Doctor of Environmental Science in *Graduate School of Environmental Science* The University of Shiga Prefecture

From Waste to Resource: Optimizing Biochar with Eggshell for Effective Phosphate Adsorption and Sustainable Fertilization

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"To myself I am only a child playing on the beach, while vast oceans of truth lie undiscovered before me."

— Isaac Newton

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ABSTRACT

Phosphorus is an important element for the plant growth, and it is used as a fertilizer. It is a limited and non-renewable resources in the earth. But when the excessive amount of phosphorus goes into waterbody, it works as a nutrient for aquatic plants and algae and causes eutrophication. So, the recovery of the phosphate from water is very important to avoid eutrophication and recover phosphate to use as fertilizer.

Phosphate recovery using adsorption is a very attractive and effective method. Nowadays different types of natural bio waste material are used for phosphate recovery. Using biochar only is not suitable for phosphate adsorption because of the negative surface charge of the biochar. But metal modified biochar has good phosphate adsorption capacity. Sometime the adsorbed material could not be used as fertilizer because of presence of heavy metal in modified adsorbent.

Eggshell decorated biochar exhibits excellent phosphate adsorption capacity than only biochar. Moreover, calcium is not toxic. That's why current study was intended to recover the phosphate from wastewater using a most convenient procedure and available materials. Bamboo and eggshell were used as an available natural ingredient which was not used for phosphate recovery before. Since bamboo char is the source of carbon and eggshell as the resource for $CaCO_3$, would be used as a metal cation which has great affinity for phosphate. So, the combination of pure biochar with calcite could be a good adsorbent material to recover phosphate from wastewater. Another objective of this study was to examine the phosphate desorption using DI water at different temperature and the effectiveness of the phosphate loaded materials as P fertilizer on Japanese mustard spinach cultivation for the sustainable management of the P adsorbed material.

Bamboo and eggshell adsorbent were prepared for different mixing ratio and temperature (600, 700, and 800°C) to find out effective ratio and calcination temperature. To investigate the feasibility of calcined bamboo and eggshell for phosphate removal, different calcination temperature, initial concentration, temperature, time, dose rate, pH, and presence of different ions was examined. Adsorption mechanism was understood by adsorption isotherm, thermodynamics study, and adsorption kinetics. Morphological changes and characterization of the adsorbent after calcination and adsorption were identified by the SEM image, EDX spectra and FTIR analysis. The maximum P adsorption capacity of the BE 1:1 and BE 2:1 was found 95.14 mg/g and 98.40 mg/g respectively. For CE, BE 1:1 and BE 2:1 adsorbent, the data

were well fitted by Langmuir model, and it indicates the monolayer adsorption on the homogenous surface of the adsorbent. Thermodynamics results revealed that the Gibbs free energy ΔG of the BE 1:1 and BE 2:1 at 298 K, ΔG was positive indicates the process was not spontaneous. But after increasing temperature the reaction was spontaneous. Langmuir separation factor (R_L) value indicates the favorable adsorption conditions for phosphate.

Characterization of adsorbent was identified by FTIR, and SEM image. From FTIR analysis the formation of the band at 1021 cm^{-1} was observed, which clearly indicated the presence of phosphate after adsorption on BE 1:1. From kinetic study it has been found that the experiment data were better fitted the pseudo second order model which explain that adsorption procedure was chemisorption process. Presence of different ions (anions and organic acids) and pH of the solution also influence the phosphate adsorption mechanism. But calcined BE 1:1 is not effective for the organo-phosphorus herbicide glyphosate removal which is beneficiary for this research because it will not compete with phosphate for active sides and don't make contamination in application of phosphate adsorbed material as fertilizer.

In this study phosphate desorption in Milli-Q water and NAC extraction method was examined. Then phosphate dropped biochar was applied on pot experiment for Japanese mustard spinach cultivation. From the experiment it was found that phosphate desorption in Milli-Q water was very low. Because the bonding between calcium and phosphate is very strong. So, the reuse of the adsorbent is not a good option. But the phosphate loaded eggshell modified bamboo char was effective as slow-release fertilizer for the Japanese mustard spinach cultivation. So, the phosphate loaded eggshell modified bamboo char has potentiality to use in plant cultivation as a phosphorus fertilizer.

CHAPTER 1

General Introduction

1. Importance of phosphorus removal

Phosphorus is the structural component of biomolecules (e. g. DNA, RNA, ATP etc) which is known as growth nutrient of the plants and other organisms (Hong et al., 2020; Santos et al., 2019). It is an important micronutrient for plant metabolism, root, and shoot growths, and reproductive development (Neelam et al., 2017). Mineral fertilizer extracted from the phosphoric rock and manure are the main source of phosphorus used for the food production (Vaccari et al., 2019). The pressure of food production due to overpopulation has been increasing the inefficient use of the phosphorus fertilizer. The rising demands of the phosphorus fertilizer will deplete the phosphorus reserve within few decades (Xie et al., 2014). Plants needs only small amount of phosphorus, but the extra residual phosphorus accumulates in the soil after plant uptake (Syers et al., 2008). This excessive amount of phosphorus enters the surface water and causes tremendous growth of algae and aquatic plants which is known as algal bloom (Lee et al., 2019). When the algae and aquatic plants die, bacteria use dissolve oxygen to decompose and deplete the dissolved oxygen. This sever water pollution is known as eutrophication. Algae blooms causes several significant negative impacts on the aquatic environment because the floating layers or surface scums may prevent photosynthesis, enormous algal biomass decomposition causes oxygen depletion and some algae such as *Microcystis* releases toxins (Bhateria et al., 2016). It is a very harmful process not only for submerged macrophytes and but also for aquatic animals due to turbidity, malodor, and hypoxic/anoxic conditions (Liu et al., 2018).

The source of phosphorus might be natural (weathering process of phosphate rock) and anthropologic. The human originated source of phosphorus are point sources (synthetic detergent in domestic wastewater) and non-point sources (agricultural run-off) (Rockström et al., 2009; Steffen et al., 2015; George et al., 2017). The discharge standard of phosphorus in Japan is 1 mg/L, China is 0.5 mg/L (GB18918-2002), and the US standard is 50 µg/L (1994) (Zhou et al., 2014). In natural water and wastewater, orthophosphate, polyphosphates, and organic phosphorus are the major form of phosphorus. Polyphosphates and organic phosphorus are converted to orthophosphate by hydrolysis/or microbial mobilization (Habiby et al., 2019). At the same time, phosphorus is a non-renewable resource and its reservation in nature are limited (Cooper et al., 2011). Sewage wastewater, sludge, manure, and other animal by-products are the biological waste contain certain amount of phosphorus which can be recovered, and European Union has exposed their attention on phosphorus recovery from wastewaters (Santos et al., 2019). Recovery of phosphorus from the wastewater might be the alternative source of the phosphorus resource. Meanwhile phosphorus removal is the eutrophication control measure for the environmental management.

2. Different Technologies for phosphate removal

Different types of technologies are available to remediate phosphorus pollution. These processes can be classified as chemical methods (precipitation, crystallization, anion exchange, and adsorption), biological methods (assimilation, enhanced biological phosphorus removal, constructed wetlands, wastewater stabilization pond), and physical methods (microfiltration, reverse osmosis, electrodialysis, and magnetic separation) (Benyoucef and Amrani, 2011; Bhojappa, 2009). But every method has some advantages and disadvantages. Physical methods are not cost effective and efficient (Karachalios, 2012).

Biological treatments have certain limitations, because this process is controlled by microorganism metabolic activity, which is influenced by environmental conditions, especially temperature. (Clark et al., 2005). Chemical precipitation generates huge amount of sludge during and post phosphate removal processes, such as separation, squeezing. To combat this side effect, sludge disposal is required (Loganathan et al., 2014). Among these, adsorption has been considered as the best option for the removal of phosphate from wastewater. Because the operation and maintenance process are simple and cost effective with high removal efficiency. This process is also environmentally friendly due to less sludge generation and low energy consumption. Moreover, it is the best technology to remove and recover phosphate from wastewater (Park et al., 2015; Lin et al., 2017).

3. Adsorption process for phosphate removal

Adsorption is defined as the accumulation of a substance at the interface between two phases such as solid and liquid or solid and gas. The substance that accumulates at the interface is called 'adsorbate' and the solid surface on which adsorption occurs is 'adsorbent'. Adsorption process occurs at the surface of the solids due to the unbalanced forces of attraction. If the adsorption happens due to weak Van der Waals forces, it is called physical adsorption. If the process is governed by chemical bonding between adsorbent and adsorbate molecule then adsorption is referred as chemisorption (Bhatnagar et al., 2010). There are diverse range of materials are used as adsorbents for the phosphate removal like, clay-based adsorbents (Othman et al., 2018), carbon alike materials (Gisi et al., 2016), metal-based materials (Zhang et al., 2017; Lin et al., 2019;) and chitosan (Xu, 2020).

Biomaterials used in adsorbent preparation are gaining interest because they are frequently biodegradable, renewable, and less toxic. Using biomass wastes for this purpose also has the advantage of ensuring agricultural waste management. (Bacelo et al., 2020). Still regeneration of phosphate from wastewater as fertilizer is an important matter for environmental sustainability. Research on the phosphate recovery using low-cost material is going on. So, it is necessary to find efficient, low cost and ecofriendly material to recover phosphorus as an alternative of the chemical fertilizer.

4. Biochar as an adsorbent

At the present time biochar has achieved the popularity as a potential adsorbent for pollutant remediation because of high efficiency, low cost, environment friendly, excellent stability, high porosity, easy preparation, and operation (Tan et al., 2015; Jeong et al., 2016). Commercial activated carbon also very effective as adsorbent but not cost effective.

Biochars are carbon-rich products produced from biomass using pyrolysis process at the temperatures below 700°C under the oxygen-limited condition (Lehmann, 2007; Zhang et al., 2011; Zheng et al., 2013). Sometime activation process has been performed in the presence of oxygen in the furnace chamber (Parez et al., 2020). This modification of the condition decreases the carbon content and positive charge of the biochar as well as concurrently increase in negative charges, oxygen content, and contents of carboxylic and phenolic functional groups (Ramola et al., 2014). The properties and functions of those biochar are highly depending on the feedstock materials and production condition (Zhang et al., 2015a).

A broad range of materials were used as a bio adsorbent such as sugarcane bagasse (Ramola et al. 2014), Soybean milk residues (okara) (Nguyen et al. 2013), Sawdust (li et al. 2018), Bamboo (Isa et al.,2016) and micro algae (Jung et al., 2016) etc. Biochar contains negative surface charge can adsorb cationic pollutants like heavy metal (Kılıç et al.,2013) and dye (Liao et al., 2012).

Pure carbon adsorbents are not efficient for phosphate adsorption due to its negative surface charge (Li et al., 2017, 2018a). To improve the phosphate adsorption capacity of the biochar researchers are searching for different methods such as, (i) cationization (e.g. metal loading, grafting with ammonium type chemicals), (ii) anionization (e.g. surface coating with sulphate), (iii) activation (e.g. thermal, chemical and steam activation) (Nguyen et al., 2014). Impregnation of exogenous metal elements into biomass through the pyrolysis under oxygen-limited condition is known as cationization process (Li et al., 2018a, 2018b; Vikrant et al., 2018). Some metal elements (Al, Fe, etc) incorporated in biomass to produced metal-based biochar show excellent adsorption of anionic pollutants (Loganathan et al., 2014).

Metal cations such as Ca^{2+}, Al^{3+}, Fe^{3+}, and La^{3+} have strong affinity for phosphate, which can significantly improve the phosphate adsorption performance of biochar (Haghseresht et al., 2009; Huang et al., 2015; Yang et al., 2014; Yin et al., 2016). However, Al^{3+}, Fe^{3+}, and La^{3+} can be released in aqueous solution under redox or acidic conditions and have toxic effects on aquatic environment and organisms (Mitrogiannis et al., 2017; Haghseresht et al., 2009).

Different calcium containing clay minerals, such as attapulgite (Kim et al., 2018), sepiolite (Yin et al., 2011, 2013), goethite (Li and Stanforth, 2000), bauxite (Altundoğan and Tümen, 2003), and dolomite (Karaca et al., 2004) have phosphate removal efficiency and nontoxic characteristic. But these are expensive.

5. Eggshell as an adsorbent

Eggshell contains calcite which is about 11% of the total egg weight (Meski et al., 2011; Oliveira et al., 2013). Every year globally eight million tons of eggshell waste has been generated and disposed as solid waste which is a big environmental concern because of creating unpleasant smell and microbial contamination (De Angelis et al., 2017). According to European Union (EU) regulations, the eggshell is a hazardous waste due to its abundance which imposes high disposal costs for the food industry (P´erez et al., 2020).

Due to the presence of $CaCO_3$, the sorption capacity of eggshell has been attracted by researchers for removal of organic (dye) (Elkady et al., 2011), inorganic (heavy metal) (Pettinato et al., 2015) pollutants and anions (nitrate, phosphate) (Ahmad et al., 2018; Photiou et al., 2021) in wastewater. Eggshell is also used as a soil amendment material (Margarida et al., 2017). It has been found that during adsorption process calcined eggshell react with phosphate and the calcined waste could not be reused because of the irreversible nature of the chemical reaction. That's why P containing eggshell possess high potentiality to use as fertilizer on agricultural field (K€ose and Kıvanç, 2011).

5.1 Raw and thermally modified Eggshell

Thermally modified eggshell has been produced using calcination process (Tangboriboon et al., 2012; Köse and Kıvanc, 2011; Torit et al., 2019; Yirong and Vaurs, 2019; Santos et al., 2019; Lee et al., 2022). Köse and Kıvanc (2011) found that calcination of the eggshell start from the 600 °C and fully calcined at 800 °C temperature. During calcination process $CaCO_3$ convert into CaO due to the higher temperature and form calcium hydroxide $Ca(OH)_2$ at longer calcination time at 900°C for 3 h due to the reactive moisture adsorption (Tangboriboon et al., 2012; Panagiotou et al., 2018). Calcined eggshell contain CaO or $Ca(OH)_2$ would adsorb more phosphate than raw eggshell powder with high content of $CaCO_3$ (Krogstad et al. 2005). Because of the high solubility of $Ca(OH)_2$ and CaO in solution could lead to the formation of $Ca_5(PO_4)_3(OH)$ and $CaHPO_4$ crystals generated by Ca-P precipitation (Yin et al., 2014).

5.2 Chemically modified eggshell

Eggshell modified with metal salt like Al, Mg, and Fe salts and hydroxides has been proven as good adsorbent. Iron hydroxide-eggshell (Mezenner et al., 2009), Al-eggshell (Guo et al., 2017; Zhang et al., 2017), Mg-eggshell (Ahmed et al., 2017), $FeCl_3$ eggshell (Xu et al., 2018), hydroxyl-Eggshell (Ribeiro et al., 2020; Almeida, et al. 2020) have been investigated and shown effectiveness for phosphate adsorption.

Before modification with metal salt and hydroxide, eggshells were cleaned and dried in oven at 100°C /105°C (Zhang et al., 2017; Guo et al., 2017; Xu et al., 2018). After that eggshell powder was immersed in 100 ml solution of $AlCl_3$ (0.29 mol/l) for 24 h with stirring speed 150 rpm at 30°C to equilibrium. Then, the particles were centrifuged and dried, screened through a sieve of 100 mesh, and subsequently used for sorption experiments (Zhang et al. 2017). Iron hydroxide-eggshell was prepared by mixing the eggshell and $FeCl_3$, $2H_2O$ (Mezenner et al., 2009; Xu et al., 2018).

5.3 Biochar with eggshell

Biochar modified with eggshell is gaining attraction because of the effective phosphate removal efficiency. Moreover, P loaded biochar could be a potential source of fertilizer. Agricultural waste-based biochar with eggshell is a low cost and ecofriendly adsorbent to treat the eutrophication problem of the waterbody (Marschner et al., 2013). Pyrolyzed eggshell with rice husk (Liu et al., 2019), palm fiber (P´erez et al., 2020), rape straw (Cao et al., 2020), tobacco stalks (He et al., 2020), sugarcane bagasse (Liao et al., 2022), Palm mesocarp fiber (Pérez et al., 2022), and potato peels (Quisperima et al 2022) were investigated as adsorbent for phosphate removal. Calcium modified biochar was prepared at high temperature under N_2

atmosphere because eggshell starts decomposition at 650°C and is completely decomposed at 800°C (Shen et al., 2018). Liu et al. (2019) suggested that eggshell modified rice straw showed good phosphate adsorption capacity and produce high amount of hydroxyapatite precipitate (HAP) on its surface or within the pores after the adsorption of phosphate. After phosphate adsorption eggshell modified rice straw rich in P, which is a necessary nutrient for plant growth. Applying it as a fertilizer to the soil can play a dual role in improving soil physical properties and increasing soil P content.

For present study, “bamboo” was used for biochar and eggshell was used as a calcium source. Bamboo is a common and available source of biomass in Asian countries. The benefit of using bamboo is after pyrolysis at high temperature it produces high density and porous structure compared to wood biochar, which enhances adsorption capacity (Zhao et al., 2008). There are over 90 genera of bamboo with more than 1200 species which occupies more than 14 million ha land of the world. Among them 80 % of all bamboo species and forests are found in South and Southeast Asia, including China, India, and Myanmar (FAO, 2007). Therefore, it is an available and cheap material to produce biochar.

6. Characterization of the adsorbent

After pyrolysis process the adsorbent material shows different physical properties and chemical compositions than the raw materials. The surface area, pore size and pore volume has been increased after addition of eggshell (Liu et al., 2019). The ratio of eggshell and fiber, temperature may affect the properties of the adsorbent materials (P´erez et al., 2020). Due to the high temperature of the calcination and pyrolysis process $CaCO_3$ of the eggshell has been changed into $CaO-Ca(OH)_2$ (Santos et al., 2019). Phosphate adsorption can be identified by the FTIR SEM, and EDX analysis. The crystal formation of phosphate on the surface of the adsorbent and disappearance of the pore space can be seen from the SEM image before and after adsorption (Liu et al., 2019; P´erez et al., 2020; Cao et al., 2020). SEM analysis showed that morphology of eggshell modified biochar has been changed after pyrolysis process. Eggshell containing biochar has broaden pores which form when $CaCO_3$ of eggshell is thermally decomposed into CO_2 during calcination process. After phosphate adsorption, pores replaced with large amounts of flocculent precipitates (Liu et al., 2019). He et al. 2020, found that Mg modified eggshell and biochar has rough surface. The surface roughness of eggshell and Mg doped biochar was also increased with granulation and macroporous structure. The presence of MgO in Mg doped biochar produces a sharp peak 459 cm^{-1} and Mg(OH)$_2$ in eggshell/Mg doped biochar produce absorption peak around 3700 cm^{-1} in FTIR analysis. And the peak appeared at 1420 cm^{-1} and 878 cm^{-1} were attributed to the vibration of CO_3^{2-} molecules. From FTIR analysis it was found that only biochar is not effective for phosphate adsorption. But for eggshell and biochar 1:1 ratio, a strong and narrow -OH stretching vibration band appears at 3641 cm^{-1} and a new stretching vibration band can also be observed at 871cm^{-1} which disappeared after phosphate adsorption. The peak appeared at 1024 cm^{-1} after the adsorption by eggshell and biochar 1:1 indicated the phosphate stretching vibration band (Liu et al., 2019; P´erez et al., 2020).

7. Adsorption Isotherm

Adsorption process of phosphate depends on the different condition that control the adsorption such as initial concentration of the adsorbate solution. The adsorption process is monolayer, or multilayer can be identified by the Langmuir model and Freundlich model. Langmuir model describes the monolayer adsorption due to precipitation and hydrogen bonding acting forces, and Freundlich model represents multi-layer adsorption process caused by Van der Waals adsorption, electrostatic attraction, etc. (Kong et al., 2018; Wang et al., 2018). From literature it has been found that the eggshell modified biochar data were better fitted by Langmuir model indicating monolayer adsorption (Table 1).

Calcined biochar shows lower adsorption capacity than the calcined eggshell and biochar mixture because of absence in active metal in the biochar (Liu et al., 2019; Cao et al., 2020). Cao et al. (2020) experimented calcined bio char, eggshell modified biochar and calcium modified biochar. Where eggshell modified biochar showed higher equilibrium adsorption amount than calcium modified biochar (109.7 mg g^{-1} and 101.0 mg g^{-1}, respectively) because eggshell contains nitrogen- rich organic matter (e.g., protein), which form hydrogen bonding and positive charge adsorption sites (Zhang et al., 2015b; Yamazaki et al., 2016).

8. Thermodynamic Study

Liu et al. (2019) found from the thermodynamic analysis that the adsorption is a endothermic reaction where phosphate spontaneously react with CaO/Ca(OH)$_2$. If the temperature of the reaction increases the phosphate adsorption capacity also increases. He et al. (2020) found that phosphorous adsorption capacity decrease with increasing temperature indicates the exothermic reaction. The ambient temperature should not be too high or too low at 100–500 mg P L^{-1} and 25 °C is the optimal temperature for the adsorption by eggshell modified tobacco. For high concentration, there is a large amount of P, and the increase of temperature intensifies the thermal movement of molecules and increases the probability of collision between phosphate and the active sites of EM-C24(Ca-Mg-Biochar), thus improving the adsorption effect. However, temperature changes disrupt thermal and chemical balance, causing dissolution/precipitation reactions to move (He et al., 2020). Excessive high temperature is not conducive to exothermic adsorption and will cause the precipitation dissolution equilibrium reaction related to chemical adsorption to move towards the dissolution direction and thus reducing the adsorption effect.

9. Adsorption kinetics

Adsorption kinetics indicates the rate of the adsorption. Adsorption kinetics can be analyzed using Pseudo first order model and Pseudo second order model. Pseudo first order model indicates the adsorption reaction is controlled by the diffusion process and Pseudo second order model indicates the adsorption reaction is controlled by the chemical adsorption process. In Chemical adsorption process the adsorbent and the adsorbate exchange or share electrons to form new compounds (Lalley et al., 2016). Table 2 shows that the eggshell and biochar-based adsorbent better fitted the Pseudo second order model which indicates the chemisorption. Liu et al. (2019) found that within 2 h fast adsorption rate was identified after that the reaction rate became slow, then adsorption equilibrium was obtained within about 6 h for all E-C and BC samples. The reason of the fast initial reaction is rapid diffusion of ions from the solution to the external adsorbent surfaces, then the slower adsorption process was explained by internal porous diffusion (Zhao et al., 2011). Since the active adsorption site of the eggshell modified biochar has increased so the diffusion process also changed into chemical sorption process. Adsorption process of only biochar is a physical adsorption process governed by a weak Van der Waals interaction (Cao et al., 2020).

10. Effects of other parameters on adsorption process

pH has a great influence on the adsorption reaction. Because the form of the phosphate varies due to the changes of the pH, while the functional group of the surface of the adsorbent also changes. The ionization constant of phosphoric acid is affected by pH of the point of zero charge (pHpzc) indicating the pH where surface charge is zero. When the reaction occurs below the pHpzc then the phosphate adsorbed by adsorbent by electrostatic attraction. The solution pH above the pHpzc creates negative charge on the surface of adsorbent from eggshell modified biochar which chemically reacts with phosphate (Liu et al., 2019; P´erez et al., 2020). Eggshell modified palm fiber showed 100 % of P removal when pH is above 10 (P´erez et al., 2020). Mg-loaded tobacco stalk biochar showed good adsorption capacity under acidic condition. In the range of pH 3-5 the phosphate adsorption capacity was 235.8–237.8 mg P g^{-1}. The adsorption capacity was decreased in alkaline condition. The first reason of this phenomenon is dissociation constant. Phosphate has three pK value such as 2.14, 7.20 and 12.37 at 25°C (Bacelo, et al., 2020). When the pH of the solution about 5.5 and 10, $H_2PO_4^-$ and HPO_4^{2-} the predominant species. When pH is greater than 12.7 then PO_4^{3-} is the predominant species (Choi et al., 2019). When pH increases $H_2PO_4^-$ is change into HPO_4^{2-} is more difficult to be adsorbed because of higher adsorption energy. That's why the adsorption capacity decreases (Li et al., 2017; Zhang et al., 2020). The second reason is that the increase of the pH value of the solution changes the degree of protonation and deprotonation which affect the electrostatic adsorption. And finally, the OH^- in the solution will compete with the phosphate ion for active adsorption sites under high pH conditions (He et al., 2020).

Wastewater contains different anions which may compete with phosphate to occupy the active site of the adsorbent. Phosphate adsorption capacity was experimented with co-existing ion NO_3^-, HCO_3^-, SO_4^{2-} and Cl^-. The anions NO_3^- and Cl^- had limited effect on the adsorption process of phosphate, even in the case of high ion concentrations up to 1 mol L^{-1} for Cl^-, the adsorption amount of phosphate remained at a high level. On the other hand, HCO_3^-, SO_4^{2-} had significant negative effect on the adsorption of phosphate on the E-C material, because they can combine with Ca^{2+} to form insoluble or poorly soluble substances to reduce the active sites on the surface of E-C 1:1(Liu et al., 2019). He et al. (2020) also found that the presence of Cl^- and CO_3^{2-} had no effect on the removal efficiency of phosphate for Eggshell modified biochar. In case of NO_3^- , removal of phosphate was increased. It has been found that SO_4^{2-} leads to the reduction of the phosphate removal efficiency of EM-C24 (Ca-Mg-Biochar).

11. Comparative study

Raw eggshell/ calcined eggshell, biochar modified eggshell and chemically modified eggshell was used by several researcher. Maximum adsorption capacity and removal efficiency has been represented as a comparative study on adsorption capacity of different types of eggshell based adsorbent in Table 3.

12. Desorption

Desorption is the inverse of the adsorption where adsorbate separates from the adsorbent substrate (Havlík 2008). Desorption study of the phosphate has been carried out to find the reusability of the adsorbent after adsorption. It is also important to understand the solubility of the phosphate in water and plant availability (Haddad et al., 2018). There are some desorption processes like thermal desorption and chemical desorption. Some chemicals are soluble in water at low pH or high pH. Desorption process depends on the types of the chemicals and their molecular bond. Phosphorus fertilizer solubility is necessary to understand the P availability for the plant. The solubility of the P fertilizer has been investigated in water, week acid and strong acid condition. Different types of organic fertilizer are used as P fertilizer like, compost, animal residue, meat and bone meal, sewage sludge and vegetable residue (Kratz et al., 2010). To understand the chemical equivalence of this fertilizer to the commercial mineral fertilizer different types of extraction method are used by researchers such as neutral ammonium citrate (NAC), Iron bag, $NaHCO_3$ and H_2O extractions method which are very effective for P extraction (Duboc et al., 2022).

13. Objective of this research

The main objective of this research is to investigate the feasibility of using Bamboo char and eggshell ash to remove phosphorus from wastewater and the applicability of phosphate containing materials as a fertilizer. The aims of this study are to prevent eutrophication of surface water by removing phosphate nutrient using natural, cost effective, ecofriendly material which is an alternative use of the agricultural waste materials. Moreover, recovery of the phosphate is beneficiary for agricultural application as fertilizer.

The objectives of the study are

1. Preparation of the adsorbent material from bamboo and eggshell powder using calcination process at high temperature and different mixing ratio.
2. Investigate the phosphate adsorption capacity and mechanism of the adsorbent materials prepared from bamboo and eggshell powder using adsorption isotherm,

kinetic, and thermodynamics study. Determine the characterization of the adsorbent before and after phosphorus adsorption process by the SEM image, FTIR analysis and XRD analysis.

3. Examine the effects of pH, adsorbent dose, adsorbent ratio, co-existing anions, and organic acids on the phosphate removal process.
4. Evaluate the desorption of the phosphate from adsorbent material and the application of P loaded material as a fertilizer in lab scale.

14. Thesis content

This study is organized into 4 sections

First chapter is general introduction which explain the importance of phosphate removal from wastewater, different types of phosphate removal methods, significance of using adsorption process and using natural waste material as an adsorbent for phosphate removal. Different types of modification process of eggshell to improve the adsorption efficiency.

Second chapter is Effects of the different mixing ratio of Bamboo char and eggshell powder on phosphorus adsorption mechanism: Adsorption isotherm and thermodynamics analysis.

In this chapter effects of initial concentration, temperature adsorbent dose, bamboo and eggshell ratio was described because these factors may affect the phosphate removal process. Adsorption mechanism was identified using adsorption isotherm (Langmuir and Freundlich isotherm model) and thermodynamic study. Adsorption nature was calculated using Langmuir separation factor. Adsorbent characteristic before and after phosphorus adsorption process was analyzed using FTIR (Fourier Transform Infrared Spectroscopy) analysis, SEM (Scanning Electron Microscope) image and EDX (Energy Dispersive X-ray spectroscopy) analysis

Third chapter is Adsorption kinetic study and influence of the pH, anions and organic matter on phosphate removal using calcined eggshell and bamboo char as adsorbent.

Where effects of time, pH, co-existing anions, and organic acids were explained. Adsorption kinetic was analyzed using Pseudo first order kinetic model and Pseudo second order kinetic model which is important to understand the adsorption mechanism. Implementation of BE 1:1 for the phosphate removal from the natural water and treated water was performed. Organic phosphorus removal efficiency of BE 1:1 was tested. Then the cost of the adsorbent preparation was estimated.

Forth chapter is Desorption study and effectiveness of the recovered phosphate after adsorption using eggshell derived bamboo char as fertilizer.

In this chapter desorption study using water extraction and Neutral Ammonium Citrate (NAC) was elucidated. After phosphorus recovery using bamboo+ eggshell 1:1 P adsorbed material was used as fertilizer and the effectiveness was illustrated in this chapter.

Table 1. Adsorption isotherm

Adsorbent	Conditions	Langmuir model			Freundlich model			Reference
		KL (L mg^{-1})	qmax (mg g^{-1})	R^2	KF (mg$^{(1-1/n)}$L$^{1/n}$g^{-1})	1/n	R^2	
EC 2:1	Calcined at 800 °C Dose: 0.01 g; Temperature: 25 °C; Time: 24 h; pH: 7	3.88	204	0.992	109	0.149	0.764	Liu et al., 2019
EC 1:1		3.74	231	0.984	122	0.152	0.752	
EC1:2		5.75	159	0.979	87.1	0.141	0.802	
EC 1:4		8.06	96.4	0.999	59.6	0.112	0.748	
BC		0.0885	5.58	0.969	1.64	0.248	0.905	
RS	0.05 g sorbent, (Initial con., 10−200mgP/L, 180 rpm 25 ± 0.5 °C for 24 h.	0.0175	3.101	0.9199	0.2156	2.1290	0.8552	Cao et al., 2020
ERS		67.3	103.9	0.9624	92.49	28.6287	0.6447	
CRS		19.41	96.56	0.9629	80.3	17.9921	0.84843	
ESF-1:10	20 mg adsorbent, Initial Conc. 5 ppm, stirring at 200 rpm (2h).	-	-	0.999	-	-	0.919	P´erez et al., 2020
M-C1	Calcined at 700°C for 2h Modified with $MgCl_2$	0.125	110.62	0.754	25.46	0.27	0.688	He et al., 2020
M-C2		0.078	206.68	0.923	34.84	0.35	0.890	
M-C3		0.099	272.37	0.850	42.30	0.41	0.812	
EM-C24		0.095	210.66	0.923	39.69	0.33	0.838	

Table 2: Adsorption kinetics of calcined eggshell and biochar

Adsorbent	Conditions	Pseudo first order model			Pseudo second order model			Reference
		K (h^{-1})	qe (mg g^{-1})	R^2	k_2 (g mg^{-1} h^{-1})	qe (mg g^{-1})	R^2	
EC 2:1	Calcined at 800 for 2h Dosage: 0.01 g; Temperature: 25 °C; Time: 24 h; pH= 7	10.5	191	0.962	0.124	196	0.983	Liu et al., 2019
EC 1:1		15.1	221	0.966	0.224	224	0.994	
EC1:2		3.46	153	0.958	0.0352	159	0.973	
EC 1:4		6.586	74.7	0.952	0.0104	81.7	0.976	
BC		1.26	5.21	0.985	0.311	5.53	0.958	
RS	0.05 g sorbent, (Initial Conc., 10−200mgP/L, 180 rpm 25 ± 0.5 °C for 24 h.	0.1417	2.173	0.8728	0.03895	2.958	0.8646	Cao et al., 2020
ERS		2.266	104.7	0.9961	0.03646	109.7	0.9906	
CRS		2.06	96.7	0.9961	0.03726	101	0.9972	
ESF-1:10	20 mg adsorbent, Initial Con. 5 ppm, stirring at 200 rpm (2h).	-	-	0.9484	-	-	0.9996	P´erez et al., 2020
M-C1	Calcined at 700 for 2h Modified with MgCl$_2$	0.46	100.35	0.926	0.0195	98.19	0.934	He et al., 2020
M-C2		0.36	196.27	0.963	0.0039	209.32	0.976	
M-C3		0.72	234.99	0.95	0.0065	245.11	0.980	
EM-C24		0.46	239.58	0.965	0.0019	271.82	0.986	

Table 3: Comparative adsorption capacity of the different types of eggshell based adsorbent

Adsorbent	P Adsorption Capacity (mg/g)	P Removal efficiency	Reference
Calcined waste eggshell	23.02	99%	Kose et al., 2011
Calcined eggshell	-	99.06 %	Tangboriboon et al., 2012
Calcined eggshell	2	-	Borhade et al., 2017
Calcined waste eggshells	-	92%	Panagiotou et al., 2018
Eggshell ash	121	90%	Torit et al 2018
Salted Calcined eggshell	3.32 ± 0.06	96.2%	Yirong et al 2019
Calcined eggshell	108.2	-	Lee et al., 2022
Eggshell and Rice straw	231	-	Liu et al., 2019
Eggshell and Rape Straw	109.7	-	Cao et al., 2020
Eggshell and Palm fiber pyrolyzed	72.0	83 %	P´erez et al., 2020
Tobacco stalks, mg, and eggshell	270	98.10%	He et al., 2020
Sugarcane bagasse and eggshell	251.16	-	Liao et al., 2022
Palm mesocarp fiber and eggshell	134	-	Pérez et al., 2022
Potato peels and eggshell	174.8	85.96%	Quisperima et al 2022
Iron Hydroxide-Eggshell	69.5	50%	Almeida et al., 2020
Magnesiothermal eggshell	43.33	100%	Mezenner et al., 2009
Aluminum-modified eggshell	6.22	-	Ahmad et al., 2017
Al-Eggshell	11.52	99.06%	Gao et al., 2017
$FeCl_3$-eggshell	3.95	99.13%	Xu et al., 2018
Iron oxyhydroxide-eggshell	328.9	-	Zhang et al., 2017

CHAPTER 2

Effects of the different mixing ratio of bamboo char and eggshell powder on phosphate adsorption mechanism: Adsorption isotherm and thermodynamics analysis.

This section is partially based on manuscript:

“Thermally modified bamboo-eggshell adsorbent for phosphate recovery and its sustainable application as fertilizer” by Sarker, P., X. Liu, N. Hata, H. Takeshita, H. Miyamura and M. Maruo published on Environmental Research (2023).

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1. Introduction

Phosphorus is a nonrenewable resource which is an essential growth nutrient for plant and aquatic algae. The main source of phosphorus fertilizer is the phosphorus rock that is depleting so fast that after few decades later future generation will face the crisis of phosphorus (Hong et al., 2020). On the other hand, eutrophication is major water pollution caused by excessive release of phosphate as nutrient from sewage effluent and agricultural runoff (Xia, et al., 2020). Phosphate released in water could be recovered and utilized as phosphate fertilizer to combat severe water pollution and meet fertilizer demand (Kumari et al., 2020).

Although physical, chemical, and biological processes are effective for phosphate removal, each process has some drawbacks, such as expensive materials and maintenance costs. (Bacelo et al., 2020). Adsorption has been used as an attractive alternative method to treat phosphorus-containing wastewater, which is easy to operate, and effective (Bacelo et al., 2020; Veni et al., 2017). Traditional adsorbents such as activated carbon and artificial organic resin polymer, as well as new type nano-adsorbents, have been found to be effective in phosphate adsorptive recovery. (Kumar et al., 2017; You et al., 2018; Zong, 2013), but these materials are not cost effective and have the disposal problem after adsorption (Nguyen et al., 2014).

Removal of phosphate using different metals like Ca, La, Mg, Mn, Fe, and Al oxides hybrid carbon composites had been introduced before. In some cases, the phosphorus adsorbed material could not be used as fertilizer because of the presence of heavy metal in modified adsorbent (Haghseresht et al., 2009; Huang et al., 2015; Yang et al., 2014; Yin et al., 2016). As a result, researchers are searching for a low-cost and environment friendly adsorbent material for phosphate recovery (Veni et al., 2017). Different types of agricultural waste material have been used effectively as adsorbents for phosphate removal (Bacelo et al., 2020).

That's the reason why the current study is planning to recover the phosphate from wastewater using a most convenient procedure and locally available biowaste materials. Bamboo and eggshells are available natural ingredients which was not used for phosphate recovery before. Bamboo is a common, cheap, and readily available source of biomass in Asian countries. There are over 90 genera of bamboo and more than 1200 species, which occupy more than 14 million ha land worldwide. Eighty percent of bamboo species and forests are found in South and Southeast Asia, including China, India, and Myanmar (Lobovikov et al., 2007). Compared with other types of biochar, such as wood, bamboo produces a high-density porous structure after pyrolysis and increases adsorption capacity which is a benefit of using bamboo as biochar

(Zhao et al., 2008). Since bamboo char is the source of carbon and eggshells contain $CaCO_3$ could be used as a metal cation which has great affinity for phosphate. Moreover, calcium is not toxic (Quina et al., 2017). Since pure biochar is not effective for the phosphate removal, the combination of pure biochar with calcium could be a good adsorbing material to recover phosphate as fertilizer (Liu et al., 2019).

Adsorption isotherm study and thermodynamic analysis is very important to reveal the adsorption mechanism. Adsorption isotherm is very important to calculate whether the reaction is monolayer or multilayer adsorption. Adsorption isotherm constant is necessary to calculate Langmuir separation factor to understand whether the adsorption nature is favorable or unfavorable (Borhade et al., 2017). Thermodynamic analysis dictates the effects of temperature on adsorption process, reaction spontaneity from Gibbs free energy (negative ΔG° indicate spontaneous reaction), and enthalpy indicates the total energy available to do work, whether the reaction is exothermic (positive enthalpy) and endothermic (negative enthalpy) nature. Some adsorption process uptake heat energy from the environment and some reaction release heat energy (Kalaitzidou et al., 2022). Entropy describes the degree of disorder and randomness of the motion of the adsorbed molecules, and its level. Enthalpy-entropy evaluate sorption reactions (physical and chemical phenomena) and the nature of the interactions between the solute and solvent to cause the reactions, and that the relationship between the enthalpy and entropy for a specific reaction is linear (Trazzi et al., 2016).

In this study, calcined eggshell powder and different mixing ratios of bamboo and eggshell at different calcination temperatures were investigated to prepare adsorbent. Then the differences in the chemical structure of the adsorbent materials after calcination and after adsorption, were identified by the FTIR, SEM Image, and EDX analysis. Then the adsorption mechanism was examined by the adsorption isotherm model and the thermodynamics analysis. Langmuir separation factor (R_L) was also calculated to understand the adsorption nature.

2. Materials and Methodology

2.1 Preparation of working solution

Working solutions of potassium dihydrogen phosphate (KH_2PO_4) for experiments was prepared by diluting the phosphate stock solution of 10 PO_4-P g/L with distilled water. Different initial concentrations of phosphate solution (5, 10, 25, 50, 100, and 150 PO_4-P mg/L) were prepared from the stock solution of 10 PO_4-P g/L.

2.2 Preparation of adsorbent

Bamboo (*Phyllostachys bambusoides*) powder was collected from the Kentomu Co., Shiga, Japan, and was oven dried at 105 °C for 24 h, then sieved through a meshes sieve (pore size: 0.3 mm) before use. Eggshell was collected from the cafeteria of The University of Shiga Prefecture, Japan. Eggshell was washed several times with tap water and then was rinsed 3 times with MQW. It was oven dried as same as the bamboo to remove moisture content (Wang et al 2010). After the treatment, dried eggshell was grounded by mortar, and was passed through the same mesh sieve as that used for bamboo. 20 g mixture of bamboo and eggshell powder was taken for calcination. To evaluate the effect of calcination temperature on eggshell decomposition from $CaCO_3$ to CaO, each sample was placed in a muffle furnace under three temperatures (600, 700 and 800 °C) for 2 h, respectively. Previous study showed that the eggshell can be completely decomposed at 800 °C (Shen et al., 2018). Then, the calcined materials were preserved in desiccator. Calcined bamboo mixed eggshell was denoted as BE; calcined eggshell as CE, and only bamboo char (BC) was also prepared. To investigate the optimal adsorption capacity of mixture of bamboo char and eggshell, different mass ratio was tested, i.e., BE 1:1, BE 2:1 and BE 10:1 at 800 °C, respectively.

2.3 Adsorption experiments

All the adsorption experiments were performed as batch experiments. Adsorbent material (0.01 g) was placed in a 50 mL polyethylene tube containing a P solution (40 mL) at pH 7, and the polyethylene tubes were agitated (220 rpm) at 25 °C. The suspension was filtered through 0.45 μm cellulose acetate filter paper (C045A047A, ADVANTEC, Japan) and the P concentration was determined by spectrophotometer (U-2000A, Hitachi, Japan) at the wavelength of 880 nm using molybdenum blue method with ascorbic acid as the reductant (Murphy and Riley, 1977).

2.4 Phosphate measurement procedure

Phosphate was measured using molybdenum blue method with ascorbic acid by spectrophotometer (U-2000A, Hitachi, Japan).

- Chemicals:
  1. Conc. H_2SO_4 70 mL+500 mL MQ water
  2. $K(SbO)C_4H_4O_6 \cdot 1/2\ H_2O$ (1.3715 g) + 500 mL MQ water
  3. $(NH_4)\ Mo_7O_{24} \cdot 4H_2O$ (20 g) + 500 mL MQ water
  4. Ascorbic acid: 1.76 g of Ascorbic acid dissolved into 100 mL of MQ water.

- Standard solution of P for the calibration curve:

0.1361 g of KH_2PO_4 was dissolved into water and adjusted the volume at 250 mL. This stock solution contains 4000 µmol/L (4 mmol/L) of P was stored in a plastic bottle in a fridge. From this stock solution, working standard solutions of 40, 20, 10, and 5 PO_4-P µmol/L were prepared in 100 mL volumetric flask.

- Working reagent preparation for phosphate measurement:

50 mL of 2.5 mol/L H_2SO_4, 5 mL of $K(SbO)C_4H_4O_6 \cdot 1/2\ H_2O$, 15 mL $(NH_4)\ Mo_7O_{24} \cdot 4H_2O$ (20 g) and 30 mL ascorbic acid solutions were mixed to prepare working solution for phosphate measurement.

Phosphate determination process:

- 8 mL of sample was taken into 10 mL of test tube, 1.6 mL of working reagent was added, then 0.4 mL of water was added and mixed well.
- After 10 min, absorbance was measured using spectrophotometer at 880 nm with quartz cell of 10 mm pathlength. Absorbance measurement should be completed within 30 min after addition of working reagent.
- Calibration carve (linier regression) was prepared in the same manner for the determination.

2.5 Phosphate adsorption capacity

The adsorption capacity (Qe, mg/g) of the sorbent material for P was calculated by mass balance as expressed in Eq. (1).

$$Q_e = \frac{V(C_0 - C_e)}{m} \text{............................}(1)$$

Where, C_0 and Ce are the initial and equilibrium concentration of phosphate in solution (mg/L), respectively; V is the volume of solution (L), and m is the adsorbent mass (g).

2.6 Adsorption Isotherm and thermodynamic analysis

Adsorption Isotherm

Adsorption isotherm was investigated by altering the initial P concentrations (0, 5, 10, 25, 50, 100, and 150 mg/L). The adsorptions were performed at 25 °C, pH 7, agitation speed at 220 rpm for 24 h using 0.01 g of BE 1:1 (800°C), BE 2:1 and CE (0.01 g) as an adsorbent. Experimental data sets were fitted with the Langmuir and Freundlich isotherm models. R Studio software was used for the isotherm models curve fitting (R Core Team 2021).

Langmuir models describe the monolayer adsorption on the homogenous surface of the adsorbent, where no interaction occurs between phosphate ion and the adsorbent surface (Habiby et al., 2019). Langmuir equation can be written as:

$Q_e = Q_{max}bCe/(1 + bCe)$ …………………………(2)

where, Q_{max} represents the maximum adsorption capacity (mg/g). The Q_e is the amount of P adsorbed per gram of adsorbent at equilibrium state, b is the Langmuir constant which is related to the amount of adsorption energy (L/g). b and Q_{max} are calculated by plotting Q_e versus C_e, where the b is the slope and the Q_{max} is the intercept of the linear Langmuir model.

The Freundlich isotherm model describes the multi-layer adsorption on heterogeneous surfaces with non-uniform energy distribution overactive binding sites of the adsorbent (Abbasi, 2017).

$\mathrm{Qe} = K_f C_e^{(1/n)}$ ………………….(3)

where, K_f represents the Freundlich affinity coefficient ($mg^{(1-n)}L^n/g$), The Q_e is the amount of P adsorbed per gram of adsorbent at equilibrium state, C_e is the equilibrium solution concentration (mg/ L) of the sorbate, and n is the Freundlich linearity constant which is related to heterogeneity of the surface. n is the adsorption intensity. If n = 1, the partition between the two phases is independent of the concentration. If the value of 1/n is below 1, it indicates a normal adsorption. On the other hand, 1/n higher than 1 indicates cooperative adsorption (Borhade et al., 2017).

Thermodynamic analysis

To examine the effect of temperature on phosphate adsorption, 0.01 g of adsorbent BE 1:1 and BE 2:1 was added in a polyethylene tube containing 40 mL of phosphate solution with different initial concentrations (0, 5, 10, 25, 50, 100, and 150 PO_4-P mg/L). Different initial concentrations were prepared from 10 PO_4-P g/L stock solution. The experiments were divided into three groups, each of which oscillated for 24 h at three different temperatures of 25 °C, 35 °C, and 45 °C, respectively. After the oscillation, the mixed solution was filtered and the phosphate concentration in the filtrate was analyzed. All experiments were performed triplicate.

2.7 Adsorbent dose

Optimum adsorbent dose was investigated by adding three different amounts (0.01 g, 0.05 g, and 0.1 g) of adsorbent of different BE ratio (CE, BE 1:1, BE 2:1, and BE 10:1) in 40 mL of phosphate solution of 100 PO_4-P mg/L. Then the solution was agitated at 200 rpm at pH 7, 25 °C temperature for 24 h. After filtration final phosphate concentration was measured. All experiments were performed triplicate.

2.8 Characterization

The morphological changes of the adsorbent before and after adsorption was analyzed by using Miniscope TM3030, (Hitachi, Japan) Scanning Electron Microscope (SEM) (Figure 1a). Fourier transform infrared spectrometer (FTIR) spectra were observed by FT/IR-4100 (JASCO, Japan) (Figure 1b) to investigate the presence of the functional group after calcination and adsorption process. EDX or energy dispersive X-ray spectrometry was analyzed for the elemental composition of the P adsorbed material by X-ray microanalyzer EMAX-7000 with Scanning Electron Microscope S-3200 N (Hitachi, Japan).

3. Result and discussion

3.1 Adsorption isotherm

The Adsorption Isotherm model curve for the CE and BE adsorbent has been shown in Figure 2 which indicates that the phosphate adsorption capacity was enhanced with increasing initial concentration of the solution. The experimental data were fitted by the Langmuir model, where R^2 value is higher than the Freundlich model and similar result was obtained by Köse and Kıvanc et al. (2011). Langmuir model describes the monolayer adsorption on the homogenous surface of the adsorbent (Habiby et al., 2019). From adsorption isotherm study, maximum P adsorption capacity (Q_{max}) values were found 95.14 and 98.40 PO_4-P mg/g for the BE 1:1 and BE 2:1 ratio respectively, compared to that in CE (68.77 mg/g) (Table 1). That means after addition of bamboo char the adsorption capacity of eggshell was increased. May be the addition of biochar increases the surface area of the adsorbent and the calcium from eggshell creates the metal modified biochar which is suitable for phosphate adsorption (Liu et al., 2019; P´erez et al., 2020; He et al.,2020). Whereas the lowest Q_{max} (24.26 PO_4-P mg/g) was obtained for BE 10:1 adsorbent which indicates addition of excess amount of biochar (BE 10:1) was not effective for phosphate adsorption. Similar result was found by Liu et al. (2019), who explained this condition because of presence of less or no active site availability in adsorbent (Liu et al., 2019).

The high values of constant b and K_f indicates that the affinity between adsorbent and adsorbate was good for the reaction. When the value of n (Freundlich linearity constant) is greater than 2, it also indicates that temperature has effects on phosphate adsorption capacity and $1/n$ was <1, indicating natural adsorption (Guo et al 2017; Ahmed et al., 2017; Borhade et al., 2017).

3.2 Effects of Temperature

The temperature has a significant effect on the phosphate adsorption capacity. At different temperatures the Langmuir model also showed that maximum phosphate adsorption capacity (Q_{max}) varies with temperature changes (Table 2). Thermodynamic analysis was calculated at different temperatures. Effects of temperature were experimented with BE 1:1 and BE 2:1 adsorbent material. After increasing temperature to 308K the adsorption capacity was decreased from 298 K temperature, then it was increased to 318K temperature (Table 2).

Effects of temperature on phosphate adsorption process were observed for thermodynamic analysis. Thermodynamic parameters describe the changes of the energy during adsorption process. From the thermodynamic equation (4) and (5), $\Delta G°$ (KJ/mol) was calculated. $\Delta S°$

(J/mol·K) and ΔH° (KJ/mol) was obtained from the intercept and slop of the linear plot of ΔG° against temperature T (K) (Figure 3) (Liu et al., 2019). Thermodynamic equation has been given bellow:

$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$........................(4)

where, ΔG° was Gibbs free energy, ΔS° was Entropy, and ΔH° was enthalpy.

$\Delta G^{\circ} = -RT \ln b$......................(5)

where, R was the universal gas constant (8.314 J/mol·K), T was temperature (K), *b* is the Langmuir adsorption constant (L/mg) (Yu et al., 2020).

In case of BE 1:1 and BE 2:1 adsorbent, adsorption reaction was not spontaneous ($\Delta G > 0$) at 298 K, (Table 2). The spontaneity of the reaction was increased with increasing reaction temperature, but the maximum adsorption capacity was decreased to 308 K temperature then increased again to 318 K temperature. Negative enthalpy indicates the exothermic reaction (Zhu et al., 2018; Abdelhay et al., 2018) and in an exothermic adsorption reaction, the high temperature decreases the phosphate adsorption capacity (Habiby et al., 2019). Positive entropy of the system means high randomness of the adsorbate and adsorbent in liquid solution (Liu et al., 2019).

Langmuir separation factor

Langmuir separation factor (R_L) calculates the adsorption nature which can be identified by the following equation (6) (Ajenifuja et al., 2017):

$R_L = \frac{1}{1+bC_0}$.............................(6)

where b is the Langmuir adsorption constant, and C_0 is the initial P concentration (mg/L).

According to the present experiment the R_L value (Table 2) was found between 0 to 1 which indicates favorable adsorption conditions for phosphate at different reaction temperatures and initial concentrations. When the initial concentration was 0, R_L value was 1 indicating linear adsorption (Table 3).

3.3 Effects of adsorbent amount

To find out the optimum dose of the adsorbent, different adsorbent amounts were used during the experiment. Different mixing ratios of bamboo and eggshell were tried to find effective adsorbent. Calcined eggshell powder and BE mixtures were found effective for phosphate removal. From Figure 4 it has been seen that the phosphate adsorption capacity decreased after adding more amount of adsorbent. high phosphate adsorption capacity was found 102.16 mg/g for 0.01 g adsorbent of BE 1:1 ratio. After addition of more doses of adsorbent the removal efficiency decreases because of less contact between phosphate ions and per unit mass of the adsorbents that means more unoccupied active sites did not take part in the adsorption process (Dragan et al., 2014). Additionally, repulsive force between active sites might slow down the reaction process (Torit et al., 2018) that's why in the present study, 0.01 g has been chosen as the optimum dose for highest phosphate removal capacity. Which may reduce unnecessary adsorbent use and cost.

3.4 Characterization

3.4.1 SEM Image and EDX spectrum

The SEM images showed morphological differences before and after P adsorption. Figures 5 and 6 show an identical difference between calcined eggshell and the BE 1:1 because of the addition of bamboo fiber. And after adsorption there were some accumulations of the precipitant on the surface of the adsorbent (Liu et al., 2019).

Figure 6 shows the changes of the SEM image of calcined BE 2:1 and BE 10:1 before and after adsorption, where the structure of the adsorbents was fiber like, because of the presence of more bamboo char (He et al., 2020). After adsorption in the SEM image of BE 10:1, no accumulations have been noticed. EDX spectrum (Figure 7 and 8) of the BE 1:1 and BE 2:1 after adsorption illustrated the presence of phosphate after adsorption and the distribution of the oxygen, calcium, and phosphate in the adsorbent material. From Figure 7 it has been seen that the green color image of calcium (Figure 7b) is more intense than yellow color image of phosphate (Figure 7a), which indicate there are some vacant active sites remaining in the material. Figure 8 also illustrates the similar results for BE 2:1. Therefore, the characterization of the material before and after adsorption confirmed that the mixture of bamboo and eggshell could adsorb phosphate from wastewater.

3.4.2 FTIR analysis

The FTIR spectrum was analyzed on FTIR spectrometer (FT/IR-4100, JASCO, Japan) in the range of 4000–400 cm^{-1}. Figure 9 (a) and (b) show FTIR spectrum within 4000–400 cm^{-1} wavenumber range for CE and BE 2:1 respectively, at different temperature 600°C, 700°C, and 800°C. The absorption peaks were observed at 1750.06 cm^{-1}, 1411.89 cm^{-1}, and 871cm^{-1} before calcination, and this fact confirmed the presence of $CaCO_3$ (Borhade et al., 2017).

From Figure 9 (a) and (b) it can be observed that eggshell calcined at 600°C contain peak at 1750.06 cm^{-1}, 1411.89 cm^{-1}, and 871cm^{-1}. That meant at 600°C $CaCO_3$ was present in the CE powder (Borhade et al., 2017), but at 700°C, 800°C the peak at about 710 cm^{-1} attributed to the presence of CaO (Torit et al. 2018). For BE 2:1 sample calcination starts at 600°C. Similar band was seen for BE 2:1 calcined at 600°C which indicate that after mixing bamboo powder with eggshell calcination process need lower temperature than only eggshell powder. After calcination the intensity of the band for $CaCO_3$ decreases. Both bands at 710 cm^{-1} and 871cm^{-1} are absent in only BC (bamboo char) samples (Figure 9 c).

This modification process is suitable for phosphate adsorption (Torit et al., 2018). From Figure 10, it can be seen the changes of the FTIR spectra after the adsorption process. A clear new band at 1024 cm^{-1} was observed after phosphate adsorption on BE 1:1 which was not visible before adsorption. Only calcined eggshell also shows small stretch for phosphate adsorption but BE1:1 shows deep band at 1024 cm^{-1} (Liu et al., 2019).

4. Summary

Modification of biochar with eggshell using calcination process is effective for P removal. From adsorption isotherm study, maximum phosphate adsorption capacity for the CE, BE 1:1 and BE 2:1 was found 68.77 and 95.14 and 98.40 mg/g at 25 °C respectively. The experimental data for the CE, BE 1:1 and BE 2:1 adsorbent was better fitted by the Langmuir model, where R^2 value is higher than the Freundlich model. That means addition of bamboo powder enhances the phosphate adsorption capacity where excess addition of biochar (BE 10:1) was not efficient for phosphate adsorption.

Thermodynamic study was performed for different initial concentration at 25 °C, 35 °C, and 45 °C temperature. Then the thermodynamic study Langmuir separation factor (R_L) was calculated.

For BE 1:1 and BE 2:1 ratio the reaction was not spontaneous at 298 K. The spontaneity of the reaction increased with increasing reaction temperature. Negative ΔH indicate the process is exothermic, and Positive entropy of the system means the randomness of the adsorbate and adsorbent in liquid solution increases. and the calculated Langmuir separation factor (R_L) indicates the favorable conditions for phosphate adsorption. After using three different doses (0.01g, 0.05g and 0.1g) of the adsorbent of different mixing ratio, 0.01g doses of BE 1:1 and BE 2:1 was found better than other doses and mixing ratio. Maximum phosphate adsorption capacity was found 102.16 PO_4-P mg/g for 0.01g doses of BE 1:1.

Adsorbent materials were prepared mixing eggshell and bamboo powder in different mixing ratio and different calcination temperatures were tried. After calcination the characterization of the materials was performed by SEM image, EDX analysis and FTIR analysis. After calcination at 600°C, 700°C, and 800°C temperature, FTIR band of CE and BE 2:1 shows difference in the formation of CaO and $CaCO_3$. The presence of stretching band at 871cm^{-1} indicates the formation of the -OH group after calcination process. Both bands at 710 cm^{-1} and 871cm^{-1} are absent in only bamboo char sample and after adsorption process, they are almost disappeared. A clear new band at 1021 cm^{-1} was observed after phosphate adsorption on BE 1:1 which was not visible before adsorption. Only calcined eggshell also shows small stretch for phosphate adsorption. But BE 1:1 shows deep band at 1024 cm^{-1}. SEM image also found difference between before and after adsorption adsorbent image. There is some aggregation of precipitate was noticed after adsorption. EDX analysis detects the presence of phosphate after adsorption in adsorbed material. From the experiment it has been confirmed that the mixing ratio of the bamboo and eggshell powder has influence on the adsorption process. So, it is necessary to study more about adsorbent preparation and adsorption isotherm and thermodynamic for different adsorbent material to find most effective adsorbent for phosphate removal.

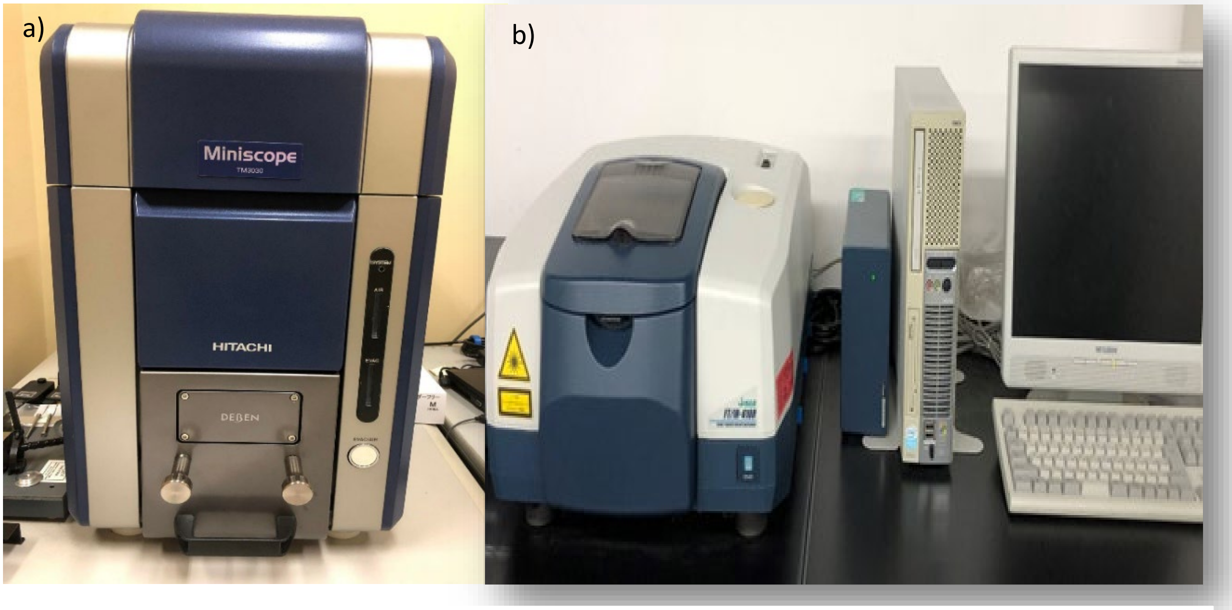

Figure 1: a) Scanning Electron Microscope (SEM). b) FTIR spectrometer

Table 1: Fitting parameters of the adsorption isotherm equilibrium for phosphate onto CE and various BE (1:1, 2:1, 10:1) samples.

	Langmuir model			Freundlich model		
Adsorbents	Q_{max} (PO_4-P mg/g)	b (L/mg)	R^2	K_f ($mg^{(1-1/n)}L^{1/n}/g$)	n	R^2
CE	68.77	0.412	0.794	43.11	9.994	0.777
BE 1:1	95.13	0.438	0.857	60.27	9.994	0.838
BE 2:1	98.40	0.041	0.920	10.94	2.350	0.819
BE 10:1	24.26	−0.180	0.464	26.07	9.994	0.094

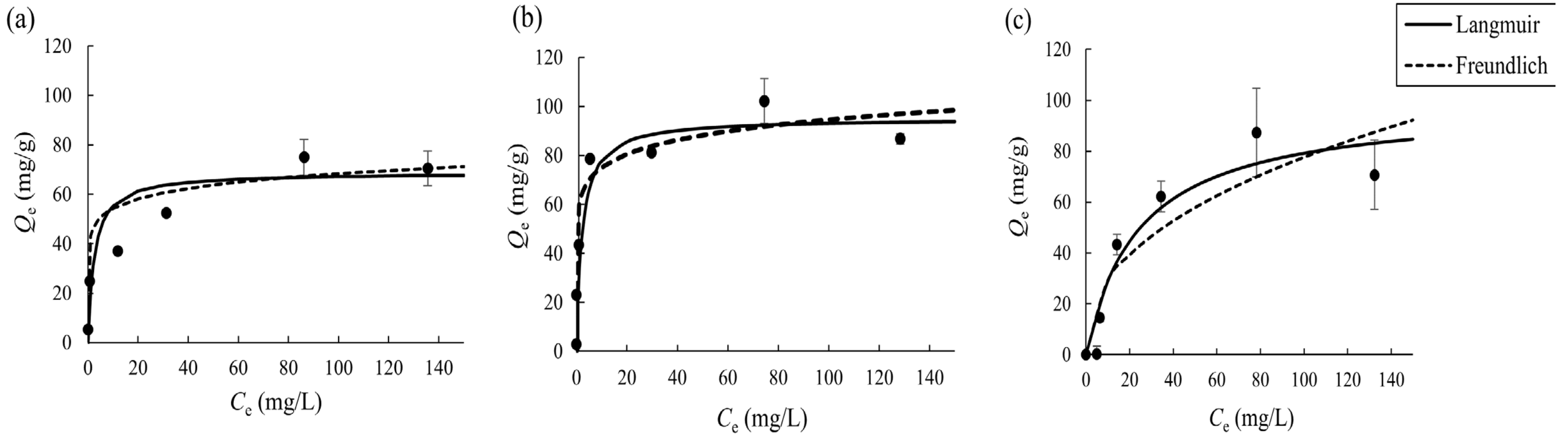

Figure 2: Adsorption isotherms of phosphate with different forms on (a) CE, (b) BE 1:1, (c) BE 2:1. The *solid* and *dashed* lines indicated the fitted Langmuir and Freundlich model, respectively. Error bar indicates standard deviation.

Table 2: Thermodynamic parameters and Langmuir separation factor for the adsorption of phosphate in different adsorbents (BE 1:1, BE 2:1).

Adsorbents	T (K)	Q_{max} (mg/g)	R_L	ΔG (KJ/mol)	ΔS (J/mol.K)	ΔH (KJ/mol)
BE 1:1	298	95.13	0.31-0.01	1.98	363.56	-0.116
	308	87.17	0.16-0.006	-0.08		
	318	112.16	0.15-0.006	-0.34		
EE 2:1	298	98.40	0.83-0.14	7.91	305.73	-0.997
	308	65.14	0.07-0.002	-2.53		
	318	76.85	0.002-7.05E-05	-12.03		

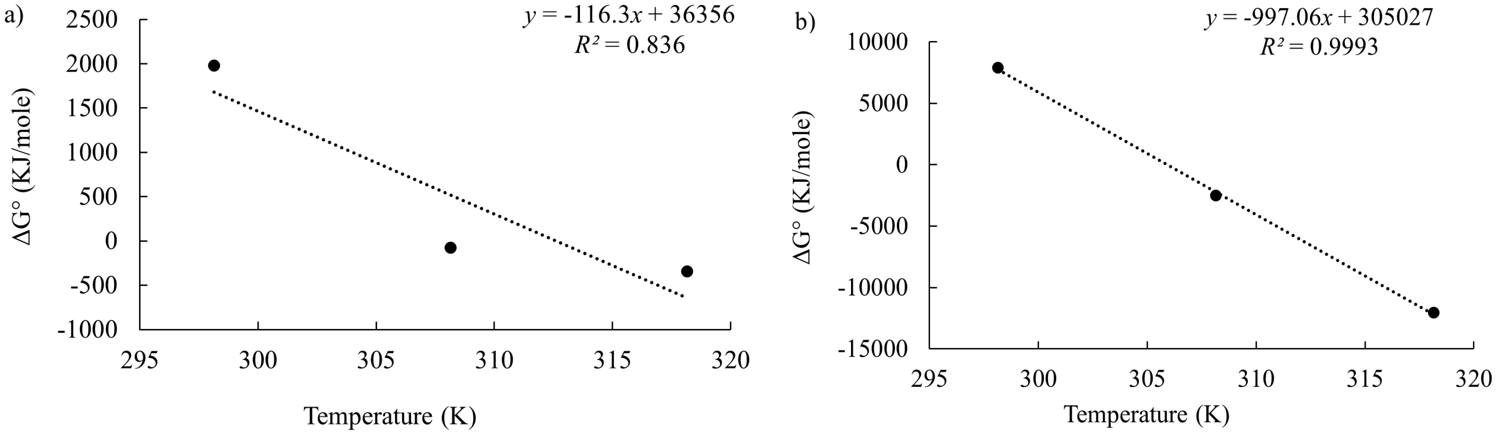

Figure 3: Linear regression of ΔG (KJ/mol) against Temperature (T), where slope ΔS (J/mol·K) and ΔH (KJ/mol) was obtained from the intercept and slop, a) BE 1:1 as adsorbent b) BE 2:1 as adsorbent.

Table 3: Adsorption nature (Langmuir separation factor)

R_L	Adsorption nature
($R_L > 1$)	Unfavorable
($0 < R_L < 1$)	Favorable
($R_L = 1$)	Linear
($R_L < 0$)	Irreversible

(Zhu et al., 2018, Ahmed et al., 2017)

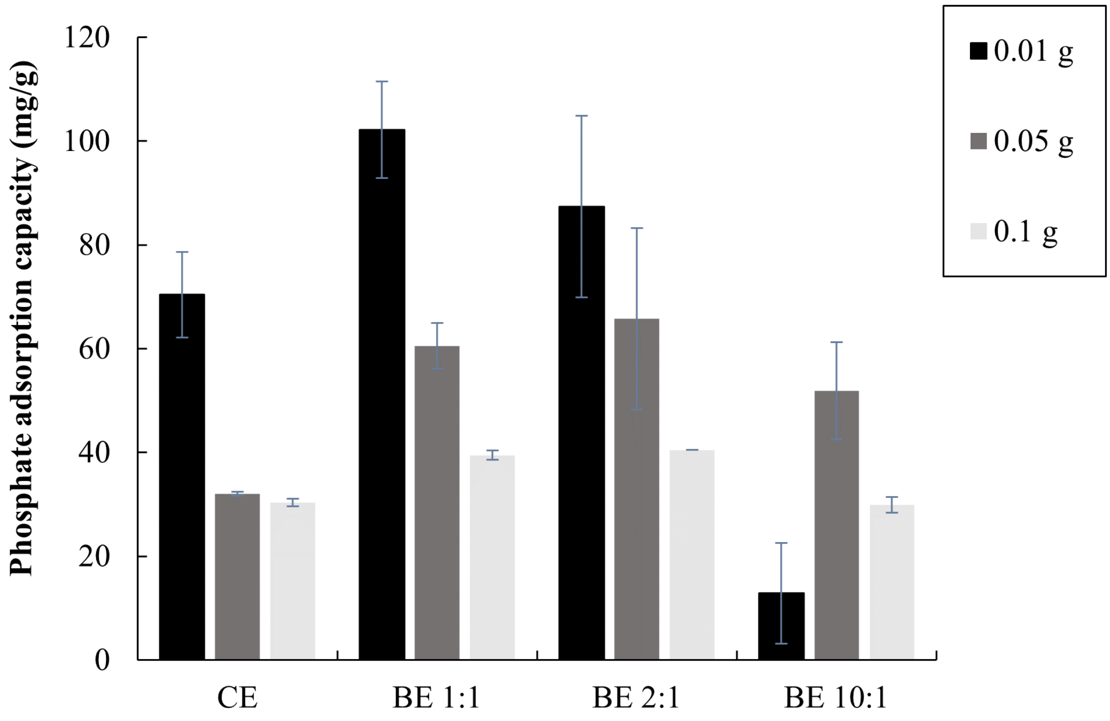

Figure 4: Phosphate (P) adsorption capacity of different adsorbent materials (CE, BE 1:1, BE 2:1, BE 10:1) for different adsorbent amount (0.01, 0.05, 0.1 g) (pH: 7; Initial P concentration: 100 mg/L; Temperature: 25 ºC; Time: 24 h). Error bar indicates standard deviation.

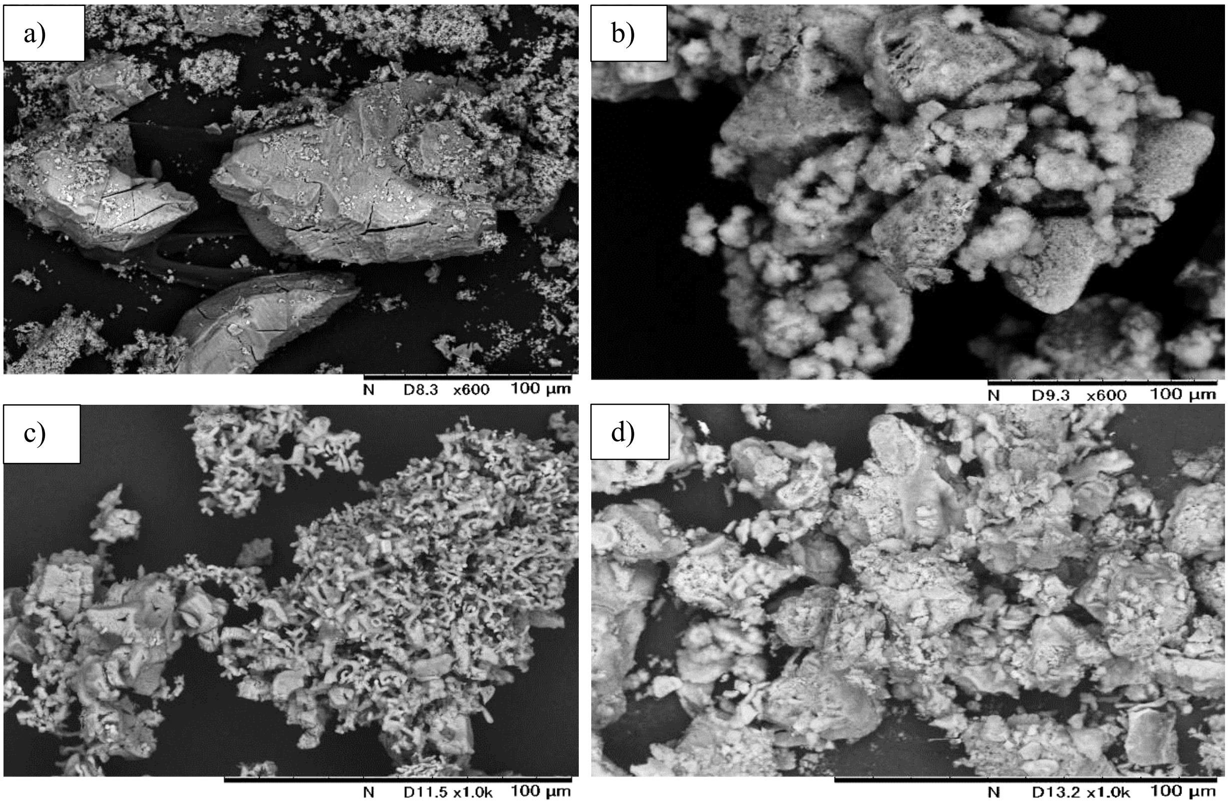

Figure 5: SEM images of CE (a, b) and BE 1:1(c, d) before and after adsorption

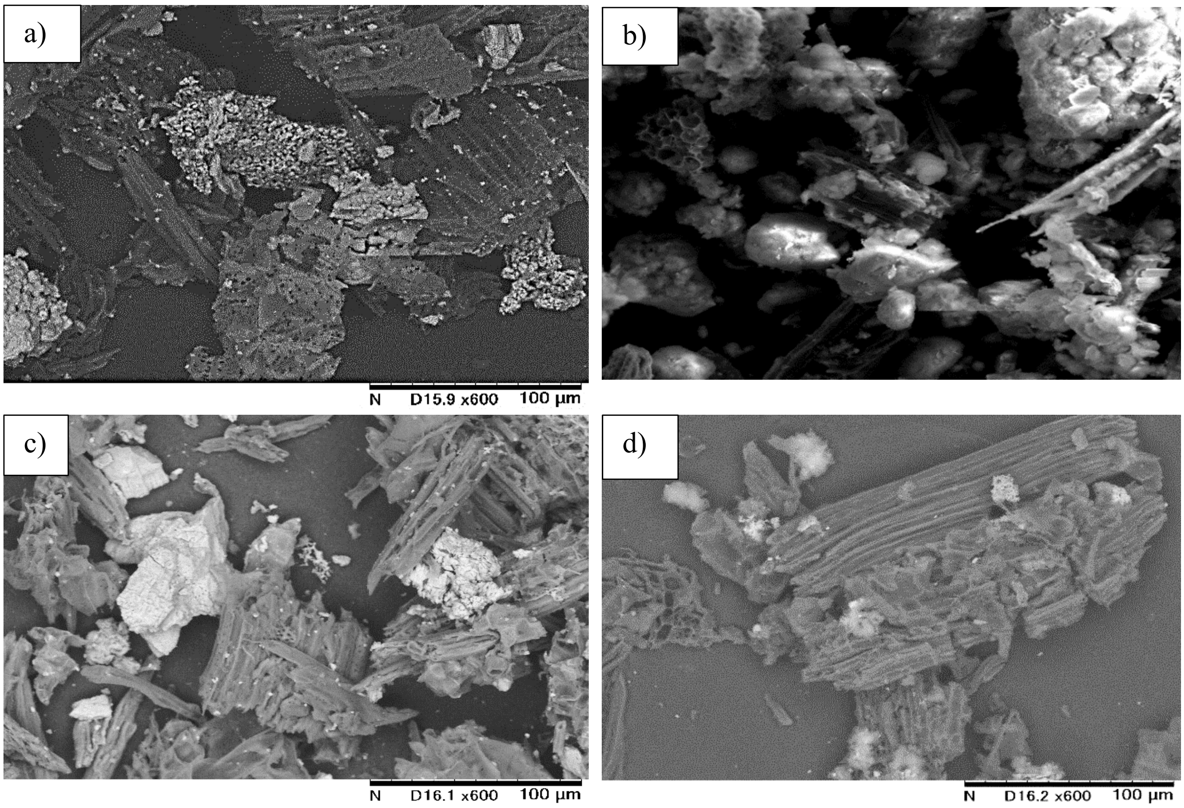

Figure 6: SEM images of calcined BE 2:1 (a, b) and BE 10:1 (c, d) before and after adsorption

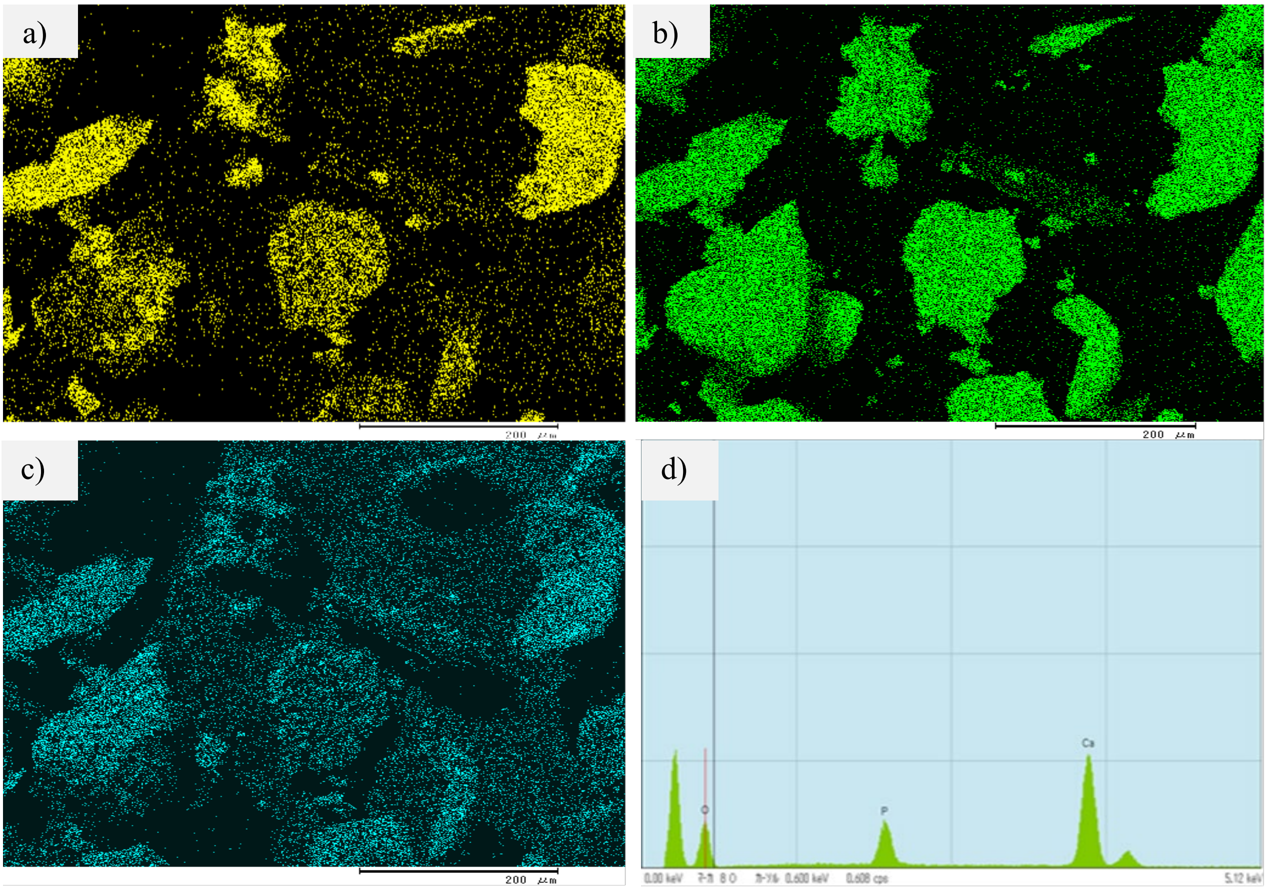

Figure 7: EDX spectrum of distribution of the a) Phosphate b) Calcium c) Oxygen d) EDX spectrum mapping for elemental composition of BE 1:1 after adsorption.

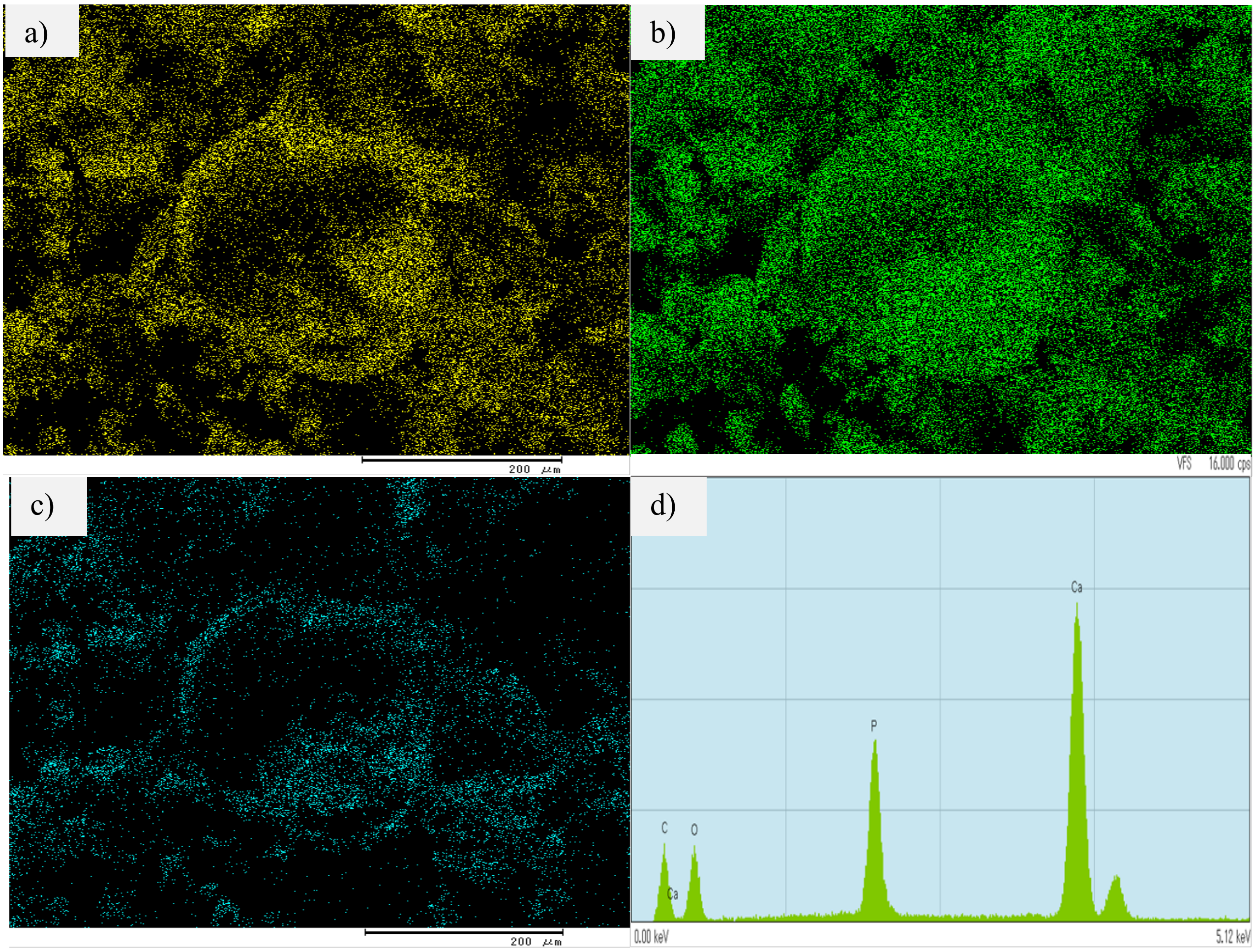

Figure 8: EDX spectrum of distribution of the a) Phosphate b) Calcium c) Oxygen d) EDX spectrum mapping for elemental composition of BE 2:1 after adsorption.

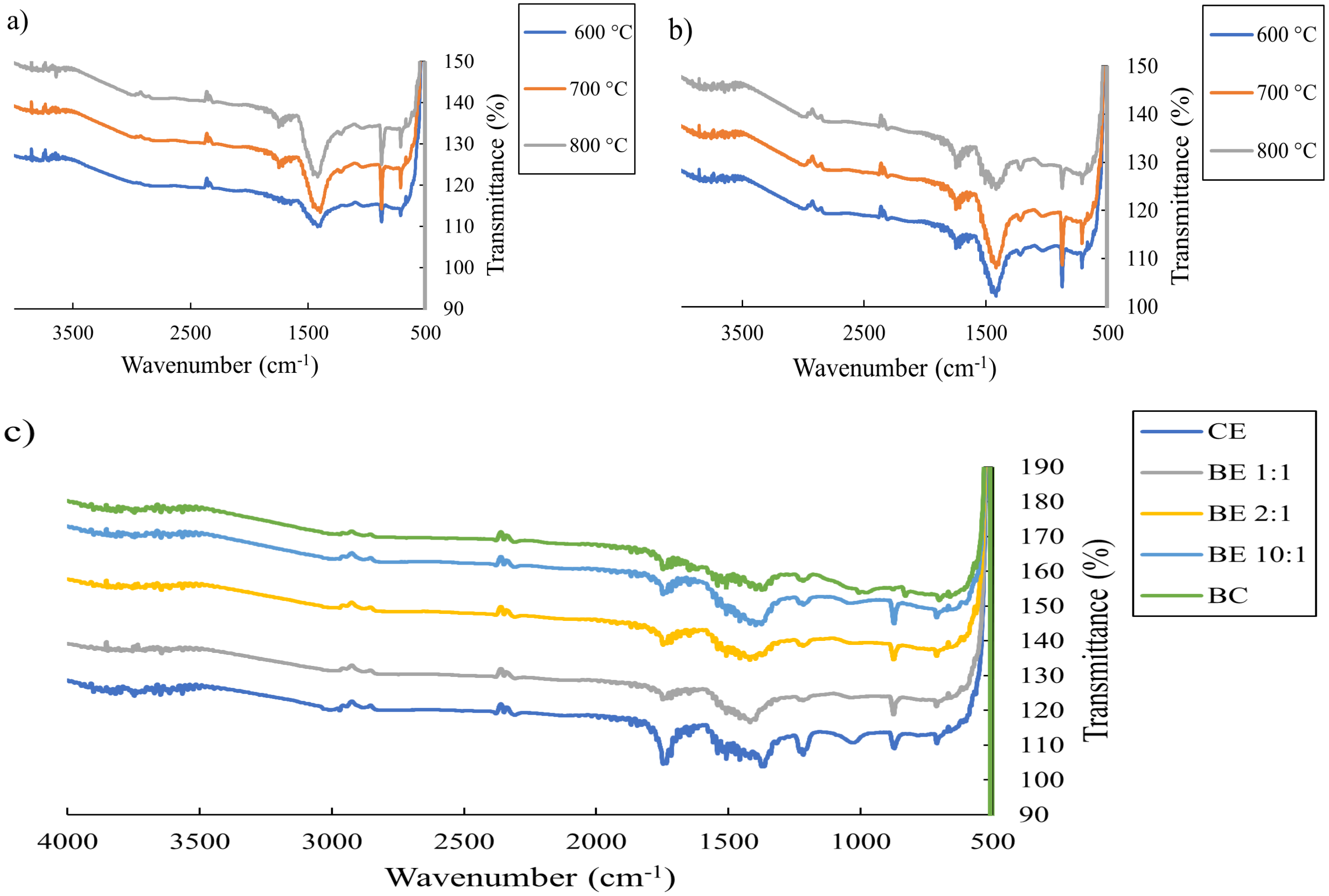

Figure 9: FTIR analysis of (a) CE and (b) BE 2:1 at 600, 700, and 800 °C, respectively, and (c) BE 1:1, BE 2:1, BE 10:1, and CE and BC at 800 °C.

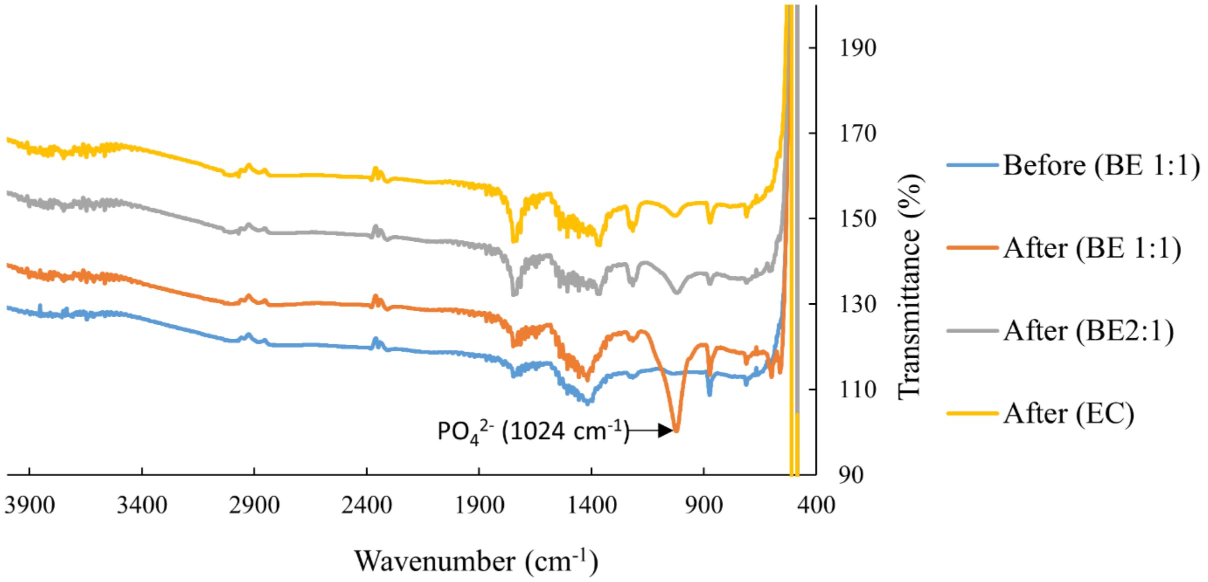

Figure 10. FTIR spectra for BE 1:1 before and after adsorption, BE 2:1 and CE after adsorptio

CHAPTER 3

Adsorption kinetic study and influence of the pH, anions, and organic matter on phosphate removal using calcined eggshell and bamboo char as adsorbent.

This section is partially based on manuscript:

"Thermally modified bamboo-eggshell adsorbent for phosphate recovery and its sustainable application as fertilizer" by Sarker, P., X. Liu, N. Hata, H. Takeshita, H. Miyamura and M. Maruo published on Environmental Research (2023).

https://doi.org/10.1016/j.envres.2023.115992

1. Introduction

Nowadays, eutrophication is a global environmental problem which is the most popular topic for researchers (Charlton et al., 2018). Anthropogenically, huge amount of phosphorus discharges into waterbody as agricultural runoff and synthetic detergent in domestic wastewater. But when the excessive amount of phosphorus goes into waterbody, it works as a nutrient for aquatic plants and algae and causes eutrophication (George et al., 2017). So, the recovery of phosphate from this source will be beneficiary for us. Among different phosphate removal technologies, adsorption is a very convenient process because several natural materials were used effectively as an adsorbent after different types of modification (Nguyen et al., 2014). Different researchers used agricultural waste-based biochar with eggshell as a low cost and ecofriendly adsorbent to treat the eutrophication problem of the waterbody (Zhou et al., 2021). Pyrolyzed eggshell with rice husk (Liu et al., 2019), palm fiber (P´erez et al., 2020), rape straw (Cao et al., 2020) and tobacco stalks (He et al., 2020) was investigated as adsorbent for phosphate removal.

The present study emphasized on using natural ingredient for phosphorus removal. Bamboo powder was used as carbon source and eggshell was used as calcium carbonate source. Pure biochar has a negative charge on the surface, which is suitable for removing heavy metals and organic pollutants (Ramola et al., 2014; Yang et al., 2016), That's why, some modification is necessary to increase adsorption capacity for negatively charged pollutants like phosphate (Nguyen et al., 2014). Phosphate adsorption process might be controlled by physical adsorption or chemical adsorption. This mechanism could be identified by the adsorption kinetics models. Adsorption kinetic models are very useful to understand the phosphate adsorption process and reaction rate, and from the results of modeling, we can know whether the adsorption process is controlled by physical adsorption or chemical adsorption mechanism (Borhade et al., 2017). Pseudo first order model indicates the adsorption reaction is controlled by the diffusion process and Pseudo second order model indicates the adsorption reaction is controlled by the chemical adsorption process. In chemical adsorption process, the adsorbent and the adsorbate exchange or share electrons to form new compounds (Lalley et al., 2016).

From literature, it was found that the eggshell and biochar-based adsorbent better fitted the pseudo second order model which indicates the chemisorption (Liu et al., 2019; P´erez et al., 2020; He et al., 2020). Liu et al. (2019) found that adsorption rate was fast within 2 h after that the reaction rate became slow, then adsorption equilibrium was obtained within about 6 h for all CE and BC samples. The reason for the fast initial reaction is rapid diffusion of ions from the solution to the external adsorbent surfaces, then the slower adsorption process was explained by internal porous diffusion (Zhao et al., 2011). Since the active adsorption site of the eggshell modified biochar has increased so the diffusion process also changed into chemical sorption process. Adsorption process of only biochar is a physical adsorption process governed by a weak Van der Waals interaction (Cao et al., 2020).

Adsorption process has been influenced by the different factors such as, pH and presence of co-existing anions (Kalaitzidou et al., 2022). pH is an important parameter which influences the phosphate adsorption procedure in several ways. The dissolved form of phosphate in water is dependent on the pH of solution. Phosphate has three different ionic stages at different pH. When pH of the solution is in the range 2.15 - 7.20, the dominant form of phosphate is $H_2PO_4^-$ (pK_{a1} as H_3PO_4: 2.15, and pK_{a2} as $H_2PO_4^-$: 7.20), in the pH range 7.20 -12.33, HPO_4^{2-} is dominant, and pH above pK_{a3}: 12.33, PO_4^{3-} becomes dominant (Mitrogiannis et al., 2017). pH below 2 and pH above 7 are not suitable for phosphate adsorption (Pandi et al., 2021).

The surface charge of the adsorbent is also affected by the pH of the solution and point of zero charge (pH_{pzc}) of the adsorbent. Surface charge of the adsorbent affects phosphate adsorption capacity. For eggshell modified biochar, pH above the pH_{pzc} creates negative charge on the surface of adsorbent which causes chemical interaction among phosphate and active site of the adsorbent (Liu et al., 2019; P´erez et al., 2020).

Natural water and wastewater may contain different types of anions and organic matter. Both waters contain chloride, bicarbonate, sulfate, and presence of these anions influences the phosphate removal efficiency because of competitive nature (Pandi et al., 2021). Domestic wastewater also contains a high concentration of nitrate and sulfate ions. Quisperima et al. (2022) used Ca-bio composites for P adsorption from real domestic water and found 91.6% removal efficiency for P removal, 53.8% removal efficiency for NO_3^{-} removal but SO_4^{2-} adsorption capacity was very low.

Dissolved organic acid may affect phosphate removal efficiency after interacting with calcium of the adsorbent material (Alsherbi et al., 2022). To understand the influence of organic matter on phosphate adsorption, it is important to examine the phosphate removal efficiency in the presence of other dissolved organic matter.

Some organic phosphorus from agricultural runoff (organo-phosphorus herbicide) and pharmaceutical wastewater also causes serious water pollution (Shushkova et al., 2016; Jiang et al., 2019). Glyphosate [*N*-(phosphonomethyl)-glycine] is a worldwide used organophosphate herbicide which contains three polar functional groups (-NH, -COOH and -PO_3H_2) (Rissouli et al., 2017). It is commonly applied to control unwanted vegetation, weeds, and grasses (He et al. 2019). But excessive amounts of pesticide and herbicide changes soil microbial community composition and ecosystems and reduces crop tolerance (Sen et al., 2019), so it is harmful for the environment.

When glyphosate enter natural water system through the agricultural runoff, it causes water pollution, and it may work as a source of phosphate for some microorganisms by utilizing C-P lyase (Shushkova et al., 2016).

If glyphosate enters the bloodstream through the stomach and the skin cause acute and sublethal and chronic toxic effect, which can be in the nerve paralysis and death of living beings (Vera et al, 2010). Moreover, it has teratogenesis, carcinogenesis, mutagenesis effects on human health (Ramrakhiani et al., 2019). It is necessary to remove glyphosate from wastewater using an effective, economic and environment friendly method.

The objectives of this study were (1) to understand the phosphate adsorption mechanism using Pseudo first order kinetic model and pseudo second order kinetic model for calcined eggshell powder and bamboo + eggshell adsorbent, (2) to examine the effects of pH and different anions such as, Cl^{-}, NO_3^{-}, CO_3^{2-}, and SO_4^{2-} on phosphorus removal capacity and the influence of different organic acids, such as citric acid, humic acid, and oxalic acid on phosphate removal efficiency, and (3) to investigate the effectiveness of the glyphosate removal (organic phosphorus) from wastewater.

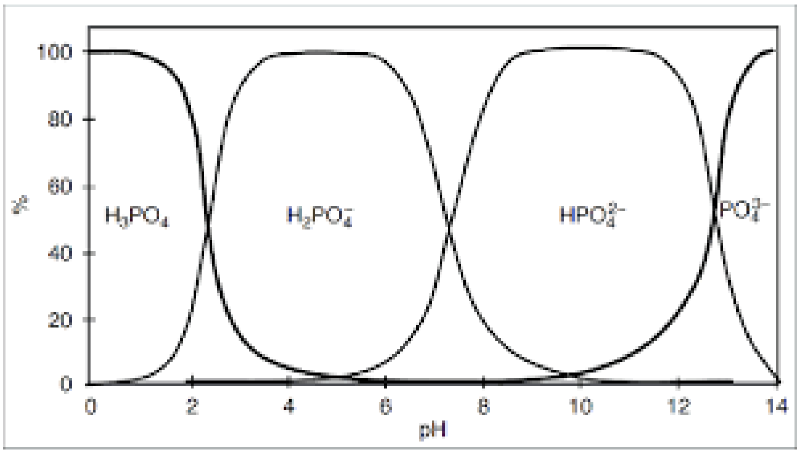

Figure 1: Distribution of phosphate species as a function of pH. (Currie et al., 2017)

2. Materials and methodology

2.1 Preparation of working solution

Working solutions of potassium dihydrogen phosphate (KH_2PO_4) for experiments were prepared by diluting the phosphate stock solution of 10 PO_4-P g/L with distilled water. 100 PO_4-P mg/L working solutions were prepared by diluting the stock solution.

2.2 Preparation of adsorbent

Bamboo (*Phyllostachys bambusoides*) powder was collected from the Kentomu Co., Shiga, Japan, and oven dried at 105°C for 24 h and finally sieved through a meshes sieve (0.30 mm) before use. Eggshell was obtained from the cafeteria of The University of Shiga Prefecture, Japan, which was washed several times with tap water and three times with distilled water, and was oven dried at 105°C for 24 h to remove moisture content (Wang et.al 2010). Then it was grounded by mortar to pass through a mesh sieve (0.30 mm).

20 g mixture of eggshell and bamboo shell powder 1:1 ratio was taken for calcination. Each sample was placed in a muffle furnace and heated to 800 °C for 2 h. The thermal treatment temperature of 800 °C was chosen since eggshell starts decomposition at 650 °C and is completely decomposed at 800 °C (Shen et al., 2018). After the furnace was cooled to room temperature, the calcined material was denoted as BE (eggshell bamboo char). Calcined eggshell (CE) was prepared using same procedure, and bamboo char (BC) was prepared also.

2.3 Adsorption kinetics

Adsorption capacity of phosphate was evaluated by mixing 0.01 g of CB, BE 1:1 and BE with 40 mL of 100 PO_4-P mg/L solution in polyethylene tubes. The mixtures were oscillated at 220 rpm, pH 7 and 25 °C temperature. At defined time (5 min, 15 min, 30 min, 1 h, 2 h, 4 h, 6 h, 8 h, 12 h, 18 h, 24 h, 36 h, and 48 h), after adsorption the mixtures were collected, filtered, and final concentration of phosphate was analyzed by measuring the absorption at the wavelength of 880 nm by molybdenum blue method using ascorbic acid (Murphy and Riley, 1977). U-2000A (Hitachi, Japan) was used as spectrophotometer, and cell pathlength was 10 mm.

2.4 Adsorption Kinetics model

Adsorption kinetics models are very useful to understand the phosphate adsorption process and rate. By fitting the empirical data, we can know whether the adsorption process is controlled by physical adsorption or chemical adsorption mechanism (Borhade et al., 2017). Pseudo first order and second order model were investigated using the data obtained from the phosphate adsorption capacity of different adsorbent time.

The adsorption capacity (Q_e, mg/g) of the sorbent material for P was calculated by the mass balance as

$$Q_e = \frac{V(C_0 - C_e)}{m} \qquad (1)$$

where, C_0 and C_e (mg/L) are the initial and equilibrium P concentration in solution, respectively, V (L) is the solution volume, and m (g) is the adsorbent weight.

In the following the linear form of the pseudo-first order relationship is shown:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \text{ ....(2)}$$

where, q_t is the amount of ion per gram of adsorbent (mg/g) at time t and k_1 is adsorption constant (min^{-1}), which is calculated by plotting the ln (qe – qt) versus t. (Foroutan et al., 2017).

The linear form of the pseudo-second order relationship is shown:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \text{ ....(3)}$$

where k_2 shows the second-order rate constant (g /mg.h). The qe and k_2 values are determined by plotting t/qt versus t (Habiby et al.,2019).

2.5 Effects of pH, co-existing anions, and organic acids

- To investigate the **effect of pH** on phosphate adsorption, 40 mL of 100 PO_4-P mg/L solution was added into a 50 mL polyethylene tube. The initial pH of the solution was adjusted to different initial pH values (3, 5, 7, 9, and 11) by adding 0.1 mol/L NaOH or 0.1 mol/L HCl solutions. Then, 0.01 g of CE and BE 1:1 adsorbent was added and oscillated at 25 °C for 24 h, after that, the mixed solution was filtered through a 0.45

μm PES (Polyethersulfone) membrane filter, and the phosphate concentration and final pH in the filtrate were measured, respectively.

- To test the **effect of co-existing inorganic anions**, 100 PO_4-P mg/L solutions with various salts (KCl, KNO_3, K_2SO_4, and $KHCO_3$ at different concentrations (10, 20, 40, 60, 80, and 100 mg/L as final concentration) was mixed with 0.01 g of BE 1:1 adsorbent in 50 mL polyethylene tube. After oscillating at 220 rpm, pH 7 and 25 °C temperature for 24 h, the supernatant was separated by filtration and analyzed. This experiment was performed triplicate.
- **Effects of organic ions**- Citric acid, oxalic acid, and humic acid of each 100 mg/L and 200 mg/L solutions were mixed with 20 PO_4-P mg/L solution. BE 1:1 adsorbent (0.01g) was added in 40 mL of the solution of 100 and 200 PO_4-P mg/L. Then the mixtures were agitated at 200 rpm, pH 7 and 25 °C for 24 h. After filtration, final phosphate concentration was measured. These experiments were performed triplicate.

2.6 Implication of BE 1:1 adsorbent on natural and treated wastewater

For this experiment 1 L of water samples were collected from three locations (Seri River: 35°16'22.3"N 136°14'19.8"E, Uso river, 35°13'58.0"N 136°12'35.4"E, and outflow of treated wastewater from Tohkubu Wastewater Treatment Plant at Hikone old harbor: 35°16'38.5"N 136°15'33.3"E). During sample collection water pH, EC and temperature was measured. pH was measured using Pack test pH-PR (Kyoritsu chemical check lab corporation, Japan). EC and temperature were measured by portable EC meter D-24 and 9382-10D sensor (HORIBA corporation, Japan). After sample collection water was filtered with 0.45 μm PES (Polyethersulfone) membrane filter. Then 5 PO_4-P mg/L phosphate was added to the sample water, because the phosphate concentration of the water sample of this location is very low. After that 0.01 g BE 1:1 adsorbent was added to the 40 ml of water sample and mixed at 200 rpm at 25 °C for 24 h, after that, the mixed solution was filtered through a 0.45 μm PES (Polyethersulfone) membrane filter. Then the final concentration of the inorganic phosphate was measured by molybdenum blue method using ascorbic acid (Murphy and Riley, 1977). U-2000A (Hitachi, Japan) was used as spectrophotometer, at 880 nm wavelength and cell pathlength was 10 mm. The anions and cations were measured using Ion Chromatography (DX-AQ, DIONEX, USA).

2.7 Organic P（Glyphosate) removal using BE 1:1 adsorbent

A stock solution (50 mg/L) of the glyphosate (Fujifilm Wako Pure Chemical Cooperation, Japan) was used to prepare different initial concentration (0, 5, 10, and 25 mg/L) of glyphosate for organic phosphate adsorption study. For this experiment 0.01 g of the adsorbent material was added to the 40 mL of the glyphosate solution in a 50 mL polyethylene tube and mixed at 200 rpm and 25° C for 24 h. The pH of the solution was maintained at 7 by adding 0.01 mol/L NaOH. After adsorption the concentration of the phosphate was measured by ICP-MS (Neu ION 1000, Perkin Elmer Co. Ltd.).

2.8 Statistical analysis

Pseudo first order kinetic model and pseudo second order kinetic model were analyzed using R Studio software (R Core Team, 2021). Graphs describe the effect of pH, anions and organic acids was produced using Microsoft-excel.

3 Results and discussion

3.1 Adsorption kinetics

To understand the effects of time on phosphate adsorption process different contact time was examined. From experimental data it was found the adsorption rates of P for CE and BE 1:1 increased after 1 h and equilibrium was reached after 4 h (Figure 2). The amounts of P adsorbed at equilibrium time were 75.95 and 98.83 PO_4-P mg/g for CE and BE 1:1, respectively (Table 1). The experimental data was fitted by pseudo first order and pseudo second order kinetic model. R^2 value was calculated and highest R^2 value was found for pseudo second order kinetic model (Figure 2, Table 1). Pseudo second order model showed good correlation with experimental data which indicates P adsorption process and adsorption rate was influenced by chemisorption (Agbovi et al., 2021), Which means calcium of the CE and BE 1:1 was reacted with phosphate to form a strong new material by electron exchange process (Liu et al., 2019).

From the experiment (Table 2) it was found that only bamboo char is not suitable for phosphate adsorption. After using bamboo as an adsorbent, the concentration of phosphate was increased at different time intervals, where initial concentration of phosphate solution was PO_4-P 100 mg/L. It was assumed that phosphate was released from the adsorbent materials. To understand whether phosphate was released from the bamboo char 0.01 g of BC (bamboo char) was added to the 40 mL of MQ water at 220 rpm and 25° for 24 h. After filtration phosphate concentration was measured, and 2.91 PO_4-P mg/L phosphate was found from the bamboo mixed water.
Literature also showes that bamboo powder contain 0.03 % phosphate from the component analysis (Table 3) (Fudano et al., 2016). Bamboo char without any modifican is not suitable for the phosphate adsorption (Du et al., 2021).

3.2 Effects of pH

Different pH solutions were tested during experiments to understand the effects of pH on phosphate adsorption process. Figure 3 shows that, For BE 1:1, at pH 5 and 7 (after adsorption final pH 6 and 7), the highest P adsorption capacities of 103.28 and 111.22 mg/g were found, respectively. At pH 3 and 9 (After adsorption final pH 6 and 10) the lowest capacities of 8.7 and 35.99 mg/g were observed, respectively. From pH 5 to 7 the dominant form of phosphate is $HPO_4{}^{2-}$. After addition of the B+E 1:1 and CE, the final pH of each solution also increased.

Calcined eggshell at 800 ºC contain $Ca(OH)_2$, which increases the pH of the solution (Santos et al., 2019). At pH below 5, physical interaction occurs between the adsorbent and phosphate ion. But above pH 5 it forms a negative ion on the surface of adsorbent which increases the chemical interaction (Liu et al., 2019).

At high pH the adsorption capacity also decreases because the dominant form of phosphate in water changes from $H_2PO_4^-$ to HPO_4^{2-} which needs higher adsorption energy compared to $H_2PO_4^-$ and difficult to be absorbed. The charge of the adsorbent also changes at high pH due to the addition and removal of the proton of the adsorbent materials causing electrostatic adsorption. At high pH the presence of OH ion decreased the phosphate adsorption because it competes with phosphate ion for the active side of the adsorbent (He et al., 2022).

3.3 Effect of Anions

Generally, wastewater contain several types of anions like Cl^-, NO_3^-, CO_3^{2-}, and SO_4^{2-}. So, the presence of these anions may influence the adsorption capacity because they could compete with phosphate for the active site of the adsorbent (Loganathan et al., 2014). From Figure 4, it has been seen that the presence of NO_3^- and Cl^- has no significant effects on the phosphate adsorption capacity (Li et al., 2022). Whereas CO_3^{2-} and SO_4^{2-} decreased the P adsorption from 94.58 to 3.2 PO_4-P mg/g as the anion concentration increased from 10 to 80 mg/L (Figure 4). This is because divalent anions may react more readily with Ca^{2+} from the eggshell than the monovalent anions (Das et al., 2006; Wang et al., 2017). It was revealed that the P adsorption capacity decreased after increasing the concentration of the anions. Similar results were also found by Liu et al., (2019) for eggshell + rice straw 1:1 ratio. This is the main limitation of this process.

3.4 Effect of organic acids

Wastewater may contain different types of organic acid. To understand the effects of the organic matter (citric acid, humic acid, and oxalic acid) on the phosphate removal efficiency different concentration of organic acids (100 mg/l, and 200 mg/L) was experimented with 20 mg/L phosphate using BE 2:1 at pH 7. The results have been illustrated in Figure 5. It has been found that organic matter has influence on phosphate removal efficiency. The phosphate removal efficiency was decreased more at high concentration (200 mg/L) of the organic acid. Generally organic acids exist in water in anionic form which would compete for the active sites on the adsorbent, thus reducing the phosphate removal efficiency (Afridi et al., 2019).

3.5 Implication on natural water and comparative study

Table 5 shows the temperature, EC and pH which was measured during sample collection. Phosphate concentration of the sample water collected from the Seri River, Uso river and treated water was found 0.078, 0.116, and 0.86 mg/L respectively. Since the concentration was very low, for investigating phosphate removal efficiency 5 mg/L inorganic phosphate was added and the concentration was found 5.22, 5.16 and 5.19 mg/L respectively. After adsorption the concentration was decreased and the removal efficiency was found 67.43, 71.12, and 67.43 %, respectfully for the Seri River, Uso river and treated water (Table 5). In chapter 2, phosphate adsorption capacity was examined for different initial concentrations. For initial concentration of 5 mg/L, P adsorption capacity was found 22.97 mg/g. For both river water and treated water, P adsorption capacity was found ~14 mg/g. This is because of the interference of the coexisting ions and organic matter that is present in natural and wastewater (Pandi et al., 2021). Table 4 shows the presence of different anions and cations in Seri and Uso river water (Table 4). Almeida et al., 2020 also found negative influence on the P adsorption process, where removal efficiency was reduced from 99 % to 51.8 % for the effluent water. Because phosphate adsorption was affected by the other anions and organic molecules.

There is very few research on the phosphate removal from real wastewater or natural water using adsorption. Table 6 shows the comparative study on the phosphate removal efficiency performed by different researchers using different adsorbent materials. It has been seen that eggshell and eggshell based material is also effective to remove phosphate from real wastewater.

3.6 Organic phosphorus (glyphosate) adsorption capacity using BE 1:1

From the experiment no adsorption of organic phosphorus (glyphosate) using BE 1:1, BC, CE and Raw eggshell powder as an adsorbent was found (Table 7 and 8). The glyphosate molecule is significantly larger than the phosphate molecule, it requires more space than phosphate. (Liu et al., 1999; Martin et al., 1999). From table 7 and 8 it has been seen that after adsorption using BE 1:1 and bamboo char the final concentration of the phosphorus was increased. Because bamboo powder contains phosphorus it has been found in literature (table 3) and experiments also. Table 7 shows calcined eggshell and raw eggshell also not effective for the glyphosate adsorption at pH 7 and 8.

This result is positive to fulfill the main objectives of this research work, Since the phosphorus loaded material will be applied as fertilizer. If wastewater contain glyphosate and inorganic phosphate, there would be no competition for the active site of the adsorbent material (De Gerónimo et al., 2022). Moreover, if glyphosate causes displacement of phosphate from adsorbent and reacts with sorption site, it will need more amount of glyphosate application than the regular application rate which is not cost effective (Barret. et al., 2007).

3.7 Cost estimation of adsorbent preparation

One of the main objectives of this work was to develop a low-cost adsorbent material from locally available waste material. Adsorbent preparation from waste material involves steps such as material correction, washing, drying, and calcination, which should be included in the cost estimation (Li et al., 2018). The adsorbent material was prepared from the eggshell waste and bamboo powder, which are available at no cost as waste materials. The adsorbent preparation cost can be estimated from the drying and calcination cost (Mondal et al., 2016). The energy used in the drying and calcination processes were calculated as 3.4 kW. However, because the cost of energy and labor varies from country to country, the production cost also varies (dos Reis et al., 2020).

4. Summary

In this study adsorption mechanism of the CE and BE 1:1 adsorbent material was analyzed using pseudo first order kinetic model and pseudo second order kinetic model whether the adsorption process is physical adsorption or chemical adsorption. For CE and BE 1:1 the data were better fitted by pseudo second order kinetic model which indicates that the adsorption process has been governed by the chemisorption process. That means the calcium and phosphate ion have a strong bonding in this reaction (Loganathan et al., 2014). Adsorption kinetics also determine the equilibrium time of the phosphate adsorption which is very important to save time (Kumar et al., 2019). In this study the equilibrium time was observed after 4 h. The amounts of P absorbed at equilibrium time were found 75.95 and 98.83 PO_4-P mg/g for CE and BE 1:1, respectively. To control the reaction environment pH of the reaction environment is a very important factor because it determines the form of the orthophosphate in the sample water. Maximum adsorption capacity was found for BE 1:1 after adsorption 103.28 mg/g at pH 5 where $H_2PO_4^-$ is the major form of the orthophosphate. At pH 7 the adsorption capacity was also high, which condition is very similar to the natural environment. That's what pH 7 was used for different experiments. After that the effects of the co-existing inorganic anions and organic acids were examined. Anion has negative charge which competes with phosphate ion for the active site and reduced the phosphate adsorption capacity. Mainly sulfate and carbonate ions decrease phosphate adsorption capacity. This is a major drawback of the adsorption process (Loganathan et al., 2014). Phosphate removal efficiency also decreases due to the presence of organic acids which also compete with phosphate ion for the active site on the adsorbent. This adsorption selectivity depends on the type of ions and their concentration. In natural or wastewater contains several types of ions which creates a complex condition for adsorption (Kumar et al., 2019). This is the primary flaw of this study which is difficult to avoid. To optimize phosphate adsorption, it is necessary to regulate optimum dose of the adsorbent. To understand the effectiveness of the BE 1:1 adsorbent for the phosphate removal from the natural water and treated water, experiment was performed on collected rivers water and treated water. Phosphate removal efficiency was found 67.43, 71.12, and 67.43 %, respectfully for the Seri River, Uso river and treated water which indicate BE1:1 adsorbent is effective to remove phosphate from natural water and wastewater. Wastewater may contain organophosphorus from pharmaceutical waste and pesticides like glyphosate. In this study the adsorbent material was applied on the glyphosate mixed water and BE 1:1 was used as an adsorbent. But after the adsorption process, phosphorus concentration was not decreased which indicates no adsorption happened. This result indicates that there is no interaction between BE 1:1 material and glyphosate. From literature it was found that the molecular structure of the glyphosate is larger than that of phosphate which inhibits the adsorption on the surface of the BE 1:1 adsorbent. So, it can be said there is no competition between phosphate and glyphosate for the active sides which is positive for this research.

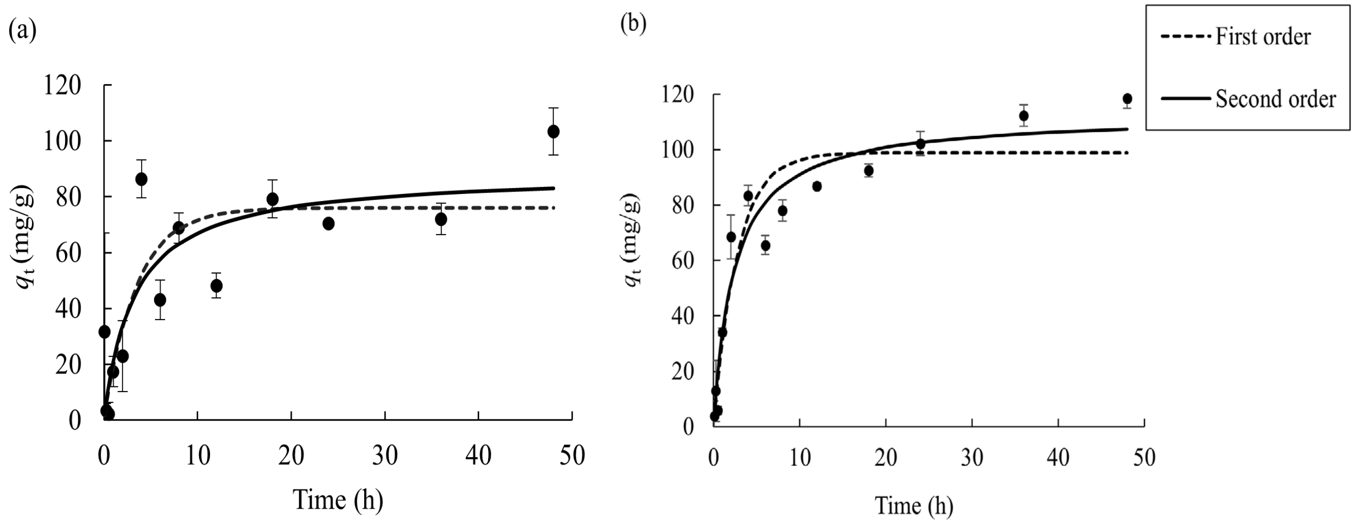

Figure 2. P adsorption kinetics on (a) CE and (b) BE 1:1 adsorbents. q_t: amount of adsorbed P ions. Error bars indicate standard deviation.

Table 1: Adsorption kinetics parameters of P on CE and BE 1:1.

Adsorbent	Pseudo first-order			Pseudo second-order		
	Q_e (PO_4-P mg/g)	K_1 (1/h)	R^2	Q_e (PO_4-P mg/L)	K_2 (1/h)	R^2
CE	75.95	0.286	0.684	88.62	0.003	0.707
BE 1:1	98.83	0.363	0.965	112.6	0.003	0.979

Table 2: Results after using bamboo char as adsorbent.

Time (h)	Initial concentration P (mg/L)	final concentration P (mg/L)
5min	100	106.9
15min	100	101.18
30min	100	103.1
1h	100	103.33
2h	100	104.49
4h	100	95.68
6h	100	112.14
8h	100	103.91
12h	100	113.39
18h	100	104.55
24h	100	112.4
36h	100	102.6
48h	100	101.59

Table 3: Component analysis of bamboo powder.

Component	Average ± Std Error
Total N (%)	0.13 ± 0.03
Total P (%)	0.13 ± 0.03
Total K (%)	0.47 ± 0.03
Total CaO (%)	0.04 ± 0.02
Total MgO (%)	0.13 ± 0.03
Total C (%)	41.68 ± 0.81
C/N	344.28 ± 51.76

(Fudano et al., 2016)

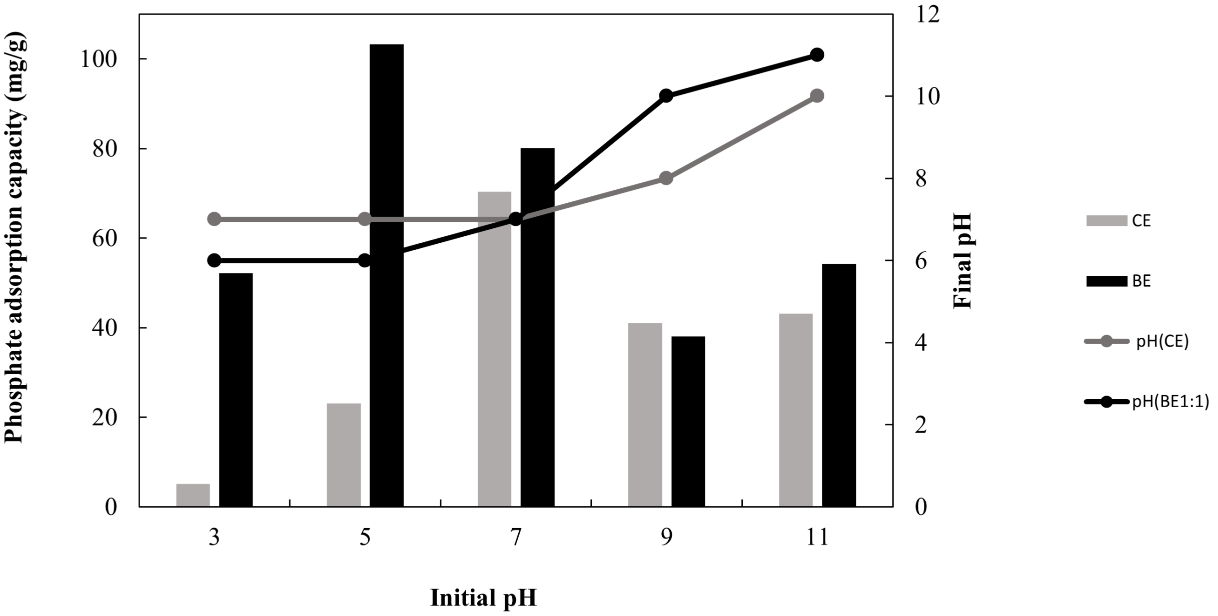

Figure 3: Effect of pH on phosphate removal using Eggshell, BE 1:1; Initial concentration 100 mg/L, Dose 0.01g, Temperature 25ºC.

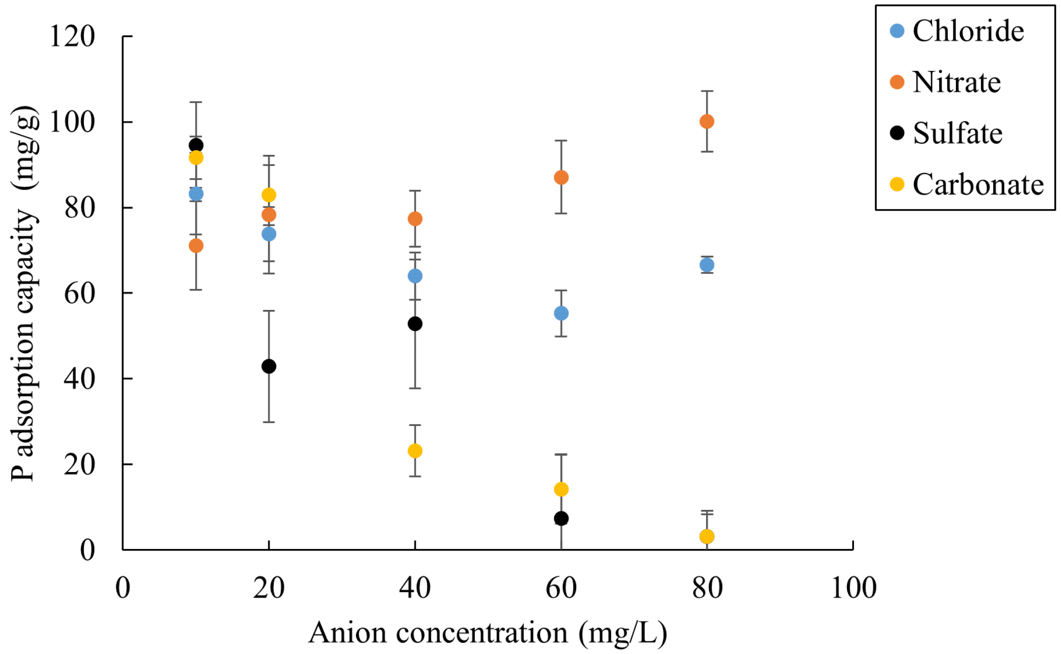

Figure 4: Effect of coexisting anions on P removal (pH: 7; initial P concentration: PO_4-P 100 mg/L; dose: 0.01 g of BE 1:1; temperature: 25 °C; time: 24 h). Error bars indicate standard deviation.

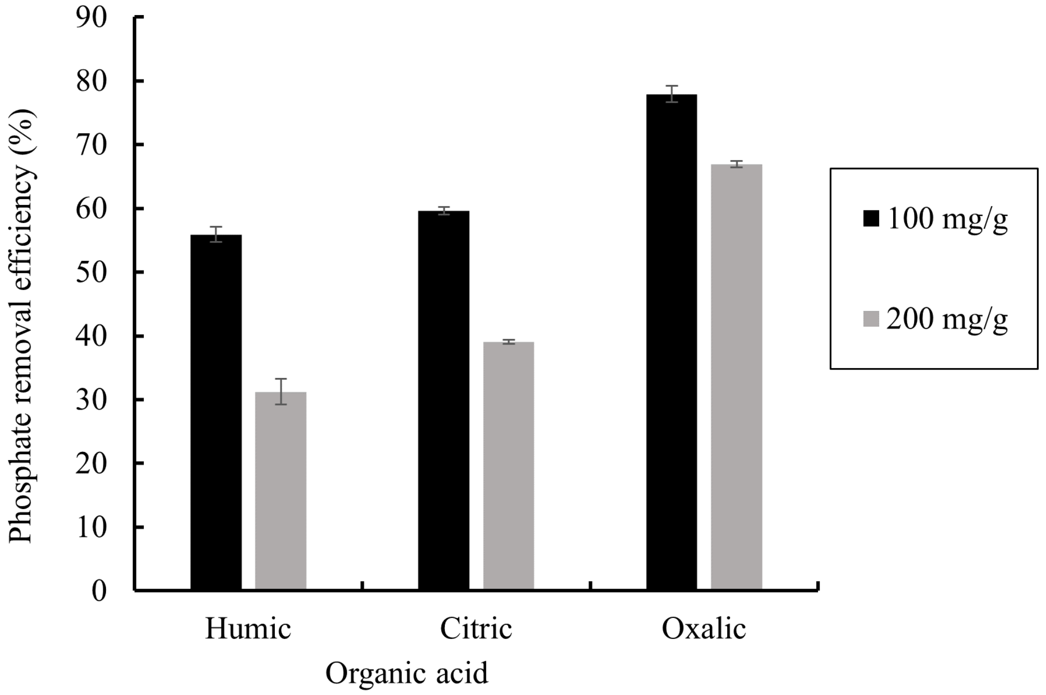

Figure 5: Effect of organic acids on phosphate removal efficiency, pH 7, Initial concentration 100mg/L, Dose 0.01g, Temperature 25 ºC.

Table 4: Anions and cations concentration of Seri and USo River.

Location	pH	PO_4 µM	Cl PPM	NO_3 PPM	SO_4 PPM	Na PPM	K PPM	Mg PPM	Ca PPM
Seri River	8.94	0.49	10.00	2.73	8.80	6.73	1.05	3.12	32.20
Uso River	8.14	1.19	14.51	5.41	27.87	14.38	2.26	3.27	18.53

Table 5: Implication of the BE 1:1 adsorbent for phosphate removal from river and treated water.

ample location	Temp ºC	EC S/m	pH	Phosphate concentration mg/L	After adding inorganic phosphate of 5 mg/L	After adsorption final concentration	Removal efficiency %	Adsorption capacity ±Std mg/g
Seri River	9.8	20.0	7.8	0.078	5.22	1.69	67.62	14.1±0.37
Uso River	9.4	20.3	7.4	0.116	5.16	1.49	71.12	14.67±0.53
Treated water	17.1	40.4	6.8	0.86	5.19	1.69	67.43	13.98±0.31

Table 6: Comparative study on the phosphate removal efficiency

Adsorbent		Sample water	Initial-final concentration mg/L	Removal efficiency %	Reference
Eggshell		municipal wastewater inlet	5.9-1	80	Oliveira et al., 2015
fumed silica powder in conjunction with pulverized oyster shell		wastewater	5-	92	Yu et al., 2010
Chitosan modified iron-cobalt nanoparticles		River water	-	58.7	Issaian et al., 2020
eggshell and potato peel		domestic water	3.8 to 0.3	85.96	Quisperima et al., 2022
Eggshell functionalized with iron oxyhydroxide		Effluent water	10-5		Almeida et al., 2020
Eggshell ash		domestic wastewater	1.7−1	80	Torit et al., 2018

Table 7: Organic phosphorus (glyphosate) adsorption capacity of BE1:1

Initial concentration (mg/L)	Final concentration Mean± sd (mg/L)
0	0.043±0.02
5	5.43±0.26
10	10.98±0.12
25	27.24±0.29

Table 8: Organic phosphorus (glyphosate) adsorption capacity of bamboo char, calcined eggshell powder and raw eggshell powder.

Adsorbent	pH	Initial concentration mg/L	Final concentration mg/L
Bamboo char	7	0	11.57
Bamboo char	7	5	12.39
Calcined eggshell powder	7	0	0.12
Calcined eggshell powder	7	5	6.95
Raw eggshell powder	8	25	25.42
Calcined eggshell powder	8	25	25.72

CHAPTER 4

Desorption study and effectiveness of the recovered phosphate as fertilizer after adsorption using eggshell derived bamboo char.

This section is partially based on manuscript:

“Thermally modified bamboo-eggshell adsorbent for phosphate recovery and its sustainable application as fertilizer” by Sarker, P., X. Liu, N. Hata, H. Takeshita, H. Miyamura and M. Maruo published on Environmental Research (2023).

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1. Introduction

Phosphorus recovery using adsorption is a very attractive and effective method (Bacelo et al., 2020). Nowadays different types of natural bio waste material are used for phosphorus recovery such as sugarcane bagasse (Ramola et al. 2014), soybean milk residues (okara) (Nguyen et al. 2013), sawdust (li et al. 2018), bamboo (Isa et al.,2016), micro algae (Jung et al., 2016), and so on. Biochar alone is not suitable for phosphorus adsorption because of its negative surface charge. But metal modified biochar has good adsorption capacity (Liu et al., 2019; P´erez et al., 2020) as it has positive charge. After adsorption the solubility of phosphorus from cation modified biochar is very low because of the stronger attraction between cation and phosphorus which decreases the availability of phosphorus for plants (Trazzi et al., 2016).

Calcium phosphate is not so much water soluble. At pH 6 and 7, P desorption using deionized water was only1.86% and 1.01%, respectively. But in acidic condition (pH 5), phosphorus release increased to 18.16% (Li et al., 2018). Sometime simple salt also was used for phosphorus desorption. But using high concentration of the salt for phosphorus desorption is not suitable for agriculture because it increases soil salinity. In alkaline solution, phosphorus was not released from calcium phosphate (Loganathan et al., 2014).

Assessing plant availability of P fertilizer is important for the proper nutrient management to reduce P fertilizer loss from agricultural fields (Elliot et al., 2005). Solubility and availability of the recovered P varies because of the chemical composition, but the assessment of the plant availability is challenging (Duboc et al., 2022). The most effective method to assess plant availability is direct application of the P recycled material on plant as fertilizer. But the growth experiment is time consuming, and results show high deviations (Kratz et al., 2019). P fertilizer solubility is measured using different extractors which indicate the P extraction capacity of plant from the soil. It is also important to determine the doses of the fertilizer (Santos et al., 2018).

From the literature it has been found that the extraction methods of phosphorus rocks vary in different country such as 2% citric acid is used in New Zealand, 2% formic acid in the EU, and 1 M ammonium citrate at pH 7 in the USA and Australia (Hedley and McLaughlin 2005). Bioavailability of the phosphorus in biochar was predicted using chemical analysis such as, 2% citric acid, 2% formic acid, and neutral ammonium citrate (NAC) extraction methods where neutral ammonium citrate method showed accurate prediction of the P solubility from the sources (Santos et al., 2018). There are some P extraction methods such as water extraction, $NaHCO_3$ extraction, iron bag extraction, NAC extraction were used to predict the phosphorus availability from different types of phosphate fertilizer. For calcium phosphate, NAC extraction method is effective (Kratz et al 2010; Duboc et al 2022). Low water solubility is a good characteristic of slow-release P fertilizer so that it could be usable for long time. Otherwise, phosphorus could be released fast and mixed with runoff to enter surface water (Duboc et al., 2022).

Plants can use P from the soil and fertilizer by different techniques such as releasing organic acids. Microbial symbiosis and activity also enhance p solubility. Sometime plant modifies its root structure to increase phosphorus uptake capacity. Solubility or release of phosphorus from fertilizer may depends on soil pH and existence of organic acid. Increasing phosphorus availability may increase fast crop production. So that recovered phosphorus could be used as an alternative of the commercial fertilizer (Rech et al., 2019).

After P recovery from the wastewater the application of the phosphorus as fertilizer is very important. Recently researchers have been emphasizing on this topic. There are very few experiments were performed to understand the effectiveness of the recovered phosphorus material as fertilizer. Li et al. (2018) used MgO-CaO Carbon composite, was produced by co-pyrolysis of sawdust and dolomite for phosphorus recovery and applied in plant cultivation. He found the effectiveness of the material as slow-release fertilizer. The average growth height and average fresh weight of Chinese brassica was measured for the phosphorus loaded materials and control. Results was found much better for the phosphorus loaded materials than control. Hong et al (2020) also used calcined sepiolite for phosphorus removal and applied as fertilizer which was proved as an effective source of phosphorus fertilizer. Because bamboo char improves soil quality (Ali et al., 2017) and eggshell powder is used as soil conditioner (Panagiotou et al., 2018), P-loaded materials could be used directly as a fertilizer to improve soil quality. Examination of the effectiveness of these materials as fertilizers is necessary before they are used in agricultural production.

In this study calcined eggshell modified bamboo char was used for phosphorus recovery from wastewater. Then the phosphorus desorption study was performed using water extraction and NAC extraction method. Then the effectiveness of the phosphorus loaded materials as P fertilizer was examined measuring the growth index of the Japanese mustard spinach.

2. Materials and methods

2.1 Desorption study

2.1.1 Water extraction

For desorption study at first adsorption was performed according to chapter 2. Where the initial concentration was 100 mg/l, 0.01 g adsorbent material was added to the 40 mL P solution and mixed at 200 rpm at 25°C temperature. After adsorption the solution was filtered by 0.45 µm PES filter paper and phosphorus concentration was measured. Then 0.01 g material was added to 40 mL MQ water and then shaken at different temperature 25, 35 and 45 °C for 1 day, 3 days, and 5 days. Then phosphorus concentration was measured by spectrophotometer (HITACHI U-2000A) at the wavelength of 880 nm by Ascorbic acid method (Murphy et al., 1977).

2.1.2 Neutral ammonium citrate (NAC) extraction

For NAC extraction 0.1g of P loaded adsorbent material was added to NAC solution at pH 7 and shaken at 65 ºC for 1h. After extraction sample was diluted with 40 mL MQ water to make the final volume 50 mL. Then the solution was filtered through 0.45 µm PES membrane filter paper and the phosphorus concentration was measured on the ICP-OES (Duboc et al., 2022).

Amount of P released from the adsorbent was calculated by equations (Haddad et al., 2017):

$$Q_{des} = \frac{C_{tdes}}{M_s V}\text{.................................}(1)$$

$$Q_{des}=C_{tdes}/M_s \times V\text{..........................}(2)$$

where, Q_{des} was released phosphorus amount (mg/g), C_{tdes} was final P concentration in the solution (mg/L), V was the volume of the used solution (L), M_s was the amount of preloaded adsorbent (g).

2.2 Pot experiment

To understand the effectiveness of the phosphorus loaded biochar several experiments were performed. In this experiment P loaded BE 1:1 material was used, because the BE 1:1 adsorbent showed the highest P adsorption capacity in chapter 2. Japanese mustard spinach was used as plant material for the cultivation. 9 cm poly pot was filled with 200 g vermiculite and mixed with 0.5 g phosphorus containing materials was placed in the incubator at 23℃ temperature, photoperiod 16-h day/8-h night cycle, Light intensity > 150 µmolm-2s-1PPFD (maximum intensity). In each experiment, four seeds were sown per pot at a depth of 5–10 mm, and thinning was started 1 week after sowing. After 2 weeks, only one plant per pot remained (Li et al., 2018). Pots should be set on trays and watered at least once every two or three days.

2.2.1 First experimental condition

1 g adsorbent (CE and BE 1:1) was added to 400 mL of 100 mg/L of P solution. After adsorption, P adsorption capacity was found 40 mg/g, that means 1g material contains 40 mg phosphorus. Then 1 g of CE and BE 1:1 with and without P was added to Soil +Vermiculite 3:1. Total 5 experiment set with triplicate was prepared for the first experiment are given bellow:

i. Mixture of Soil and Vermiculite in 3:1 ratio with BE 1:1 loaded with phosphorus (SVer3:1 + BE 1:1 + P)
ii. Mixture of Soil and Vermiculite in 3:1 ratio with BE 1:1 material (SVer3:1+ BE 1:1)
iii. Mixture of Soil and Vermiculite in 3:1 ratio with CE loaded with phosphorus (SVer3:1 + CE 1:1 + P)
iv. Mixture of Soil and Vermiculite in 3:1 ratio with CE adsorbent material (SVer3:1 + CE 1:1)
v. Mixture of Soil and Vermiculite in 3:1 ratio (SVer3:1) (Control)

2.2.2 Second experimental condition

0.5 g adsorbent (BE 1:1) was added to 400 mL of 500 mg/L of P solution. where 1 g material contains 90 mg phosphate. In this experiment vermiculite was used as nutrient free material which was used for control. Then 0.5 g P adsorbed materials were used mixed with vermiculite to examine the effects of the phosphorus adsorbed material as fertilizer. In this experiment was performed without adding others nutrient and total 3 experiment set with triplicate were prepared as follows:

i. Vermiculite with BE 1:1 loaded with phosphorus (Ver+BE 1:1+P)
ii. Vermiculite with BE 1:1 material (Ver+BE 1:1)
iii. Vermiculite (ver) (Control)

2.2.3 Third experiment

0.5 g adsorbent (BE 1:1) was added to 400 mL of 500 mg/L of P solution. where 1g material contains 90 mg phosphate. After adsorption process, P containing adsorbent material was applied as a fertilizer to evaluate its effectiveness as a fertilizer. Two experiments with triplicate were conducted as follows:

i. vermiculite only (Ver) (Control)
ii. mixture of vermiculite and BE 1:1 with P addition (Ver + BE 1:1 + P)

Third experiment was performed using additional micro and macronutrients. The control experiment was performed without phosphorus loaded material. In this experiment half-strength Hoagland's Solution was used as additional nutrient for continuous irrigation (Yan et al., 2013). After 21 days the plant growth index was measured. Root and shoot length were measured by scale. Then wet and dry weights were weighed (IUW 200-D, As One, Japan).

2.3 Half-strength Hoagland solution preparation

In this experiment Half- strength Hoagland solution was used to supply additional nutrient to the experimental plants. It was prepared from the 4-stock solution of the mixture of different nutrients (Yan et al. 2013). A detail preparation process has been given bellow-

Stock Solution 1: Mixture

Add gram amounts to distilled water to make 500 mL of stock solution:

- KNO_3 3 mmol/L
- NH_4Cl 0.5 mmol/L
- $MgSO_4$ 1 mmol/L

Stock Solution 2: Calcium Nitrate

- Add gram amounts to distilled water to make 500 mL of stock solution:
- $Ca(NO_3)_2$ 2.5 mmol/L

Stock Solution 3: A-Z (micronutrients)

Add gram amounts to distilled water to make 100 mL, then put 45/4 mL (11.25 mL) solution in 500mL bottle, fill to 500 mL liters using distilled water (discard excess):

- H_3BO_3 (boric acid) 2.9 grams
- $MnCl_2.4H_2O$ (manganese chloride) 1.8 grams
- $ZnSO_4.7H_2O$ (zinc sulfate) 0.2 grams
- $CuSO_4.5H_2O$ (copper sulfate) 0.08 grams
- $H_2MoO_4.H_2O$ (molybdic acid) 0.09 grams

Stock Solution 4: Iron

Dissolve gram amounts in 100 mL of distilled water by heating to 60°C for one hour; let cool slightly and add distilled water to reach total volume of 500:

- $FeSO_4.7H_2O$ (iron sulfate) 2.5/4 grams (0.625 g)
- Na EDTA (ethylene diamine tetra-acetic acid) 3.3/4 grams (0.825 g)

This nutrient solution used for continuous irrigation is a modified half-strength (0.5X) Hoagland's solution. To make half-strength Hoagland's for Fast Plants, mix the following quantities of the four stock solutions and add distilled water to make a total volume of 1 L:

- 2.0 mL Mixture (Stock Solution 1)
- 2.5 mL Calcium Nitrate (Stock Solution 2)
- 2.0 mL A-Z (Stock Solution 3)
- 2.0 mL Iron (Stock Solution 4)

3. Result and discussion

3.1 Desorption capacity

The phosphorus desorption amounts from the BE 1:1 adsorbent were shown in Table 1. After 1 day desorption, the released phosphorus amount was found higher than after 3- and 5-days desorption into MQW. At 45 °C the desorption was comparatively higher than at 25°C and 35°C. Overall, the phosphorus desorption in MQW is very low, because the bonding between calcium and phosphate is very strong which makes it water insoluble. For increasing the desorption rate the pH of the solution must be below 5.5 (Loganathan et al., 2014). After extraction using NAC extraction method the amount of desorbed phosphorus was found 48.68 mg/g was higher than water extraction process. In this process citric acid forms complex bond with calcium and release phosphate which increase the solubility of calcium phosphate in NAC solution (Barrow et al., 2017).

3.2 Effectiveness of the phosphorus containing biochar as fertilizer (Pot experiment)

3.2.1 First experiment

After 21 days of the experiment the plant growth index was measured. From Figure 1 and Table 2, it has been found that length of the root, shoot and largest leaf and the wet and dry weight of the root and shoot for 5 experiment set was very similar. This may be because of using nutrient enriched soil material which was sufficient for plant growth.

3.2.2 Second experiment

After 21 days of the experiment the plant growth index was measured. From Figure 2 and Table 3, it has been found that length of the root, shoot and largest leaf and the wet and dry weight of the root and shoot for 3 experiment set was also very similar. This is because of using nutrient free vermiculite which was not efficient for plant growth. Only phosphorus is not enough for plant growth. Other macro and micronutrients are necessary for plant growth (Ebelhar et al 2008).

3.2.3 Third experiment

Length of the root, shoot, largest leaf, wet and dry weight of the root and shoot was measured after 21 days of seedling. There this a noticeable difference between two sets of experiment. The length and weight of the plant cultivated with phosphorus dropped biochar was higher than without phosphorus vermiculite (control). In the control experiment all other nutrients were provided except phosphorus. Without phosphorus plant root and shoot development was not enough (Figure 3). From table 4, it has been seen that the length of the root and height of shoot for B+E 1:1 with P was 30.3cm and 11.5cm which is higher than the length of the root(19.3cm) and height of shoot (7.3cm) of plant cultivated without phosphorus. The wet root weight and shoot weight for B+E 1:1 with P was 4.3g and 6.3g which was comparatively higher than the without phosphorus plant's wet root weight (0.68g) and shoot weight (0.16g). According to Justus von Liebig if one of the essential plant nutrients is deficient, plant growth will be poor even when all other essential nutrients are abundant. In the 19th century, the German scientist Justus von Liebig formulated the "Law of the Minimum" (Figure 4) (Ebelhar et al., 2008).

3.3 Discussion

Phosphorus is a vital plant nutrient which is a major component of ATP and DNA. ATP is the plant 'energy' which is necessary for photosynthesis, protein synthesis, nutrition distribution, nutrient uptake, respiration, and genetic characteristics transportation. Phosphorus enhances root growth and influences early maturity, straw strength, crop quality and diseases resistance. Phosphorus deficiency has significant negative impact on crop production (Upadhyaya et al., 2017). Using phosphorus fertilizer is a common practice for optimum crop production. There are many commercial phosphorus fertilizers like rock phosphate, phosphoric acid, calcium orthophosphates, ammonium phosphates, ammonium polyphosphate and nitric phosphates which are generated from phosphorus rock mine. Traditionally animal bone was used as phosphorus fertilizer. Total reserve of phosphorus in the world is very limited compared to the current demand. For this reason, recovery of phosphorus from waste material is a good alternative way to meet the huge demand of phosphorus (Samreen et al., 2019).

From the desorption study it has been found that phosphorus release with MQ water was very low. because the bonding between calcium and phosphate is very strong. For this reason, calcium phosphate is water insoluble (Loganathan et al., 2014). But NAC extraction method is effective for phosphorus extraction from calcium phosphate because citrate ion replaces phosphate ion and release phosphate from adsorbent (Duboc et al., 2022). Soil property has great influence on phosphorus release. Soil organic matter and acidic condition enhance the phosphorus solubility. The slow-release property of this material is also suitable for agricultural application. Because plant has different technique to uptake phosphorus from soil (Rech et al., 2018). The growth of plant of experiment 3 also proved that plant was capable to uptake phosphorus from soil. That's why there was huge difference in plant growth rate. Plant roots release different types of low molecular weight compounds into the rhizosphere which is important for the chemical, physical, and biological interaction between roots of the plants and the rhizosphere. These low molecular weight compounds help microorganisms to improve nutrient uptake capacity, plant growth development and stress/ diseases resistance capacity (Yadav et al., 2015). Spinach plants release citric acid and malic acid in p deficient environment which might be effective for phosphorus release from P loaded bio adsorbent material (Romar et al., 2001). Brassica species also release different types of organic acid where citric acid and malic acid are the most abundant (Sousa et al., 2009). *Brassica napus* is a mustered family plant release organic acid from the roots to use phosphorus from phosphate rock fertilizer (Haynes 1992). Hong et al. (2020) found that calcined sepiolite effectively removed phosphate and P-loaded sepiolite was applied to rice crop production. The P-loaded material increased plant growth and biomass. Li et al. (2018b) synthesized a CaO-MgO carbon hybrid composite (sawdust and dolomite) and reclaimed phosphate fertilizer has been proven effective as a slow-release fertilizer for agricultural production. The higher plant growth in the current study also indicated that P-loaded material could be used as an alternative source of phosphate fertilizer.

4. Summary

This study revealed that phosphorus loaded eggshell modified bamboo char has potentiality to use in plant cultivation as a phosphorus fertilizer. Since the desorption capacity is very low in MQ water. But in soil environment plants have mechanism to improve the P uptake capacity. Which might influence the root and shoot development of the plants. So, the phosphorus recovered from wastewater is applicable as a slow-release fertilizer. Further study should be developed to enhance the solubility of the P loaded adsorbent material. So that it could be used as commercial phosphorus fertilizer. A lab-scale fertilizer experiment was performed here, and thus the practical agricultural application of the material as a fertilizer should be examined before commercial applications could be considered.

Table 1: Results of P desorption using water extraction and NAC extraction method.

Extraction method	Time	Q_{des} (mg/g)		
		25 °C	35 °C	45 °C
MQW	1 day	1.54	0.79	1.97
	3 days	0.52	0.67	1.77
	5 days	0.54	0.29	0.48
NAC	1 h	48.8	-	-

Table 2. First Experiment. Growth parameter of the Japanese mustard spinach in the four experimental conditions (Exp I-IV). LR: length of the root; HS: height of shoot; LL: length of the largest leaf; WRW: wet root weight; DRW: dry root weight; WSW: wet shoot weight; DSW: dry shoot weight. SD: standard deviation.

Experimental condition	LR	HS	LL	WRW	DRW	WSW	DSW
	Mean ± sd (cm)			Mean ± sd (g)			
Exp. I: SVer 3:1 + BE 1:1 + P	23.0±2.16	11.0±0.94	10.0±0.94	0.8±0.12	0.22±0.07	6.5±0.64	1.24±0.06
Exp. II: SVer3:1+ BE 1:1	30.0±4.08	11.0±0.82	9.6±0.47	0.83±0.17	0.23±0.06	7.1±1.05	1.25±0.06
Exp. III: SVer 3:1 + CE 1:1	25.0±2.2	10.3±0.47	9.8±0.21	0.86±0.08	0.23±0.07	7.0±0.86	1.17±0.19
Exp. IV: SVer 3:1 + CE 1:1 + P	23±2.9	10.17±0.62	9.33±0.47	0.7±0.08	0.25±0.045	6.5±0.41	0.86±0.24
Exp.V: SVer 3:1	25.0±0.94	11.0±0.47	10.0±0.47	0.7±0.08	0.24±0.04	6.5±0.48	1.34±0.12

Figure 1: Plants growth for first experiment.

Table 3. Second experiment, Growth parameter of the Japanese mustard spinach in the four experimental conditions (Exp I-IV). LR: length of the root; HS: height of shoot; LL: length of the largest leaf; WRW: wet root weight; DRW: dry root weight; WSW: wet shoot weight; DSW: dry shoot weight. (Without additional nutrient).

Experimental condition	LR	HS	LL	WRW	DRW	WSW	DSW
	Mean ± sd (cm)			Mean ± sd (g)			
Exp. I: Ver	5.66±0.47	2.17±0.23	1.36±0.26	0.01±0.001	0.006±4.7E-05	0.05±0.003	0.01±9.4E-05
Exp. II: Ver + BE 1:1+P (unsaturated)	4.6±0.94	2.0±0.00	1.4±0.14	0.012±0.003	0.0014±0.0002	0.067±0.002	0.01±0.006
Exp. III: Ver + BE 1:1 + P (saturated)	72.0±0.82	2.0±0.00	1.16±0.24	0.063±0.061	0.002±0.0002	0.061±0.003	0.01±0.002

Figure 2: Plants growth for second experiment.

Table 4. Third experiment. Growth parameter of the Japanese mustard spinach in the four experimental conditions (Exp I-IV). LR: length of the root; HS: height of shoot; LL: length of the largest leaf; WRW: wet root weight; DRW: dry root weight; WSW: wet shoot weight; DSW: dry shoot weight. (Using Half-strength Hoagland solution for other plant nutrients)

Experimental condition	LR	HS	LL	WRW	DRW	WSW	DSW
	Mean ± sd (cm)			Mean ± sd (g)			
Exp. I: Ver	19.3±1.70	7.3±0	5.5±0	0.68±0	0.06±0.71	1.02±0.12	0.16±0.05
Exp. II: Ver + BE 1:1 + P	30.3±3.30	11.5±0.47	11.0±0.47	4.3±0.41	0.28±0.09	6.3±0.03	1.2±0.01

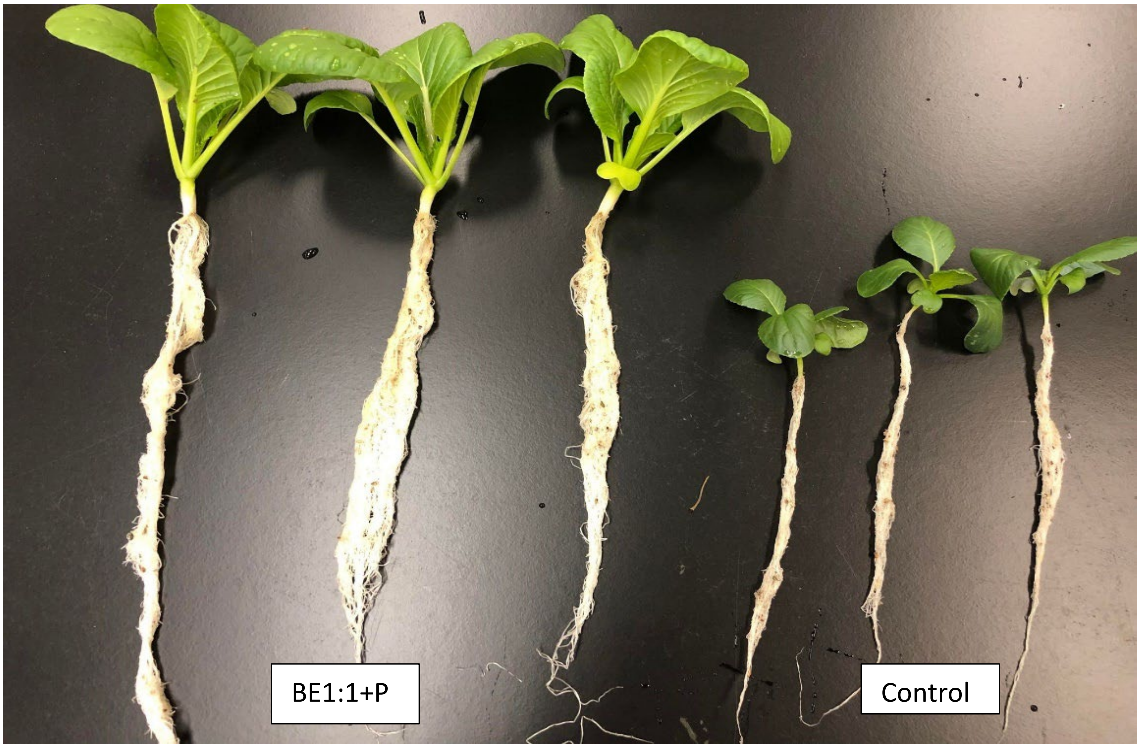

Figure 3: Effects of BE(1:1)+P on plant growth (experiment).

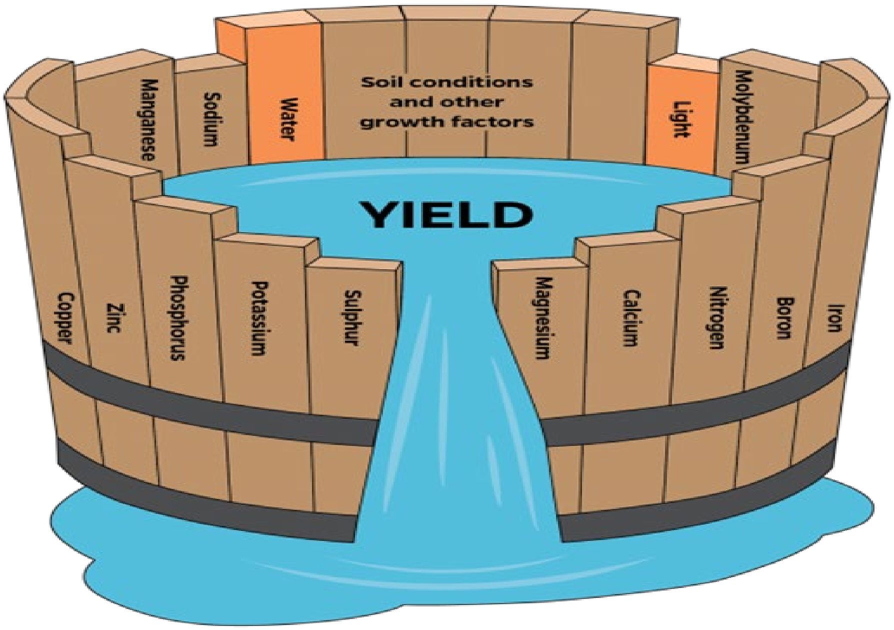

Figure 4: Law of the Minimum (Ebelhar et al 2008)

CHAPTER 5

Conclusion

1. Conclusion

This PhD research investigated the preparation of the adsorbent from locally available biowaste material, where eggshell waste and bamboo waste was used to produce low-cost, and environment friendly adsorbent material. Effectiveness of the adsorbent material to recover phosphorus and implementation of the P loaded adsorbent material as fertilizer after adsorption was examined. Eggshell modified bamboo char after calcination has been proven as a good adsorbent for phosphate removal from wastewater. From this experiment at the same time three environmental problems were tried to be solved. First, using waste material for adsorbent preparation is a good solution for solid waste and environmental management. Second, removing phosphorus using adsorption process is beneficiary to reduce severe water pollution (eutrophication). Third, after adsorption the P loaded material could be used as fertilizer to meet the huge demand of the phosphorus fertilizer.

In **chapter 2**, At first adsorbent material was prepared using different calcination temperature (600, 700, and 800°C) and mixing ratio of eggshell and bamboo powder (CE, BE 1:1, 2:1, 10:1 and BE). After calcination, SEM image and FTIR analysis was performed to understand the morphological and physicochemical changes. Then the materials were applied as adsorbent to understand its effectiveness under different initial concentration and temperature. Optimum dose (0.01g) and effective mixing ratio (BE 1:1) was found from the experiment. Then the adsorption isotherm and thermodynamics was calculated and maximum phosphorus adsorption capacity for the BE 1:1 and BE 2:1 was found 95.14 and 98.40 mg/g at 25 °C and non-spontaneous reaction was found for the BE 1:1 at 25°C. The reaction was spontaneous at 35 and 45 °C. Adsorption process was calculated by adsorption isotherm, where experimental data were better fitted by the Langmuir adsorption isotherm model, indicating monolayer adsorption on homogenous surface. Langmuir separation factor indicated favorable condition for the phosphorus adsorption in different initial concentration and temperature.

After phosphate adsorption experiments, presence of phosphorus in the adsorbent was examined using FTIR, SEM image and EDX analysis. From FTIR analysis, a clear new band at 1024 cm^{-1} was observed after phosphate adsorption on BE 1:1. SEM image showed morphological changes and EDX analysis ensured the presence of phosphorus after adsorption using adsorbent materials.

In **chapter 3,** influences of pH and co-existing anions in the phosphorus adsorption process was investigated. Adsorption mechanism was calculated by adsorption kinetics, where experimental data were better fitted by the pseudo second order model. This result indicates that the adsorption process was controlled by the chemisorption process. Calcium ion has strong affinity to the phosphate ion, and it created an intermolecular interaction on adsorption. The amounts of P adsorbed were 75.95 and 98.83 mg/g for CE and BE 1:1, respectively.

Phosphate adsorption process was influenced by the pH of the reaction. Maximum adsorption capacity was found from pH 5 to 7. Where pH 7 is neutral pH and like natural water. Presence of different anions and organic acids in wastewater is usual. In presence of CO_3^{2-}, and SO_4^{2-} phosphate adsorption capacity decreases. Presence of organic acids like humic acid, citric acid and oxalic acid also affects phosphorus adsorption capacity.

BE 1:1 adsorbent was applied on river water and treated wastewater. Where, 67.43, 71.12, and 67.43 % phosphate removal efficiency was obtained for the Seri River water, Uso River water, and treated wastewater of Tohokubu Wastewater Treatment Plant (Matsubara, Hikone, Shiga), respectively. For river water and treated wastewater, the removal efficiency was also affected by co-existing matters. But the phosphate removal efficiency from river and treated wastewater using BE 1:1 was good, and it was effective for real wastewater application. It is not easy to avoid the influence of the co-existing ion. So, it is necessary to control the amount of the adsorbent to increase the phosphorus adsorption capacity.

Organic phosphorus removal efficiency was investigated using BE 1:1 adsorbent material on glyphosate containing water and no adsorption of organic phosphorus from glyphosate was found from the experiment which is positive for the objective of this research. BE 1:1 is efficient for inorganic phosphorus removal and safe for fertilizer use because of no competition and contamination of glyphosate from wastewater.

Cost estimation of adsorbent preparation is an important part of this study to apply in commercial scale. Since the labor cost and material cost varies country to country, energy used for the adsorbent preparation was estimated. Total energy consumption was 3.4 KW.

In **Chapter 4,** Desorption study using water extraction method and neutral ammonium citrate (NAC) extraction method was performed. The desorption capacity in milli Q water was found lower than the NAC extraction method (48.68 mg/g). This low solubility of the P loaded materials is suitable to use as slow-release fertilizer. Then the P loaded BE 1:1 was applied on

Japanese mustard spinach cultivation in different soil condition. Vermiculite (nutrient free material) was used for the cultivation where half strength Hoagland solution (without P) was added to provide other macro and micronutrient. Plant growth was found higher for the P loaded BE 1:1 than the control.

Though the phosphate of the adsorbed material release in water is very low because of strong bond between calcium and phosphate. But the plant growth was good which indicates that the phosphate was taken up by plants. Plants have some mechanisms to uptake phosphate by releasing organic acid which increase the plant availability of the phosphorus to uptake. In nutrient enriched soil, there is no effects of P loaded biochar on plant growth. The slow-release property of P-loaded BE 1:1 material is suitable for long-term uses as sustainable fertilizer. Our results demonstrate that adsorbent preparation from waste materials could convert waste into a resource to control eutrophication and use the recovered P as a valuable fertilizer.

2. Recommendation

In future study, it is necessary to give emphasize on the improvement of the adsorption capacity and quality of the phosphorus loaded material to use as fertilizer.

1. Since the objective of this study was recovery of phosphorus from wastewater, research should focus on the interference of the other ions and organic matters like pharmaceutical contamination which could interfere with the maximum phosphorus removal capacity.

2. The current experiment of the fertilizer application was performed in lab scale, but practical application of the phosphorus loaded material as fertilizer in the agricultural field is needed before commercial application. Farther experiment is necessary to improve the plant availability of the fertilizer to make it commercially applicable.

3. Another future study could focus on the investigation of the preparation of the adsorbent using different waste material. So that at the same time we can control water pollution and solid waste. Proper use of agricultural and industrial waste could convert the waste material into resources. It will reduce the cost of the adsorbent preparation and improve the economic feasibility.

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