be classed as homopolymer or copolymer based on the different polymerization processes such as suspension, block, solution, and emulsion. Homopolymers have just one kind of monomer in their structure, and depending on the nature of the monomer and the polymerization process employed, they may have a cross-linked structure. Copolymeric hydrogels are made up of two types of monomers, at least one of which is hydrophilic. An interpenetrating network (IPN) can be formed by joining two polymers, provided that one of them is already present in the solution [6, 10]. Hydrogel is found in three different types: resins, films, and nanocomposites, and in an attempt to improve its adsorptive properties, many other chemicals can be integrated into the network. According to the literature survey, it is visible that hydrogels have a high potential to succeed with their applicability in wastewater treatment for intended anion removal [11]. The morphology of hydrogel beads suggests that their size can vary from 20nm – 5mm with porous, rough outer surfaces [12]. Their swelling ratio is mainly dependent on the pH of the solution and retention time. Biopolymers such as polysaccharides and polypeptides have garnered a serious welcome in the hydrogel bead production industry.

2.2.6 Biopolymers

There are various biopolymers incorporated in biodegradable research work nowadays. Within an organism, these various polymers are made up of numerous individual monomers or units. They are often sourced from plants and animals, making them both biodegradable and easily reusable for different purposes. Incorporating this feature of biodegradability came into use after the era of sustainable engineering started. Hence researchers have thrived in finding engineering solutions incorporating biodegradable materials. Attempting the use of biopolymers in adsorptive studies came into light around the early 2010s. Since its application has improved vastly in fields such as tissue engineering. Hydrogels are employed in a variety of industries due to their unique architectures and compatibility with various operating conditions. Hydrogels are distinguished from other biomaterials by their flexibility, and their versatility is unparalleled since their applications vary from industrial to biological. Drug delivery, dye, and heavy metal removal, scaffolds in tissue engineering, and even contact lenses are some of the major uses of hydrogels [6, 10]. Biopolymers, as previously discussed, are critical in the development of useful and novel hydrogels with improved biocompatibility [13]. Sugar-based polysaccharide biopolymers and protein-based polypeptides have both been used extensively in the development of novel biodegradable and biocompatible hydrogel materials. Polysaccharides utilized in the creation of hydrogels include chitosan, cellulose, alginate, and glycosaminoglycans. Polypeptides may contain collagen, gelatine, and other proteins [14].

2.2.7 Hydrogel bead application in wastewater treatment

There is a considerable number of works done in the area of hydrogel beads incorporated in wastewater treatment. However, there were some articles which provided an insight for the research. A study on phosphate removal from a complex water environment study incorporated Zr-bentonite hydrogels [15]. Testing on anion selectivity was further carried out by introducing other multivalent anion salts. Another study discusses the application of polyacrylic-based hydrogel beads for heavy metal removal [16]. These acrylic-based polymer hydrogel beads have garnered attention due to their applicability in pollutant adsorption and heavy metal extractions. This research further elaborates on the different approaches that can be taken into consideration when synthesizing acrylic hydrogels. An in-depth analysis of the thermodynamic factor affecting the hydrogel beads is also explained. Researchers attempted the removal of boron using modified chitosan hydrogel beads [17]. This was done using a synthesis of manganese chitosan hydrogel beads. This research was done in an attempt to clear freshwater samples entering irrigation systems. Results show a potential in commercial application for improving water quality.

2.2.8 Materials of application

Chitosan (CS), Copper nitrate trihydrate (CNT), Aluminium chloride hexahydrate (ACH), Microcrystalline cellulose (MCC), and Cellulose Nanofiber were used in this study to synthesize hydrogel beads (CNF). They are chosen after careful examination of the selected pollutant - 'Phosphate' in water, its affinity to the metallic ions inside the hydrogel beads, the ability of the biopolymer to absorb and desorb water without hesitation, the adaptability of the biopolymer and enhancers, and the required strength of the hydrogel beads. Furthermore, extensive research and theories advanced by other researchers' work on hydrogel beads, such as [8,15,16] and many others, aided in finalizing the proper salts of application for each metal and the methodology of application of each additive and enhancer to the hydrogel prior to bead preparation.

Chitosan: Chitosan is a polysaccharide with high antibacterial properties that is biocompatible, biodegradable, and non-toxic. Chitosan, hence, has many uses, including those in medicine, agriculture, food preservation, nutritional supplementation, cosmetics, and wastewater treatment. A polysaccharide generated from chitin is chitosan.

Copper: Copper is a reddish-brown metal with a cubic crystalline structure. It is malleable, ductile, and an extremely good conductor of both electricity and thermal energy. It has a low chemical reactivity and falls under the category of transition metals in the periodic table. The molecular weight of copper is 63.55 g and has a density of about 8.9 gcm^{-1}. The most common ionic form is when the atom releases 2 electrons in the hope of ionic bond formation. Therefore, the most abundant cation type is the Cu^{2+} ion. In this research this ion type is used as the metal dispersed in the hydrogel beads. Why use copper is due to its high affinity to form an attraction with negatively charged phosphate ions. This has promoted the amount of phosphate removed from the water sample drastically. The copper nitrate trihydrate of 2+ copper was the best choice since it showed very good results during experimentation.

Aluminium: Although it makes up 8.1% of the Earth's crust, aluminum is rarely encountered in nature alone. It is typically present in minerals like cryolite and bauxite. These are aluminum silicate minerals. The Hall-Héroult technique is used to remove the majority of aluminum used in commerce. Given that aluminum is not a particularly strong metal on its own, it is frequently utilized as an alloy. Copper, manganese, magnesium, and silicon alloys are light but robust. They play a crucial role in the development of hydrogel and is often used in drug delivery and dye removal applications of hydrogel. The introduction aluminum can enhance the hydrogel's water affinity percentage by high numbers. One of the reasons it is utilized as a crosslinker in the experimentation for some types of beads.

Microcrystalline cellulose: Cellulose ($C_6H_{10}O_5$) n is one of the most widely distributed organic polymers in nature. It is a crucial structural component of oomycetes, many kinds of algae, and green plants' main cell walls. The polysaccharide is composed of a linear chain of (1-4) linked d-glucose units numbering from several hundred to several thousand. Utilizing various processes, including oxidation, etherification, and esterification, which transform generated celluloses into derivatives of cellulose, many techniques of cellulose extraction have been developed [18].

Cellulose nanofiber: Emerging nanomaterials called naturally generated cellulose nanofibrils (CNFs) have high strength, large surface area, and variable surface chemistry, enabling regulated interactions with the biological, nanoparticle, small molecule, and polymer materials. While the hydrophilicity of the nanocellulose interface has made it challenging to use CNFs as reinforcing agents in conventional plastics, it has been a significant advantage in the development of reinforced or structured hydrogel composites (or, when dried, aerogels) that exhibit mechanical reinforcement as well as a variety of other desirable properties [19]. The banana pseudo Cellulose nanofiber (CNF) used in this research was obtained by a master's student at Swinburne University of Technology Sarawak.

3. Methodology

The fabrication procedure was conducted in 4 separate parts, which include the preparation of Control CS – CNT/ACH beads, the preparation of MCC CS – CNT/ACH beads, the preparation of CNF CS – CNT/ACH beads, and lastly, the conditioning of the film. The testing procedures include FTIR analysis, Absorbance performance, Temperature sensitivity, and Batch adsorption study. All the beakers, flasks, crucibles, and petri dishes were washed with distilled water and dried in an oven for 1 hour at 60ºC prior to use.

3.1 Fabrication of hydrogel beads

Preparation of control CS – CNT/ACH beads: 9g of CS were dissolved in 450 ml of 2% (v/v) acetic acid solution to create a chitosan solution of 2% (w/v). Following complete CS dissolution, the solution was separated into 9 samples of 50ml given in Table 1. The beads were synthesized into 9 different types by using the below additive amounts.

Table 1. Distribution of additives for Types A – I

Type	A	B	C	D	E	F	G	H	I
CS (w/v)	2%	2%	2%	2%	2%	2%	2%	2%	3%
CNT (g)	0.2	0.4	0.2	0.4	0.2	-	-	2.7	2.7
ACH (g)	-	-	0.2	0.2	0.4	0.4	0.2	-	-

Homogenous distribution was achieved by continuous stirring at 300rpm for 24 hrs of each hydrogel mixture. 18g of SH is dissolved in 900ml of DI water to create a 2% (w/v) SH solution and divided into 9 samples of 100ml SH solution. The hydrogel mixtures were added dropwise into each of the SH samples using a micro dropper to form the hydrogel beads. The prepared beads were left at continuous stirring at 300rpm for 24 hrs inside the SH solutions to ensure cross-linking.

Preparation of MCC CS – CNT/ACH beads: The same steps for the hydrogel mixture preparation are carried out for Types A – F as control hydrogel beads. Then, prior to leaving for continuous stirring, 0.2 g of MCC is added. Steps are repeated from then onwards.

Preparation of CNF CS – CNT/ACH beads: The CNF pulp is prepared by soaking 0.3g of CNF in 30ml of DI water and letting to soak for 2 hrs. Using the sonicator machine, preparation of CNF pulp is done, the settings used are 40% - 50% amplitude (gradually increase), elapsed time 8 mins 20 secs, Pulse 5/10 and total energy used is 8184Joules. The same steps for the hydrogel mixture preparation are carried out for Types A – F as control hydrogel beads. Then, prior to leaving for continuous stirring 5 ml of CNF pulp is added. Steps are repeated from then onwards.

Conditioning of hydrogel beads: The 21 types of hydrogel beads synthesized were washed with DI water till pH 6.5 – 7.5 is reached (tabulated in Table 2). The washed beads must be dried in an oven at 60 for 4 hrs. After drying, the beads are stored in a desiccator to avoid contact with air.

Table 2. Twenty-one types of synthesized hydrogel beads

Control Type A	Control Type B	Control Type C	Control Type D	Control Type E	Control Type F	Control Type G
MCC Type A	MCC Type B	MCC Type C	MCC Type D	MCC Type E	MCC Type F	Control Type H
CNF Type A	CNF Type B	CNF Type C	CNF Type D	CNF Type E	CNF Type F	Control Type I

3.2 Testing procedure

Fourier transform infrared analysis: The chemical alterations and bonding of the different types of composite films were analyzed using FTIR spectra. The equipment used to conduct the FTIR was a Perkin-Elmer Spectrum 400 FTIR spectrophotometer.

Absorbance performance: The absorptive studies were carried out on the percentage weight of water of the soaked beads and the percentage of phosphate removal using titration. A solution of 0.01M SDP is prepared by adding 1.56g of SDP in 1000 ml of DI water. Sixty-three samples of 15ml, each 0.01M SDP, are distributed, and 10 beads of each of the 21 types of beads are suspended into 3 solutions per type. For water absorbance testing the dry weight before soaking and wet weight after soaking of the hydrogel beads are obtained. For the phosphate removal efficiency testing, the 21 types, each out of the 63, are kept for 12 hrs, 24 hrs, and 48 hrs, respectively. Using a 0.1M SH solution the samples of SDP are titrated in the presence of phenolphthalein and pH meter for accuracy. The experiment is repeated for 3 rounds to reduce the error percentage.

Temperature sensitivity: Once the absorbance and phosphate removal efficiencies are calculated, the best type of beads can be identified. A selective experimentation is done to observe the absorbance performance of the beads under temperatures lesser than room temperature and higher than room temperature. The same steps as absorbance testing are carried out for Type A control beads to prepare 9 samples of 15ml 0.01M SDP and 10 beads each. Three samples are left in the refrigerator set at 15 for 24hrs, 3 samples at room temperature for 24 hrs, and 3 samples sealed inside the oven at 45 for 24 hrs. The same steps of titration are followed at the end of 24 hrs using 0.1M SH.

Batch adsorption study: Using the same selection Type, A control, selective experimentation is done to observe the absorbance performance of the beads as a pack of 10 beads, 15 beads, and 20 beads for comparison of the absorbance fluctuations with the varying of no: of beads. The same steps as absorbance testing are carried out for Type A control beads to prepare 9 samples of 15ml 0.01M SDP and let 10 beads each of 3 samples for 24 hrs, 15 beads each of 3 samples for 24 hrs, and 20 beads 3 samples for 24 hrs. The same steps of titration are followed at the end of 24 hrs using 0.1M SH.

4. Results and discussion

4.1 Fourier transform infrared analysis

According to the FTIR results, Figures 1, Figure 2, and Figure 3 display the FTIR spectra of the produced chitosan composite beads packed with Copper (II) particles and the Al (III). The amide (C=O) stretch, the C-N stretch, the bending owing to N-H stretching, and the absorptions due to C-H stretching at around 3000 cm^{-1} and the C-H bending at around 1300 cm1 are the characteristic peaks for chitosan. The C-O skeletal stretch typical of polysaccharides can be seen at 1100 cm^{-1}, and C-O antisymmetric stretching can be seen at 1000 cm^{-1}. Copper and Aluminium exhibit absorption bands at 700 cm.

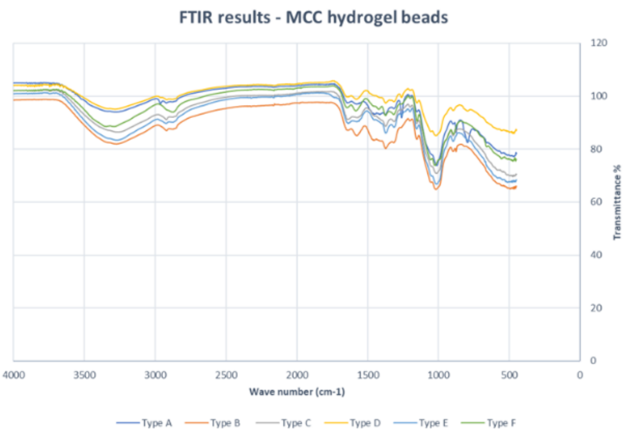


Figure 1. FTIR plot of MCC hydrogel beads

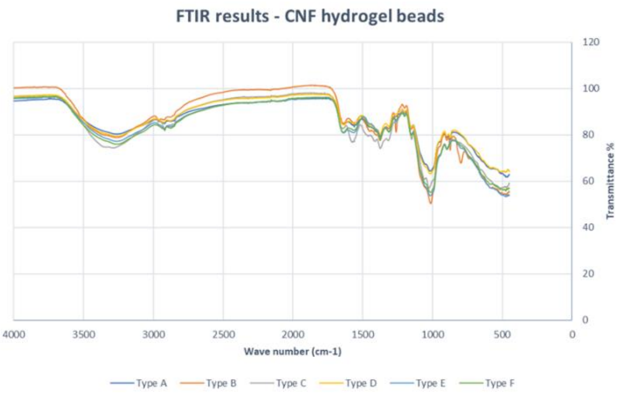


Figure 2. FTIR plot for CNF hydrogel beads

Absorbance performance

According to the graph, it is visible that the percentage weight of water absorbed is highest in Type F CNF beads. This type consists of CNF and Aluminium as additives in the hydrogel mixture. Also, the lowest water absorbed is by Type A control beads. This type consists of only copper as an additive. These results suggest that the water absorbance when only copper is integrated is very low compared to the other samples with high water affinity moving from Types C to F. Types C to F are consisted of aluminium, and types C, D, E are consisting of both copper and aluminium. Also, it is noticeable that water affinity slightly increases with the addition of MCC into the beads. However, the affinity reduces when CNF is tallied with copper suggesting strong bonds between copper and CNF as a structure more than hollow spaces with lower bonding percentage.

Types H and Type I show a high affinity towards water due to their high concentration of chitosan compared to Type H with the usual chitosan concentration. In testing the percentage removal of phosphate, calculations were done using a simple titration of acid base. The first set of results was tested after 12 hours, and 5 types of beads had a percentage removal higher than 50% already. Then, after 24 hours, the results showed that 13 samples had a removal percentage of 50% and above, but already 7 samples showed more than 60% removal efficiency. At the end of 48 hours, 10 samples recorded a removal efficiency of above 60%. This result shows as shown in Figure 4, the experiment was indeed a success in recording more than 10 bead types with the effective removal of phosphate from controlled wastewater samples. Discussing further, the bead type A had the best-recorded removal percentage since the beginning of testing. It had a 66.67% removal percentage after 12 hours, a 73% removal percentage after 48 hours, and successful removal of 80% phosphate at the end of 48 hours (Figures 5, Figure 6, and Figure 7). This can be due to the fact that it has the least amount of copper and no other additives blended, ensuring a strong hydrogel network. The fewer the additives, the better the percentage removal across each bead type from A to I.

4.2 Temperature sensitivity

As the Type A control beads showed the best results in the general titrations, it was used to test the effects of the bead when external stimuli changed. Temperature fluctuations were chosen for the matter. The same type of bead was distributed into 9 samples and were placed at three different temperatures. The samples at room temperature showed the highest phosphate removal at the end of 48 hours.

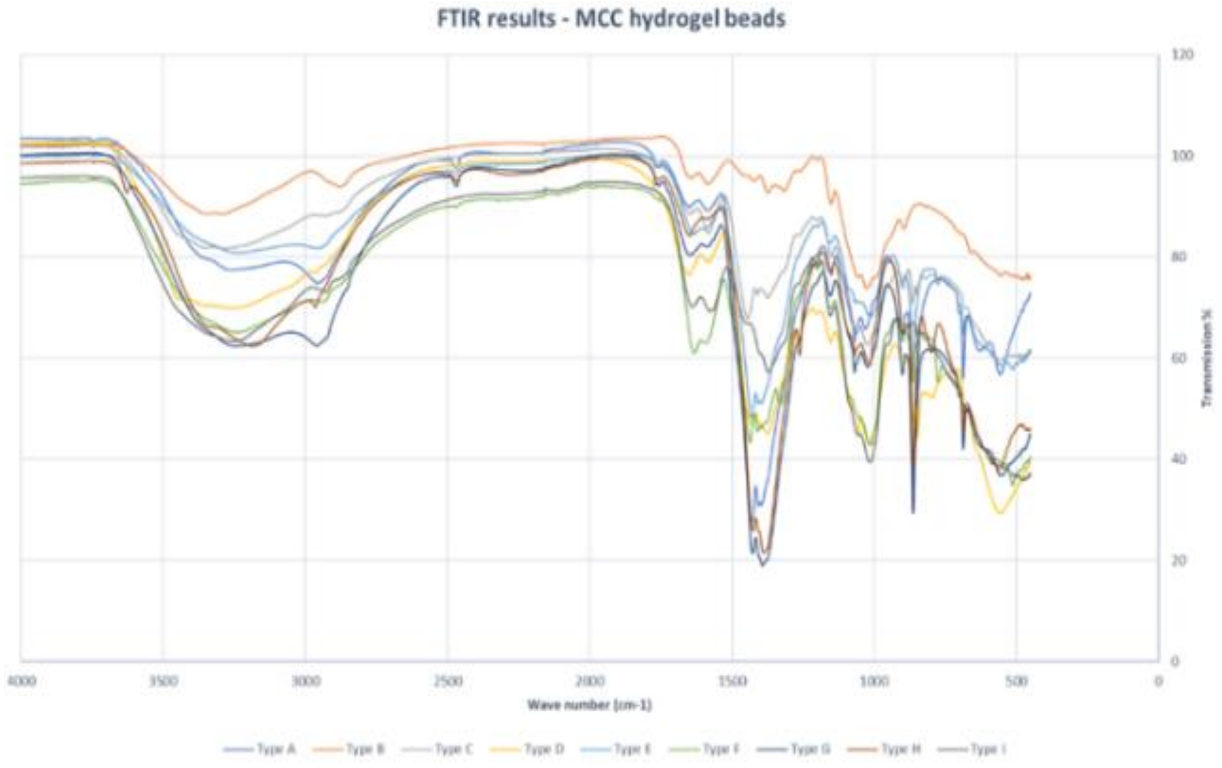


Figure 3. FTIR plot of control hydrogel beads

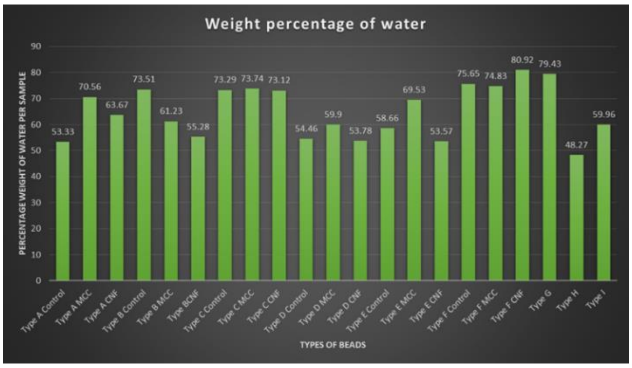


Figure 4. Plot of percentage weight of water per bead type

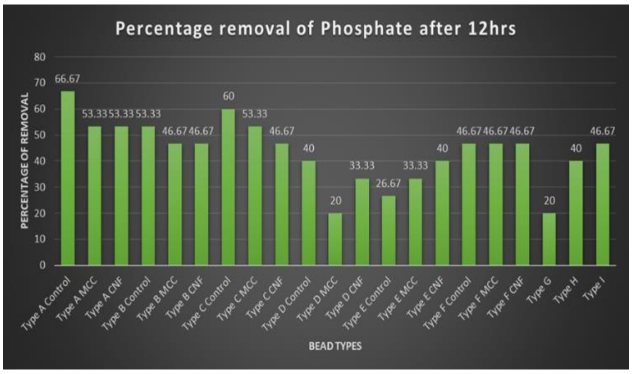


Figure 5. The plot of percentage removal of phosphate after 12 hrs

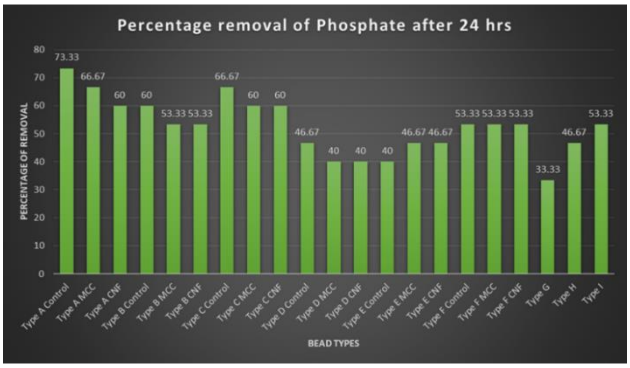


Figure 6. The plot of percentage removal of phosphate after 24 hrs

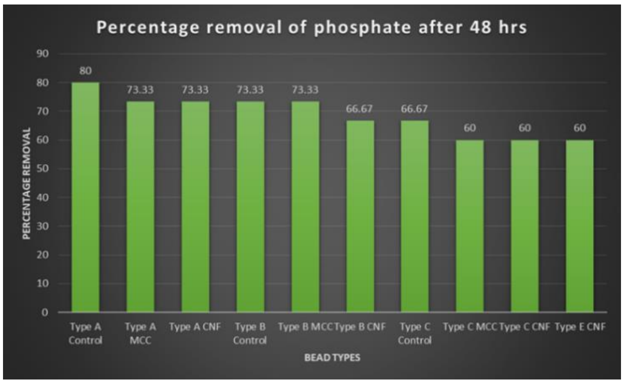


Figure 7. The plot of percentage removal of phosphate after 48 hrs

Table 3. Percentage removal of Phosphate at different temperatures

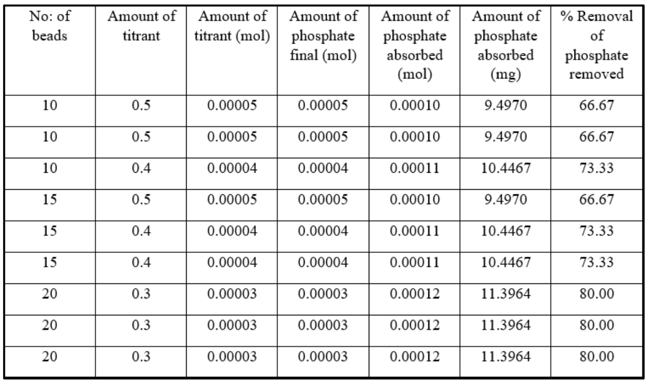
Temperature of the samples (Celsius)	Amount of titrant	Amount of titrant (mol)	Amount of phosphate final (mol)	Amount of phosphate absorbed (mol)	Amount of phosphate absorbed (mg)	% Removal of phosphate removed
15 - A	1.4	0.00014	0.00014	0.00001	0.9497	6.67
15 - B	1.4	0.00014	0.00014	0.00001	0.9497	6.67
15 - C	1.2	0.00012	0.00012	0.00003	2.8491	20.00
30 - A	0.3	0.00003	0.00003	0.00012	11.3964	80.00
30 - B	0.3	0.00003	0.00003	0.00012	11.3964	80.00
30 - C	0.3	0.00003	0.00003	0.00012	11.3964	80.00
45 - A	0.5	0.00005	0.00005	0.00010	9.4970	66.67
45 - B	0.6	0.00006	0.00006	0.00009	8.5473	60.00
45 - C	0.5	0.00005	0.00005	0.00010	9.4970	66.67

The sample set at a lower temperature did not show any progress toward phosphate removal since the percentage was very poor, somewhere around 6.7%. The samples set at a higher temperature still was able to absorb some amount of phosphate. Compared to that of the samples at room temperature, it was less. However, the removal of 66.67% shows good numbers. This shows that the beads lose their anion removal efficiency, which is very noticeable at lower temperatures (Table 3). Anyhow, a slight increment would not affect the case of anion removal as much as low temperatures. This could be due to the gel's tendency to harden at lower temperatures, limiting the amount of water absorbed. Further resulting in lesser adsorption of phosphate. However, the best temperature for anion removal is room temperature.

4.3 Batch adsorption study

Similar to section 4.3, the batch adsorption study utilized the same type of bead, Type A control, for the study of the effect of the beads per sample. The results showed good progress when compared to one another. When the no of beads increased the absorption, the cap was reached at 12 hours. When using 10 beads, the sample was only able to recover 66.67% of the total phosphates in the solution. However, as expected, when the number of beads was increased by 5, the absorption percentage was increased to 73% (Table 4). As per expectation, the sample with 20 beads was titrated with just 0.3 ml of titrant. This means that it reached the absorption cap of 80% over the time period of 12 hours.

Table 4. Percentage removal of Phosphate for batch adsorption studies



No: of beads	Amount of titrant	Amount of titrant (mol)	Amount of phosphate final (mol)	Amount of phosphate absorbed (mol)	Amount of phosphate absorbed (mg)	% Removal of phosphate removed
10	0.5	0.00005	0.00005	0.00010	9.4970	66.67
10	0.5	0.00005	0.00005	0.00010	9.4970	66.67
10	0.4	0.00004	0.00004	0.00011	10.4467	73.33
15	0.5	0.00005	0.00005	0.00010	9.4970	66.67
15	0.4	0.00004	0.00004	0.00011	10.4467	73.33
15	0.4	0.00004	0.00004	0.00011	10.4467	73.33
20	0.3	0.00003	0.00003	0.00012	11.3964	80.00
20	0.3	0.00003	0.00003	0.00012	11.3964	80.00
20	0.3	0.00003	0.00003	0.00012	11.3964	80.00

5. Conclusions

This experimental research was a success, considering the fact that 10 bead types had a phosphate removal percentage higher than 60%. From the FTIR results, the favorable bonding of Chitosan to Copper and Chitosan to Aluminum was observed. Also, with the introduction of cellulose matter, the rigidness of the beads increased considerably. However, the enhancers did not show any progress towards the affinity of phosphate anion surpassing the control set of beads. The best bead type at the end of the experiment was identified to be Type A control, which successfully eliminated 80% of the phosphate in all samples. The same bead was then tested for temperature sensitivity and batch adsorption studies where at room temperature, the beads still showed an 80% removal rate, at 45 Celsius, it had lowered its affinity by almost 13%, dropping the percentage of phosphate removal up to 60.67% at 15 Celsius the beads did not show any affinity towards the phosphate anions resulting the percentage of removal to be as low as 6.67. In the batch adsorption studies, the same type of bead showed that the maximum adsorption capacity was 80%, where 10 beads in 12 hours resulted in 66.67% absorbance, 15 beads in 12 hours resulted in 73% absorbance, and 20 beads in 12 hours resulted in 80% absorbance.

Ethical issue

The authors are aware of and comply with best practices in publication ethics, specifically with regard to authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests, and compliance with policies on research ethics. The authors adhere to publication requirements that the submitted work is original and has not been published elsewhere.

Data availability statement

The manuscript contains all the data. However, more data will be available upon request from the authors.

Conflict of interest

The authors declare no potential conflict of interest.

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