



Utilization of cockle shell powder as an adsorbent to remove phosphorus-containing wastewater

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ABSTRACT

The paper demonstrates the capability of using cockle shells as an adsorbent for phosphorus removal from simulated petrochemical wastewater, focusing on the actual condition of the petrochemical facultative pond. In this study, the physicochemical properties of shell powder were determined, such as the functional groups, surface morphology, crystalline structure, and surface area using FTIR, SEM, EDX, XRD, and BET. It was observed that the optimum conditions for effective phosphorus removal are under the presence of rotational speed (125 rpm), higher dosage (7 g/L), and larger surface area (smaller particle size) of the shell powder. Fine powder achieved up to 52.27% of phosphorus removal after 40 min compared to coarse powder which could only give 16.67% removal. Additionally, calcined shell powder demonstrated a higher phosphorus removal rate, i.e., up to 62.37%, compared to raw shell powders. The adsorption isotherm was studied using Langmuir and Freundlich models, but the isothermal data fit better for the Freundlich model ($R^2 = 0.9836$). Overall, this study has successfully generated a greener and low-cost adsorbent.

1. Introduction

Phosphorus is an essential nutrient for aquatic life. Phosphorus in natural water is usually found in the form of phosphates, PO_4^{3-} . It is needed for growth and required for many metabolic reactions in plants and animals. Phosphorus is a limiting nutrient in freshwater aquatic systems (Blaas and Kroeze, 2016; Douglas et al., 2016). Plant growth will be disturbed if phosphorus were used even though nitrogen content is high. However, an excessive amount of phosphorus can lead to algae bloom known as eutrophication (Blaas and Kroeze, 2016). The over-supply of phosphorous can cause reduction of water transparency, oxygen diminution or anoxia due to the decomposition of organic matter, variations in species composition, increased occurrence of fish kills, decreased species diversity and a decline in harvestable fish (Fink et al., 2018).

Cockles, scientifically referred to as *Anadara granosa*, is a type of seashell that is well-known in Malaysia for being served in local dishes (Izzah Ahmad et al., 2016; Saharudin et al., 2018). In addition, studies done by Zuki et al. (2014) and Bharatham et al. (2014) had proven that the mineral contents in cockle shells are similar to the corals. Cockle shells have become an important protein source in the Southeast Asian

region and one of the calcium carbonate ($CaCO_3$) sources in Malaysia (Mailafiya et al., 2019; Saharuddin et al., 2019). Due to the significant demand for marine-based seafood, it has generated a massive amount of shells. However, most of the shell wastes are dumped in landfills which contribute to pollution. In Malaysia, shell wastes are often abandoned without proper treatment, leading to unpleasant smells (Mohamed et al., 2012). In this study, cockle shell powder was chosen as an adsorbent to treat wastewater. This is because they can be considered cheap, environmental-friendly and under-utilized materials containing high calcium sources (Hajar Saharudin et al., 2019; Mahmood et al., 2017; Saharudin et al., 2019). A few studies have been done to utilize waste cockle shells as valuable materials. For example, the mineral content of $CaCO_3$ in shell wastes can be converted into lime to be used as a heterogeneous catalyst in biodiesel production (Marwaha et al., 2018), bio lubricant production (Ghafar et al., 2019) and also as an adsorbent in wastewater (Kasim et al., 2020; Kim et al., 2018; Qalyoubi et al., 2021).

The current research aimed to investigate the feasibility of cockle shells as adsorbent for phosphorus removal from petrochemical wastewater. Some analyses were done to achieve the objectives of the study. First, the physicochemical properties such as surface area, crystalline structure, surface morphology and functional group of raw and calcined

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cockle shell powder as adsorbent were analyzed and studied. Second, a phosphorus removal study through the adsorption process was conducted focusing on the effects of raw and calcined cockle shells as adsorbent. In addition, the effects of shell powder concentration, particle size and rotational speed were also studied using Langmuir and Freundlich isothermal equations.

2. Experimental section

2.1. Materials

Cockle shells were collected from a local market in Kuantan, Pahang, Malaysia. Potassium phosphate monobasic (98% purity, Sigma-Aldrich, USA) was used to prepare synthetic wastewater. Phosphorus in the samples was measured using a Hach spectrophotometer (Hach DRB200, USA) and Hach kits (Hach CO., Loveland, CO, USA). The pH reading was taken using the pH meter (pH 150, Eutech Instruments, Singapore).

2.2. Pre-treatment of cockle shells

First, the cockle shells were cleaned thoroughly using hot water to remove dirt and residue of cockle flesh. After that, the cockle shells were oven-dried for 1 h at 110 °C to remove the moisture content (Hajar Saharudin et al., 2018). Then, they were crushed into powder using a grinder machine (Retsch ZM 200 Grinder, Germany) to obtain fine particles. Lastly, the powder was sieved into several sizes (fine, 60–70 µm; coarse, >125 µm) using a sieve shaker (Retsch AS200, Germany).

2.3. Calcination of shell powder

The calcination process was carried out in a furnace. The shell powder was placed in a ceramic crucible and heated at 900 °C for 5 h of holding time to complete calcination. According to previous studies, cockle shells were calcined between 700 °C and 900 °C (Mohamad et al., 2016; Suwannasingha et al., 2022). However, higher temperature is required for a complete calcination and maximum yield of CaO (Shariffuddin et al., 2013). The samples were weighed before and after the heating to evaluate the conversion of shell powders.

2.4. Characterization of cockle shells

Fourier transform infrared spectroscopy (FTIR) (Bruker vector 33, USA) was determined to check the presence of a functional group on the adsorbent. The analysis was carried out within 380–4000 cm⁻¹, and 15 scans were taken for each sample. X-ray diffraction (XRD) was performed using a Bruker D8 Advance diffractometer with a 40-kV Cu Kα X-ray source, scanning within a 2θ range of 20–80° with a 0.02° step (Ji et al., 2019; Shariffuddin et al., 2013). The scanning electron microscopy (SEM) analysis was performed using Benchtop scanning electron microscope (TM3030 Plus, Hitachi, Japan) with 15 kV accelerating voltage and image analysis. Three magnifications (500, 1000 and 3000) were used to obtain the SEM image for each powder sample. At the same time, energy dispersive X-ray spectroscopy (EDX) (SwiftED3000, Hitachi, Japan) was used simultaneously with SEM to determine the relative composition and elements present in the sample powder.

Brunauer-Emmett-Teller (BET) analysis was conducted using a high-performance adsorption analyzer (ASAP, 2020; Micromeritics, USA) to determine the powder's pore size, specific surface area (SSA), pore-volume and pore size distribution. The SSA was calculated from the N₂ adsorption data based on a formula developed by Brunauer, Emmett and Teller, and the P/P₀ value ranged between 0.05 and 0.2.

2.5. Preparation of synthetic wastewater

Synthetic wastewater was prepared by weighing 10 mg of potassium phosphate monobasic and dissolved in 1 L of deionized water to form a

phosphate solution.

2.6. Adsorption experiment

The method of conducting the adsorption experiment in the batch reactor was carried out under ambient temperature and pressure to imitate the condition of the facultative pond in a petrochemical wastewater treatment plant. Initially, 3 g/L of raw shell powder was added to the wastewater sample. The solution was stirred magnetically throughout the experiment for 60 min. Then, 5 mL of the sample was withdrawn at every 5 min time interval to analyze the pH reading using the pH meter, and the sample was added into a phosphorus vial. Then, the phosphorus content was determined by using Hach spectrophotometer. Finally, the experiment was repeated using calcined shell powder, with different concentrations of the adsorbent (5 g/L and 7 g/L), particle sizes (fine, 60–70 µm; coarse, >125 µm) and rotational speeds (125 rpm and 0 rpm). The parameters were obtained from previous studies on removal experiments using CaO catalyst or nanoparticles (Khoo and Esmaeili, 2018; Tamjidi and Esmaeili, 2019). No rotation was used to imitate the actual condition of the petrochemical's facultative pond. At a certain time (t), the adsorbed amount was calculated using Eq. (1), and Eq. (2) was used for the calculation of removal percentage.

$$q_t = \frac{C_i - C_t}{M} \times V \quad 1$$

$$\text{Removal \%} = \frac{C_i - C_t}{C_i} \times 100 \quad 2$$

C_i and C_t are initial concentration of the adsorbate and concentration at a given time. M is the weight of adsorbent dosage in g and V is the volume of the solution used in the adsorption studies.

2.7. Isothermal study

Isothermal study for adsorption was used to describe the molecular distribution adsorbate between the solid-liquid interface. Critical information, including the affinity, mechanism and favorability of the removal process can be explained from the adsorption isotherm (Khan et al., 2021; Nallakukkala et al., 2020; Senthilkumar et al., 2022). In this study, Freundlich and Langmuir isothermal equations were used to understand the adsorption process. As cited in Al-Ghouthi and Da'ana (2020), the Langmuir isotherm presumes a surface with homogeneous binding sites, and the mathematical expression is,

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \quad 3$$

In Eq. (3), C_e stands for the adsorbate concentration (mg/L) at the equilibrium time. The amount of adsorbate (mg/g) adsorbed at equilibrium time and maximum capacity (mg/g) are denoted by q_e and q_m. A graph of C_e/q_e vs C_e illustrates a straight line, where 1/q_m and 1/q_mK_L are expressed by the slope and intercept, respectively. R_L is a dimensionless equilibrium parameter (Eq. (4)), which indicates the favorability of the removal process (Al-Ghouthi and Da'ana, 2020).

$$R_L = \frac{1}{(1 + K_L C_0)} \quad 4$$

Freundlich isothermal model explains the multilayer adsorption on heterogeneous sites (Al-Ghouthi and Da'ana, 2020). The mathematical expression is given in Eq. (5)

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_f \quad 5$$

Adsorption capacity and intensity of adsorption are expressed by n and K_f, respectively, which are described as Freundlich constants. The two values are obtained from the slope and intercept of ln q_e vs ln C_e.

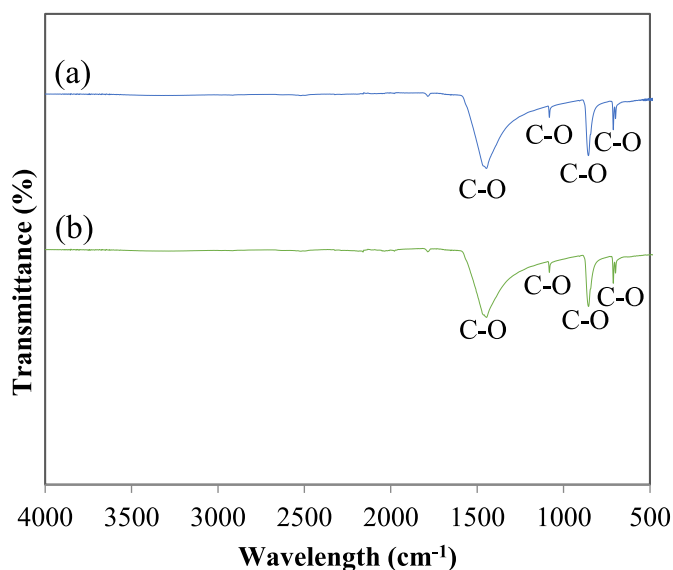


Fig. 1. FTIR spectra for raw shell powder (a) pre-treatment and (b) post-treatment.

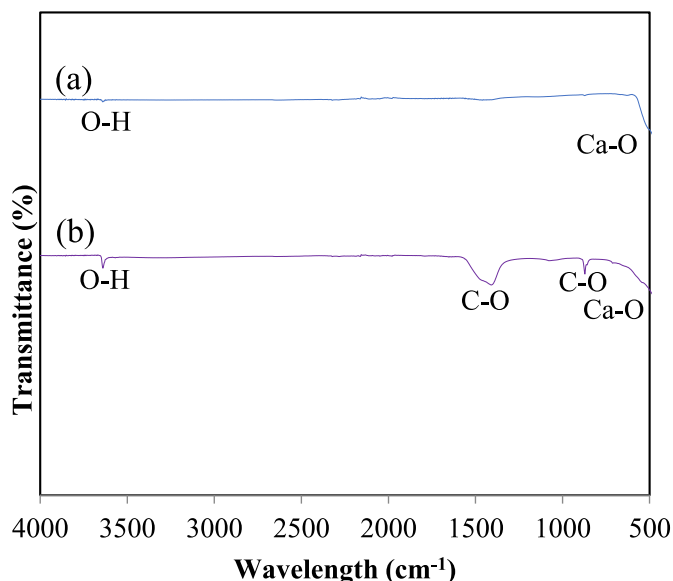


Fig. 2. FTIR spectra for calcined shell powder (a) pre powder and (b) post-treatment.

3. Results and discussion

3.1. Characterization of cockle shells

The characterization of shell powders was done using FTIR, SEM, EDX, XRD and BET. Fig. 1 describes the FTIR spectrum of the raw shell powder representing the CaCO_3 spectrum for pre-treatment and post-treatment. Referring to the FTIR spectrum, the sharp bands around 1450 cm^{-1} , 1100 cm^{-1} , 860 cm^{-1} and 710 cm^{-1} indicated the presence of C–O group in the raw shell powders. The result illustrated that the powder derived from cockle shells has the properties of carbonate group. Comparing the pre- and post-treatment for raw shell powder, the results revealed no changes nor other functional groups were present in the powder.

Fig. 2 displays the FTIR spectrum of calcined shell powder. The pre-treatment spectrum revealed a weak band at 3640 cm^{-1} that

represented hydroxyl group (O–H) due to the low moisture available in the powder. However, after the treatment, the spectrum clearly showed that there were changes in the peaks. The sharp O–H bands implied the reaction between calcium oxide (CaO) with water and formed calcium hydroxide ($\text{Ca}(\text{OH})_2$). Also, an intense band was noticed around 858 cm^{-1} , corresponding to the carbonate functional group.

SEM micrographs were used to study the morphological changes in raw and calcined shell powders. Fig. 3 (a) clearly exhibits that the raw shell appeared to be aragonite with typical layered sheets commonly found in molluscs. Needle-like and rod-like shapes could be identified from the figure, which proved the presence of aragonite polymorph (Ghafar et al., 2017; Jaji et al., 2017). In addition, from the EDX spectra, three main elements were present in the raw shell powders: calcium, carbon and oxygen. Meanwhile, Fig. 3 (b) displays the post-treatment image. An additional peak found in the EDX spectrum represented a phosphorus element (P). The observation proved phosphorus adsorption using raw cockle shells.

Fig. 4 (a) shows the morphology of calcined shell powder heated up to $900\text{ }^\circ\text{C}$ for 5 h. The morphology changed from layered sheets into a porous structure with rhombic shape due to transformation from aragonite to calcite (Ghafar et al., 2017; Jaji et al., 2017). The cavities that appeared in the calcined shell powder were formed possibly due to the release of carbon dioxide gas during the calcination process described in a study done by Buasri et al. (2013). Calcite polymorph tends to be more stable at room temperature compared to aragonite (Declat et al., 2016). The EDX spectra of calcined powder showed that only calcium and oxygen were present in the pre-treatment spectrum. However, there was a trace of carbon in the post-treatment spectrum, as indicated in Fig. 4 (b). The findings of FTIR also verified the carbon tracing as there was carbonate growth due to the de-ionization of Ca^{2+} and OH^- with carbonic acid which formed calcium carbonate.

Fig. 5 illustrates the XRD patterns of raw shell powder and calcined shell powder heated at $900\text{ }^\circ\text{C}$ for 5 h. Fig. 5 (a) presents that the peaks identified were CaCO_3 with aragonite polymorphs without any calcite and vaterite existed in the raw shell. Aragonite polymorphs of CaCO_3 were reported to be metastable under geological conditions and can be easily transformed into calcite at $380\text{--}470\text{ }^\circ\text{C}$, which is more stable (Ghafar et al., 2017).

Fig. 5 (b) shows peaks at 32.49° , 37.59° , 53.99° , 64.28° , 67.72° and 79.54° were claimed as CaO that formed due to the calcination of CaCO_3 , which transformed aragonite polymorph into CaO. However, the peaks at 48.06° and 51.4° were identified as CaCO_3 that was retained as calcite due to insufficient heat supplied to the powder during the calcination process (Shariffuddin et al., 2013). A few conditions must be complied with to achieve the maximum yield of lime. Calcination temperature must be beyond the CaCO_3 dissociation temperature. Adequate reaction time for complete calcination and carbon dioxide must be removed entirely to prevent the reversible reaction.

Table 1 illustrates the summary of the BET analysis. The surface area of the raw shell was determined to be $3.6598\text{ m}^2/\text{g}$, whereas the surface area of the calcined shell was observed to be $1.4197\text{ m}^2/\text{g}$, which was smaller after being calcined at $900\text{ }^\circ\text{C}$. CaO is more porous than CaCO_3 , according to Maya et al. (2018). The differences in porosity are due to the molar volumes' inequality. Calcination at high temperature reduces the surface area, thus develops the porosity. In fact, at elevated temperatures, particles tend to change and shrink in pores (Maya et al., 2018).

3.2. Phosphorous removal from wastewater

3.2.1. Effects of raw and calcinate shell powder

Fig. 6 shows the effects of raw and calcined shell powders on the percentage of phosphorus removal and pH. It demonstrates that calcined shell powder gave a higher phosphorus removal rate, up to 62.37% at minute 20, compared to raw shell powders. Phosphorus removal reaction by lime was more thorough under alkaline conditions as the

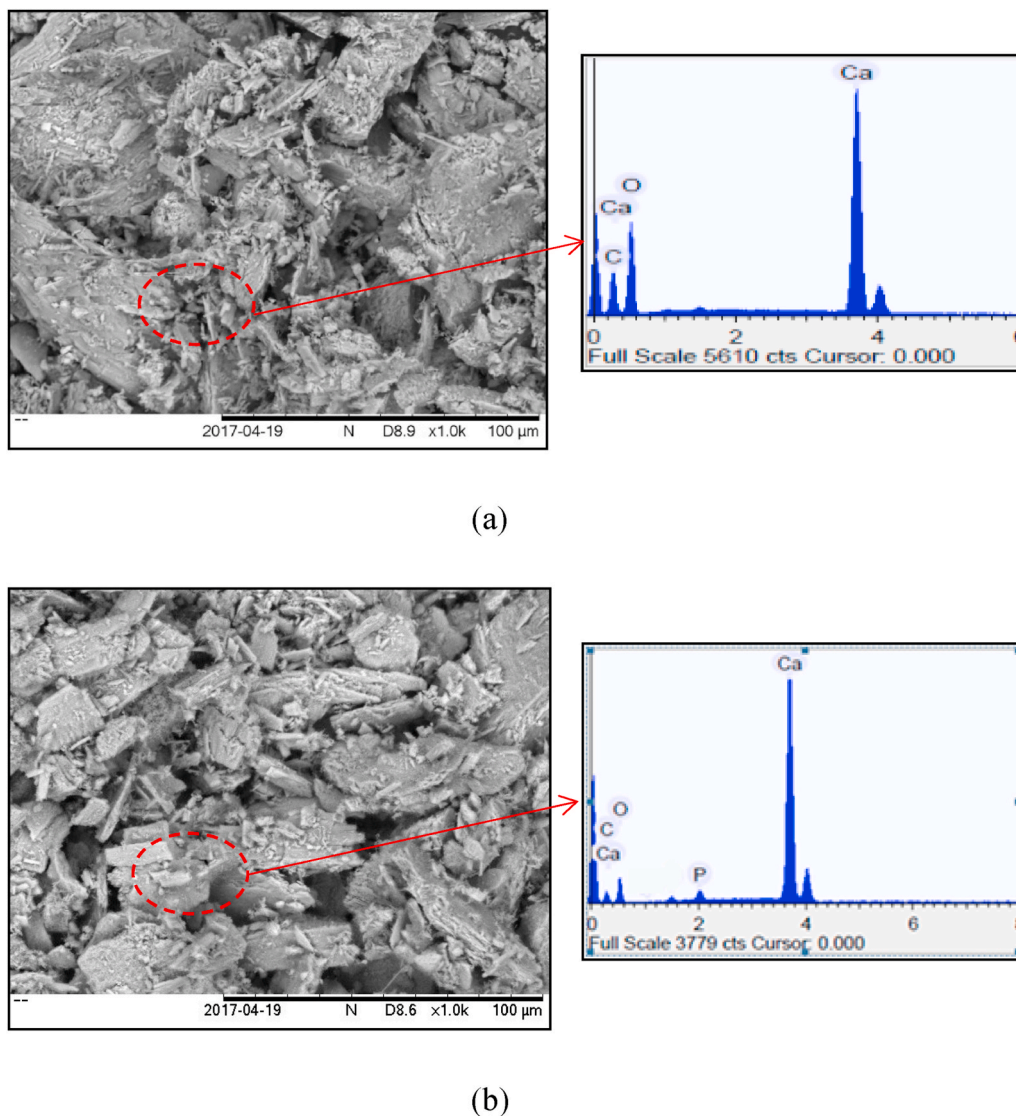
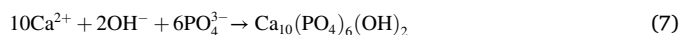
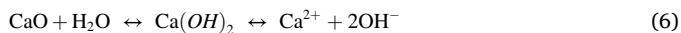


Fig. 3. SEM-EDX image of raw shell powder in the particle size range of 60–70 µm for (a) pre-treatment (b) post-treatment.

abundant presence of calcium ion and hydroxide ion stimulated the reaction in the direction of precipitation (Kasim et al., 2020), either heterogeneously on the particles' surface or homogeneously within the solution as followed by the dissolution of lime. The phenomena differed from the removal mechanism of raw powder, which was through adsorption. $\text{Ca}(\text{OH})_2$ has low solubility in water, which disassociates calcium and hydroxide ions (Kim et al., 2018).

Depending on the pH, insoluble hydroxyapatite (HAP) can be formed via the following reactions, which are (Equation (6)) and (Equation (7)),



The precipitation took place at higher pH (14). Greater pH favored HAP formation as the concentration of hydroxide and phosphate ions increased pH. It should be noted that the current study concerned with the pH. Even though calcined powder gave higher phosphate removal, but the pH boosted up to 10.71, which turned the solution into a very alkaline pH. The formation of $\text{Ca}(\text{OH})_2$ from the reaction of CaO with water was responsible for the phenomenon. Compared to the pH of the solution treated by raw shell powder, the pH was maintained throughout the 60 min under natural conditions. Due to this, the wastewater treatment with calcined shells was not further studied.

3.2.2. Effects of shell powder concentration

Fig. 7 shows the effects of shell powder concentration on the percentage of phosphorus removal and pH. The graph demonstrates that a concentration of 7 g/L gives the highest phosphorus removal, up to 52.27% after 40 min, and remains constant till 60 min, compared to the 3 g/L and 5 g/L. Higher concentration referred to more adsorbent dosage, increasing the number of active sites in unit volume (Kasim et al., 2020; Kim et al., 2018). Adsorption is dependent on the availability of binding sites for phosphate (dos Reis et al., 2020). Therefore, more binding sites available at higher concentrations allow more phosphate to be attached to the adsorbent surface. The trends started to decrease at minutes 40 for 3 g/L and 5 g/L due to the re-dissolving of phosphate as the system settles at equilibrium (Kasim et al., 2020). For the Effect of shell powder concentration on pH, the trends show no significant increases in pH for all adsorbent dosage initially and remain constant throughout the 60 min, which is due to the small amount of calcium ions dissolution (Kasim et al., 2020).

3.2.3. Effects of particle size

Fig. 8 shows the effects of particle size on the percentage of phosphorus removal and pH. The dimensions used were 60–70 µm (fine) and >125 µm (coarse). Referring to the results, higher phosphate removal could be achieved by using fine powder. Finer sizes give a larger total

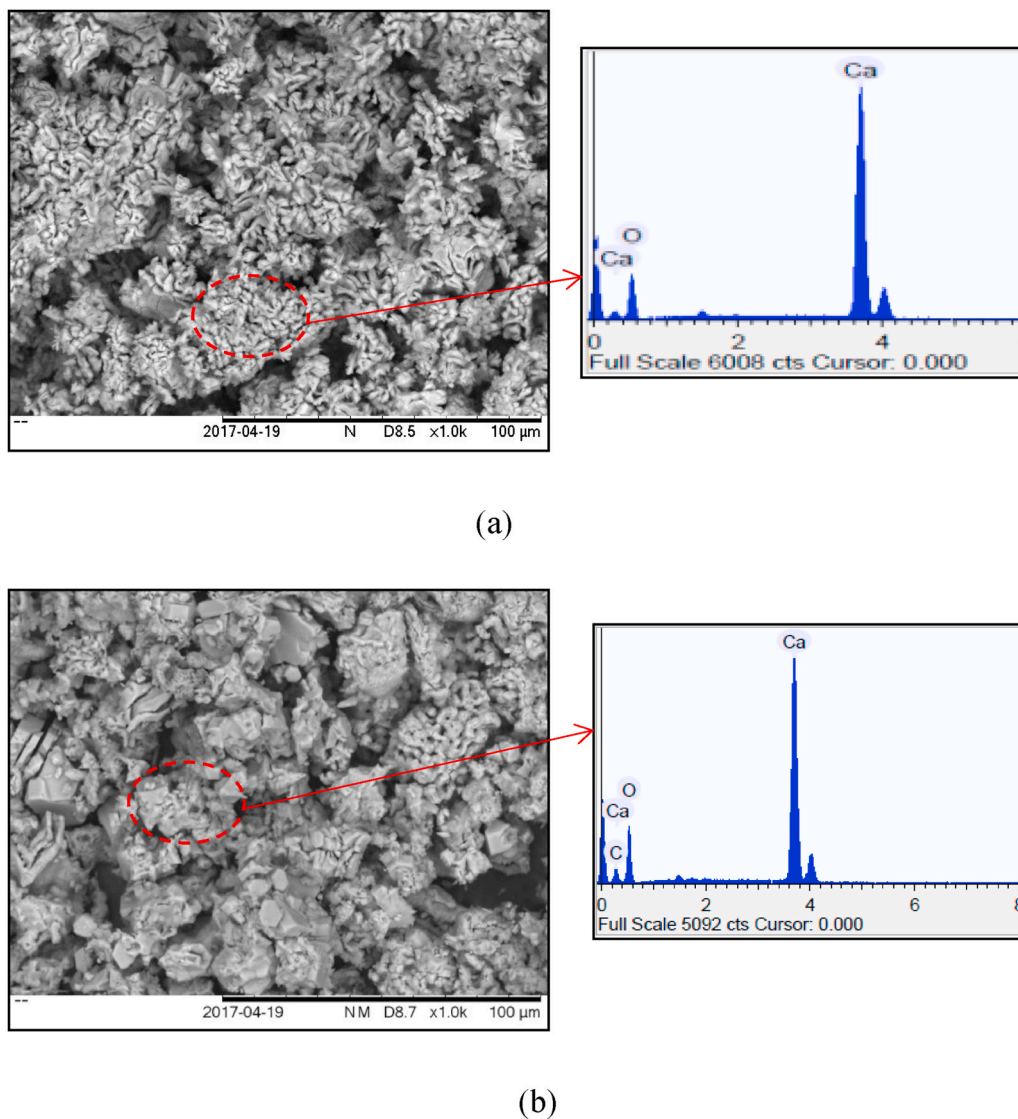


Fig. 4. SEM image of calcined shell powder in the particle size range of 60–70 μm for (a) pre-treatment, (b) post-treatment.

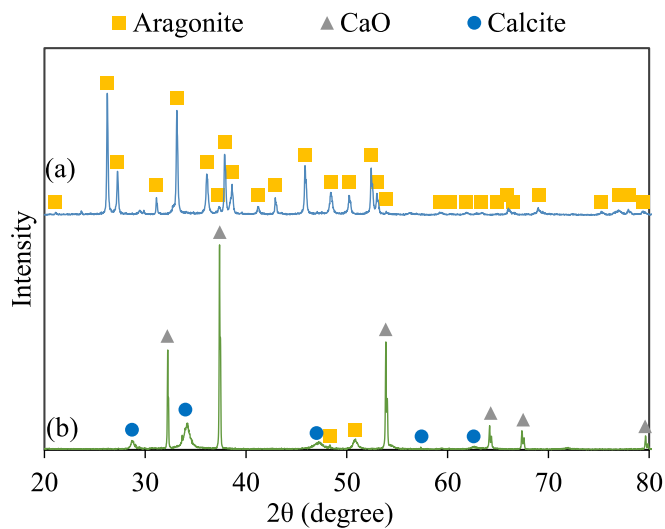


Fig. 5. XRD pattern of changes in the crystal structure and chemical composition of shell powder; (a) raw shell powder, (b) calcined shell powder.

Table 1

Summary of specific surface area (SSA), pore volume and adsorption average pore width of calcined shell powder by BET.

Sample	Specific Surface Area (SSA) m ² /g	Pore volume cm ³ /g	Adsorption average pore width (4 V/A by BET) nm
Raw shell, CaCO ₃	3.6598	0.003003	28.7477
Calcined shell, CaO	1.4197	0.002113	59.5247

surface area compared to coarse size (dos Reis et al., 2020; Kasim et al., 2020). Therefore, more active sites are available for the adsorption of phosphate (dos Reis et al., 2020). Fine powder in this study achieved up to 52.27% of phosphorus removal after 40 min compared to coarse powder that could only give 16.67% removal. For the effect of particle size on pH, the trends showed that pH remained constant throughout the experiment as the experiment was run using raw shell powders.

3.2.4. Effects of rotational speed

Fig. 9 shows the effects of rotational speed on the percentage of

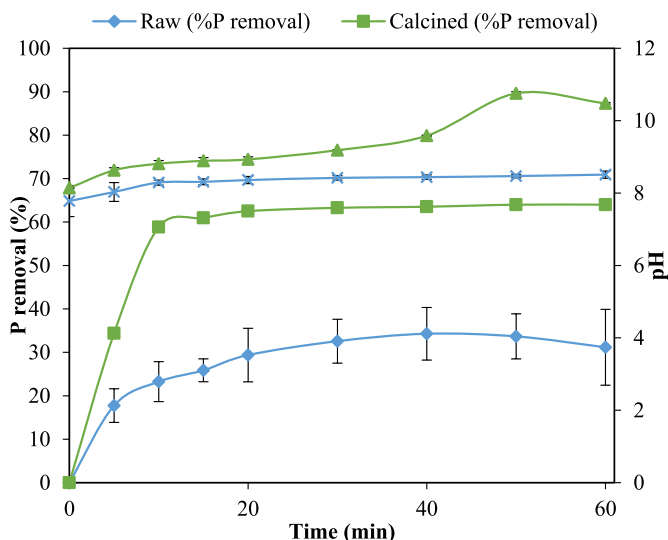


Fig. 6. Effects of raw and calcined shell powder on percentage of phosphorus removal and pH (particle size = fine powder, powder concentration = 7 g/L, rotational speed = 125 rpm).

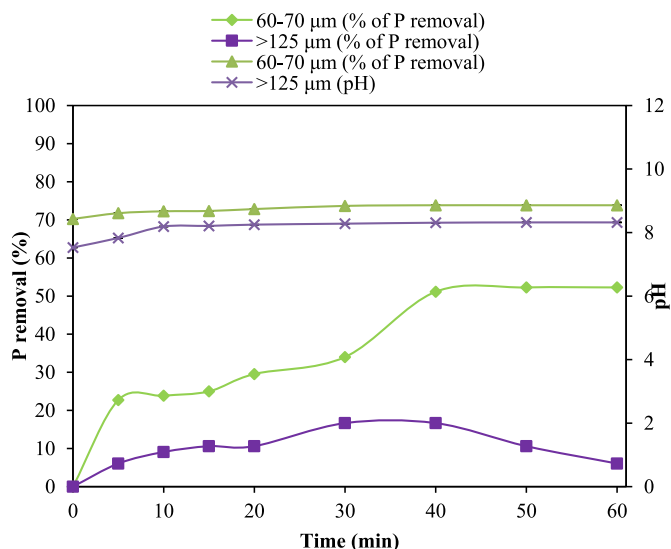


Fig. 8. Effects of particle size on percentage of phosphorus removal and pH. (type of powder = raw shell, powder concentration = 7 g/L, rotational speed = 125 rpm).

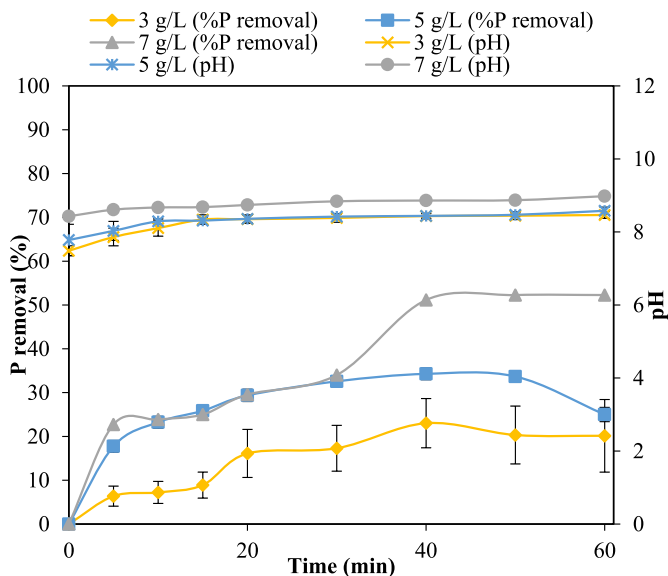


Fig. 7. Effects of shell powder concentration on percentage of phosphorus removal and pH (particle size = fine powder, type of powder = raw shell, rotational speed = 125 rpm).

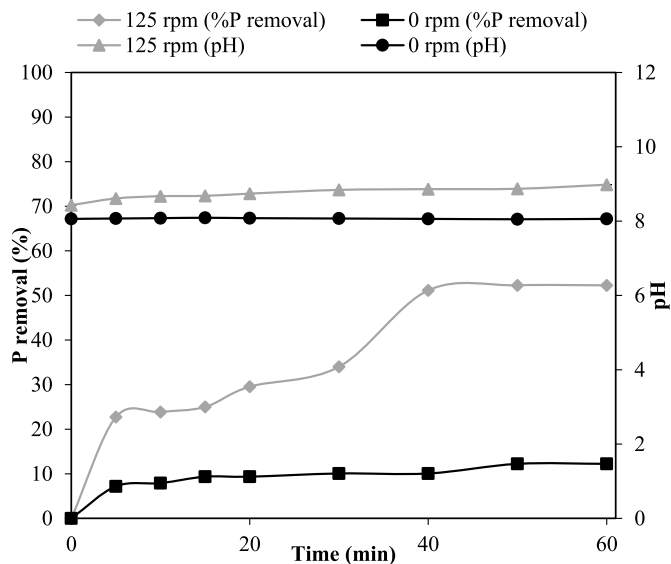


Fig. 9. Effects of rotational speed on percentage of phosphorus removal and pH (particle size = fine powder, powder concentration = 7 g/L, type of powder = raw shell).

phosphorus removal and pH. The rotational speeds used were 0 rpm (no stirring) and 125 rpm. From the graph, it can be observed that there was a significant difference when stirring was applied. The percentage of phosphorus removal could achieve up to 52.27% compared to no stirring that could only achieve the highest removal of 12.23% after 60 min of reaction. Stirring has a significant impact on mass transfer resistance (Deniz, 2020). When stirring is applied, it creates a turbulence flow as the fluid velocity increases, thus decreasing the boundary layer thickness and increasing Reynold number, as well as reducing the external mass transfer resistance into a negligible value. Therefore, a higher rotational speed will increase Reynold number, which provides a higher mass transfer rate, increasing the percentage of phosphorus removal. However, in industrial's facultative ponds, no agitation is applied. Therefore, the study with no stirring was preferable and suited the industrial condition. On the other hand, the trends revealed that the pH remained constant throughout the experiment as it was ran using raw

Table 2

List of calculated constants and parameters from Langmuir and Freundlich isothermal models.

Isotherms	Constant	Value in this study
Langmuir	q_m (mg/g)	0.1603
	K_L (L/mg)	-0.31
	R_L	-0.58
	R^2	0.9681
Freundlich	K_f	7.104
	N	-0.61
	R^2	0.9836

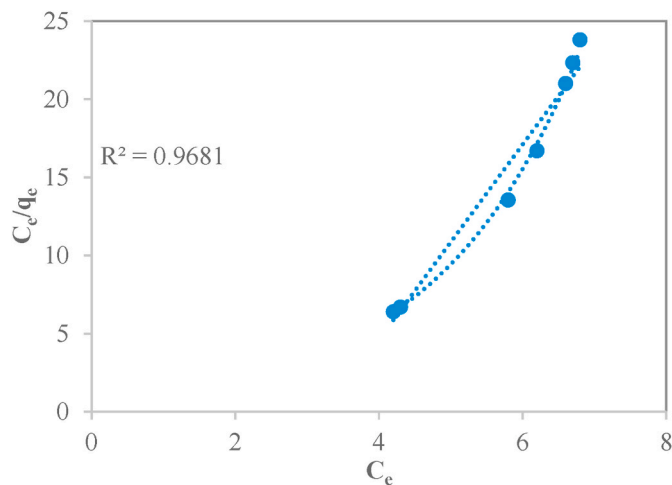


Fig. 10. Langmuir isotherm model for the removal of phosphorous using calcined cockle shells.

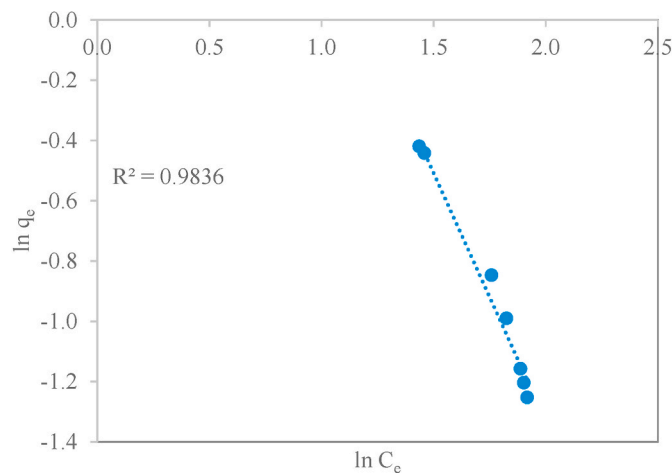


Fig. 11. Freundlich isotherm model for the removal of phosphorous using calcined cockle shells.

shell powder which gave slightly no changes in pH.

3.3. Adsorption isotherm

The parameters calculated from Langmuir and Freundlich isothermal models are listed in Table 2. The plots of Langmuir and Freundlich isothermal models are displayed in Figs. 10 and 11, respectively.

The adsorption of phosphorous using cockle shells occurred mostly onto heterogeneous sites (multilayer) rather than monolayer adsorption according to the R^2 value of Freundlich isotherm (0.9836). However, monolayer uptake played a key role as well ($R^2 = 0.9681$). The maximum uptake calculated from Langmuir isotherm was 0.1603 mg/g. The inadequate surface area obtained from BET analysis explained the phenomenon of low uptake. R_L was less than 1, which explains the favorability of the adsorption process.

4. Conclusion

The study was conducted to assess the capability of cockle shells in removing phosphorous from petrochemical wastewater through adsorption. The adsorbent characteristic was analyzed via FTIR, SEM, EDX, BET and XRD, which confirmed that the shells consisted of CaCO_3 , specifically in aragonite polymorph. Furthermore, the produced powder

from the cockle shells was used in the adsorption experiment that was carried out in a batch reactor under ambient pressure and temperature to study the optimum condition for optimum phosphorous removal.

Several parameters were studied, such as the effects of raw and calcined powders, adsorbent dosages, particle sizes and rotational speeds. It was observed that the optimum condition for effective phosphorous removal is under the presence of rotational speed, which can minimize mass transfer limitation. Besides, a considerable amount of adsorbent with smaller particle size can deliver better results as it will increase the total surface area of the adsorbent. As could be seen, using calcined shell powder can boost up the removal of phosphorous up to 50% removal. However, it is vital to consider the actual condition of the petrochemical facultative pond that concerns pH. The use of calcined shell powder can also boost the pH up to 12, which is inconsiderable for wastewater to be discharged. Therefore, raw shell powder is preferable as it can maintain the pH at neutral, but still can remove some amount of phosphorous.

In conclusion, the current study proved that cockle shells consist of CaCO_3 with aragonite polymorph that can act as adsorbent to remove phosphorous from wastewater. Therefore, the findings from this study are essential to promote the reusing of shell wastes to treat wastewater and at the same time reducing the environmental damage brought by the disposal of waste shells. In future, enhanced performances can be achieved by using other adsorptive materials such as chitosan, including zeolites with calcined cockle shells to increase the specific surface area.

Credit author statement

Abdullah Nayeem: Writing – original draft, Reviewing and Editing Farahin Mizi: Conceptualization, Methodology, Mohd Faizal Ali: Supervision, Funding acquisition, Jun Haslinda Shariffuddin: Conceptualization, Writing- Reviewing and Editing, Validation, Supervision, Project administration

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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