# Blood Cockle Shell: an agro-waste for N and P Removal of Shrimp Farm Effluent

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**Abstract**

This research investigated the removal efficiency of burned (activated) blood cockle shells (BBCS) of the total nitrogen (N) and phosphorus (P) effluent from shrimp farms, in comparison with novel activated charcoal (AC) and natural (unactivated) blood cockle shell (grinding, NBCS). All shell types (BBCS, NBCS) performed well as adsorbents The removal efficiency varied with shell particle size and effluent flow rate. The shell particle size of BBCS at 0.85-2.0 millimeters had the highest removal efficiency of total N and P at 86.66% and 87.63%, respectively. The best flow rate of effluent for N and P removal efficiency through adsorbency were 300 ml/hour. Moreover, the equilibrium model study for adsorption isotherm of BBCS performed better fitted to the Langmuir model in nitrogen removal, and to both Langmuir & Freundlich model in phosphorus removal. Our findings indicated that the higher surface area and larger average pore size of the adsorbents as BBCS (Bunauer, Emmett and Teller method: BET) produced more N and P removal efficiency than the lower one as NBCS.

*Key Words:* Nitrogen / Phosphorus / Removal/ Shrimp effluent / Burned/ Blood cockle shell

## 1. Introduction

Effluent from aquacultural farms is a significant problem with an impact on natural bodies of water, such as lakes, rivers, and seas. The cause is the high level of nutrients in effluent, such as nitrogen (N), ammonia ($NH_3$), and phosphorus (P). When these elements are released into a body of water, they will introduce nutrients, and consequently raise the level of the Eutrophication phenomena. This then initiates plankton bloom: plankton bloom is a consequence of a lack of dissolved oxygen in the water. Whenever there is no oxygen exchange process together with no surface wind in a body of water, a so called red water condition or red tide will occur. This red tide creates many problems as water can become poisonous to living organisms due to the accumulation of toxins in shells that can be transferred to shell consumers, which can include humans (Sirirattanachai and Thongra-a, 1993). Hence, at present there is an announcement from the Natural Resource and Environment Ministry on the standard of effluent release from coastal aquacultures (Ministry of Natural Resources and Environment (MNRE), 2004). The purpose of this announcement is to control the quality of water quality before it is released into a natural body of water. Therefore, every aquacultural farm has to establish such a process, so that their effluent conforms to standard before being released into a natural body of water.

Though there are many methods for the removal of N and P in effluent, they are not viewed favorably by local people due to the cost and skills required. However, all of those methods employ the adsorption medium principle, the method of adsorption is determined by the nature of the adsorption medium: surface area, pore structure, particle size, and nature of the adsorbent (ability in the dissolution, molecular weight and size, and polar of molecule, etc.) (Bhatnagar and Sillanpää, 2010). The Department of Fisheries

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reported (Department of Fisheries (DOF), 2009) that the blood cockle annual consumption was 81,959 tons in 2005. Consequently, the remnant shell after consumption was leftover in the environment without any sort of management. The main element of blood cockle shell (BBCS) is calcium carbonate ($CaCO_3$), its physical and chemical characteristics should be the same as oyster shell, which has been reported to have a good P adsorption capacity (Kwon et al., 2004). Moreover, increasing the capacity of adsorption can be introduced by increasing the surface area and decreasing particle size, and by a burning process. (Chang et al., 2000)

Therefore, it is the attempt of this study to investigate whether the natural structure of blood cockle shell (grinding, NBCS) or unactivated blood cockle shell and the modification of burned shell structure of BBCS can be used as an adsorption medium for N and P, similar to oyster shells. In particular, we aimed to confirm the removal of N and P of shrimp farm effluent, in comparison with activated carbon or activated charcoal (AC).

## 2. Methodology

### *2.1 Conceptual framework*

To test whether BBCS and its modified structure has the capability of total N and P removal of shrimp farm effluent, we designed the methodology shown in Figure 1.

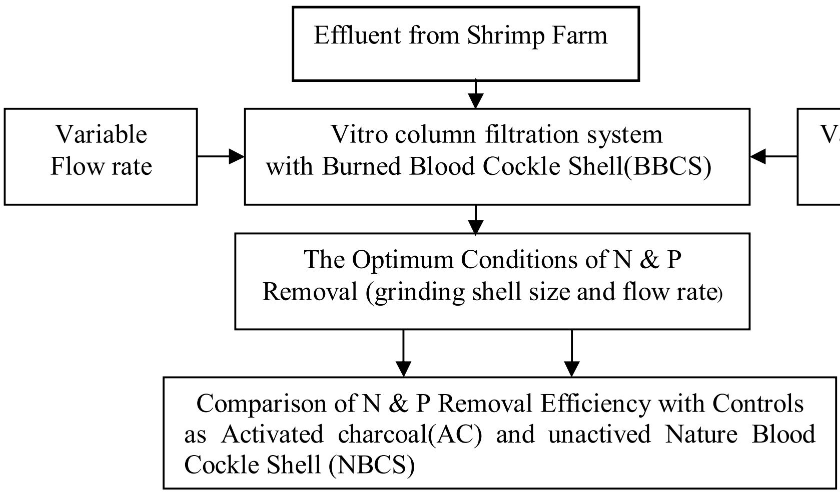



**Figure 1** Conceptual Framework of the Study

### *2.2 Blood cockle shell preparation*

Blood cockle shells (BCS) were immersed into clean water for 12 hrs., then they were brushed until clean, and dried in an open space. For BBCS production, some of them were put into an oven at 750°C for 1 hr. (Chaiyakam and Tunvilai, 1992). Then the burned shell was separated into 3 parts ground to sizes of 0.85-2.0, 0.3 – 0.35, and larger than 2.0 millimeter by a sieving method.

### *2.3 Vitro column filtration system preparation*

The vitro column filtration system (continuous adsorption system) was designed with a contact time of 8 hours, a flow rate of 300-900 ml/hour, in columns of diameter 75 mm. and 1 m in height. Filled adsorbents (BBCS, NBCS) of each size (0.85-2.0 mm. 0.3-0.35 mm. and >2.0 mm.) of each samples were of 60 cm. in height following previous research (Patpu, 2004; Wuttiyingyong, 1999).

### *2.4 Effluent quality of shrimp farm*

The effluent from the shrimp farm was collected from Black Tiger shrimps (Mr. Dacha Saeheng farm, Samutsakorn Province) at nearly the exact time of the experiment. The analysis was conducted by the Standard Method (American Public Health Association (APHA), 1992) collecting the below values:

1) pH (measured by numeric pH and temperature meter)

2) Alkalinity (indicator method)

3) Total P (Persulfate digestion/ Ascorbic acid method)

4) Total N rate (total Kjedahl Nitrogen; TKN)

5) BOD (Azide modification: 20°C: 5 days)

### *2.5 Blood cockle shell's physical properties*

Specific surface area and density of BCS was conducted by Bunauer machine, Emmett and Teller method (BET). The shell's structure pore size was estimated by Scanning Electron Microscopy (SEM).

### *2.6 Total N and P removal efficiency*

*2.6.1 With various burned blood cockle shell's sizes (BNBCS)*

1.1) We placed 0.85-2.0 millimeter of burned blood cockle shell in a glass column at 60 cm high. The effluent was released into the column with a constant rate, collecting samples after passing effluent through the column every hour for 8 hrs. Finally we analyzed the total P and N adsorbed by the samples. .

1.2) Repeated step 1.1, but changed the BBCS to be 0.3 – 0.35 mm.

1.3) Repeated step 1.1, but changed the BBCS to larger than 2.0 mm.

All 1.1, 1.2, 1.3 this process was repeated 3 times.

Then the adsorbent controls using natural blood cockle shell (NBCS) in the same various sizes and activated carbon (AC: AR grade 300 micron) were placed in the glass columns, released effluent passed through and analyzed N , P concentration, the experiment was repeated 3 times, in the same manner as above.

*2.6.2 With various flow rates of effluent*

The BBCS size with the highest adsorption ability was placed in No.2.5.1 in a glass column at 60 cm. in height. The effluent was released into the column with a constant flow rate at 300 ml/hour. Samples collected after the effluent had passed through the column every hour for 8 hours, was analyzed for the amount of total N and P. The experiment was repeated with the higher flow rate at 600, 900, 1200 ml/hours, samples were collected having had the effluent pass through the sample every hour for 8 hours and the samples were analyzed as mentioned. All processes were undertaken 3 times.

*2.6.3 Determination of nitrogen and phosphorus removal efficiency of burned blood cockle*

The removal efficiency of BBCS was determined through comparison by rate of total N and P removal with NBCS and AC in the best conditions of the above effluent flow rate and shell size. The experiment of the removal process was undertaken 3 times.

### *2.7 Adsorption Isotherm Study*

The Langmuir and Freundlich model (Song et al., 2012; Ghabbour and Davies, 2011; Okeola and Odebunmi, 2010; Bolster and Hornberger, 2007) was applied to describe the characteristics of adsorbents of BBCS. The Langmuir equation is

$$Q = Q_m K_a C / 1 + K_a C \qquad (1)$$

Where; Q is the substance quantity per adsorption weight,

$Q_m$ is the substance quantity per adsorption weight for complete monolayer,

C is the concentration of solute at equilibrium point,

$K_a$ is the state of adsorption heat.

The Freundlich equation is

$$X / M = K_f C^{l/n} \qquad (2)$$

Where; X is the quantity of solute adsorbed,

M is the weight of adsorption,

C is the concentration of solute at the equilibrium point, and

$K_f$ and N are constant values dependent on the temperature of the adsorption substance.

The constants $Q_m$ and $K_a$ via the Langmuir equation and K, 1/n via Freundlich equation were calculated. Finally, the linearized equation for Langmuir and Freundlich was conducted and the least square fit ($R^2$) in each equation was estimated.

The study was conducted fulfilling the best conditions of BBCS size (later performed with the size of 0.85-2.0 mm.) in the glass column of 60 cm. height. The synthesis effluents with concentration of 1 mg. N / liter and 1 mg. P/liter were poured into the column at the best constant flow rate (later performed at the rate of 300 ml/hour). Collected the passing effluent every hour for 8 hours, and analyzed the N and P concentrations. Then, the same method was conducted, but the synthesis effluents we changed with the concentration of i) 5 mg N/ liter, 5 mg. P/ liter, ii) 10 mg. nitrogen/ liter, 10 mg P/ liter and iii) 15 mg. N/ liter, 15 mg P/ liter. All processes were repeated 3 times.

## 3. Results

### *3.1 Effluent qualities of shrimp farm*

All of the collected effluent produced alkaline conditions in the ranges of 8.3-8.5 and BOD in 4.68-5.65 mg/l, both of which were within permitted levels (MNRE, 2007), but the total N, P exceeded permitted levels by 2 – 5 times (Table 1)

**Table 1** Effluent qualities of shrimps farm

| Parameters | Unit | Values | Maximum Permission* |
|---|---|---|---|
| pH | - | 8.3 – 8.5 | 6.5 -9.0 |
| Hardness | mg/L | 11.7 – 12.1 | - |
| Total Phosphorus | mg/L | 0.85 – 2.21 | 0.4 |
| Total Nitrogen | mg/L | 7.84 – 12.6 | 4.0 |
| BOD | mg/L | 4.68 – 5.65 | 20 |

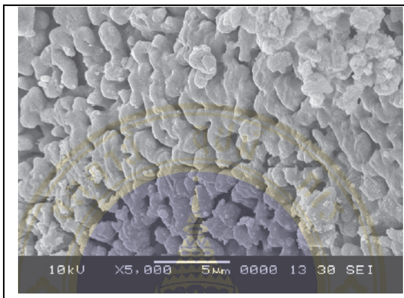
*Source: Pollution Control Department, 2001.

### *3.2 Blood cockle shell's physical properties*

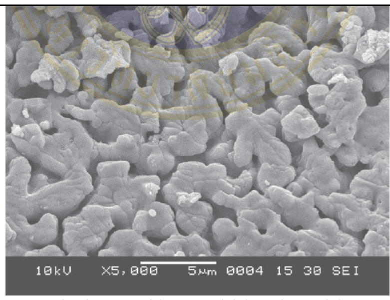
The BET method revealed that the BBCS had a BET surface area of 1.85 $m^2$/g, with an average pore volume of 0.002 $cm^3$/g., and an average pore size of 38.39 angstroms. BCS (not burned) had a surface area 1.72 $m^2$/g., an average pore volume of 0.002 $cm^3$/g. and an average pore size 37.24 angstroms (A°) (Table 2 and Figure 2).

**Table 2** Blood cockle shell's physical properties

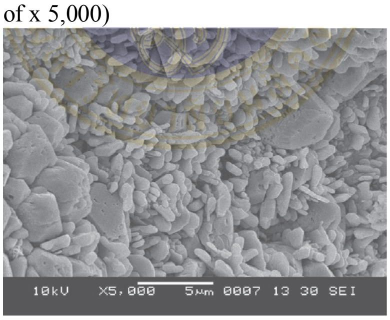
| Samples | BET Surface Area ($m^2/g$) | Average Pore Volume ($cm^3/g$) | Average Pore Size (A°) |
|---|---|---|---|
| Burned Blood Cockle Shell | 1.85 | 0.002 | 38.39 |
| Nature Blood Cockle Shell | 1.72 | 0.002 | 37.24 |



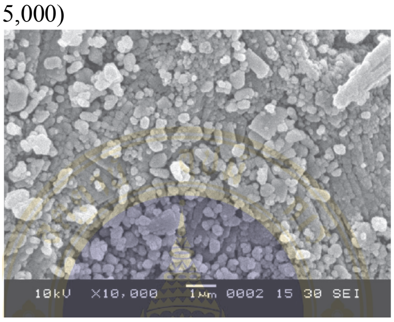

Morphology of burned blood cockle shell at size > 2.0 mm. (magnification of x 5,000)




Morphology of burned blood cockle shell at size 0.85 – 2.0 mm. (magn. of x 5,000)




Morphology of burned blood cockle shell at size 0.3 – 0.35 mm. ( magn. of x 5,000)




Morphology of natural blood cockle shell (magn. of x 10,000)

**Figure 2** Morphology of burned and natural blood cockle shell

### *3.3 The optimum conditions of nitrogen and phosphorus removal by BBCS*

Within the 3 sizes of blood cockle shell (0.3 - 0.35 mm., 0.85-2.0 mm., and >2.0 mm.), the size of 0.3 - 0.35 mm. performed the powder look. In the packed column, it obstructed the input effluent which could not move down, so we had to cancel this experiment. However, with the other 2 sieved shell sizes the water flowed quite well. The size of 0.85-2.0 mm. resulted in maximum efficiency for a total N removal of 86.66 % during the 4 hours, as well as 87.63 % of P during the same 4 hour measuring time. We also found that BBCS size of more than 2.0 mm. produced the maximum efficiency with a total N and P removal as high as 70.23% and 77.53%, respectively (Table 3).

**Table 3** Removal Efficiency of nitrogen and phosphorus of various burned shell sizes

| Time (hrs.) | Nitrogen removal | | | | Phosphorus removal | | | |
|---|---|---|---|---|---|---|---|---|
| | Burned size 0.85-2.0 mm. | | Burned size > 2.0 mm. | | Burned size 0.85-2.0 mm. | | Burned size > 2.0 mm | |
| | Concentration (mg/L) | Efficiency (%) | Concentration (mg/L) | Efficiency (%) | Concentration (mg/L) | Efficiency (%) | Concentration (mg/L) | Efficiency (%) |
| 0 | 12.6 | - | 7.84 | - | 2.21 | - | 2.21 | - |
| 1 | 4.76 | 62.22 | 5.6 | 28.57 | 2.17 | 1.81 | 0.97 | 56.26 |
| 2 | 3.92 | 68.88 | 5.13 | 34.52 | 1.81 | 14.03 | 0.84 | 61.99 |
| 3 | 2.52 | 80.0 | 3.64 | 53.57 | 1.76 | 48.42 | 0.54 | 75.41 |
| 4 | 1.68 | 86.66 | 2.33 | 70.23 | 0.27 | 87.63 | 0.5 | 77.53 |
| 5 | 3.36 | 73.33 | 2.52 | 67.86 | 0.55 | 74.96 | 0.64 | 70.89 |
| 6 | 3.64 | 71.11 | 2.8 | 63.09 | 0.68 | 69.23 | 0.8 | 63.80 |
| 7 | 4.2 | 66.66 | 3.73 | 52.38 | 0.88 | 60.18 | 0.84 | 61.99 |
| 8 | 4.29 | 65.92 | 5.13 | 34.53 | 1.17 | 47.21 | 1.03 | 53.55 |

### *3.4 The efficiency of the N and P removal at various flow rates*

We found an initial flow rate of 300 ml/hour (Wuttiyingyong, 1999), which was too low and not appropriate for shrimp farming practice. Hence, the study designed the experiment to cover a more rapid flow rate at 1, 2, 3 and 4 times higher than the initial flow rate (300, 600, 900 and 1200 ml/hr.). The efficiency of N and P removal is shown in Tables 4 and 5.

**Table 4** Efficiency of nitrogen removal by burned shell size 0.85-2.0 mm. at various flow rates

| Time (Hours) | Flow rate 300ml/hr. | | Flow rate 600ml/hr. | | Flow rate 900ml/hr. | | Flow rate 1,200ml/hr. | |
|---|---|---|---|---|---|---|---|---|
| | Concentration (mg/L) | Efficiency (%) | Concentration (mg/L) | Efficiency (%) | Concentration (mg/L) | Efficiency (%) | Concentration (mg/L) | Efficiency (%) |
| 0 | 12.6 | - | 12.6 | - | 8.12 | - | 7.48 | - |
| 1 | 4.76 | 62.22 | 6.72 | 46.66 | 5.69 | 29.87 | 5.23 | 33.33 |
| 2 | 3.92 | 68.88 | 5.69 | 54.81 | 5.13 | 36.78 | 4.57 | 39.29 |
| 3 | 2.52 | 80.00 | 5.13 | 59.26 | 4.48 | 44.83 | 4.48 | 42.86 |
| 4 | 1.68 | 86.66 | 4.20 | 66.66 | 3.92 | 51.73 | 4.23 | 46.43 |
| 5 | 3.36 | 73.33 | 3.92 | 68.89 | 4.01 | 50.57 | 4.67 | 40.47 |
| 6 | 3.64 | 71.11 | 4.39 | 65.18 | 4.67 | 42.53 | 5.23 | 33.33 |
| 7 | 4.20 | 66.66 | 4.76 | 62.22 | 5.23 | 35.63 | 5.60 | 28.57 |
| 8 | 4.29 | 65.92 | 6.72 | 46.66 | 5.69 | 29.89 | 6.16 | 21.43 |

**Table 5** Efficiency of phosphorus removal by burned shell size 0.85-2.0 mm. at various flow rates

| Time (Hours) | Flow rate 300ml/hr. | | Flow rate 600ml/hr. | | Flow rate 900ml/hr. | | Flow rate 1,200ml/hr. | |
|---|---|---|---|---|---|---|---|---|
| | Concentration (mg/L) | Efficiency (%) | Concentration (mg/L) | Efficiency (%) | Concentration (mg/L) | Efficiency (%) | Concentration (mg/L) | Efficiency (%) |
| 0 | 2.21 | - | 2.0 | - | 2.2 | - | 0.85 | - |
| 1 | 2.17 | 1.81 | 1.96 | 1.83 | 2.01 | 8.49 | 0.66 | 21.96 |
| 2 | 1.81 | 14.03 | 0.47 | 78.0 | 1.1 | 49.85 | 0.32 | 62.35 |
| 3 | 1.76 | 48.42 | 0.42 | 79.0 | 0.53 | 75.76 | 0.19 | 77.65 |
| 4 | 0.27 | 87.63 | 0.40 | 80.0 | 0.46 | 79.09 | 0.33 | 61.57 |
| 5 | 0.55 | 74.96 | 0.47 | 76.67 | 0.48 | 78.18 | 0.37 | 56.08 |
| 6 | 0.68 | 69.23 | 0.51 | 74.50 | 0.53 | 75.90 | 0.44 | 48.24 |
| 7 | 0.88 | 60.18 | 0.53 | 73.50 | 0.68 | 69.09 | 0.49 | 42.75 |
| 8 | 1.17 | 47.21 | 0.53 | 73.50 | 0.85 | 61.36 | 0.51 | 40.39 |

The efficiency of N removal by BBCS size at 0.85 –2.0 mm. at a flow rate of 300 ml/hr. obtained the highest removal efficiency at 86.66%, followed by 600, 900, 1,200 ml/hr. at the maximum peaks of 68.89%, 51.73% and 46.43%, respectively. Most removal occurred in the 4th.hour. The P removal at a flow rate of 300 ml/hour showed the highest efficiency (87.63%) in the 4th. hour. Measuring hourly, followed by 600, 900, 1,200 ml/hr at the maximum peaks of 80.0%, 79.09% and 61.53%, respectively. Most of the removal also occurred in the 4th hour.

### *3.5 The potential removal efficiency of BBCS*

The potential efficiency of N and P removal of BBCS was determined through an efficiency comparison with the actual adsorbents of activated charcoal (reference adsorbent, size 300 micron), and its NBCS (natural structure). NBCS produced a gradual increase of N removal from 4.88% during the 1st hour, to 12.19 % in the 2nd. hour and 19.51 % in the 3rd hour. A peak efficiency occurred at 31.71 % for 3 hours (for the 4th, 5th, 6th hours), and gradually decreased from the 7th hour measuring at 19.51% during the 8th hour. Although the P removal efficiency also gradually increased from the first hour at 46.27% and reached a peak efficiency at the 3rd hour, then gradually decreased to 33.83% during the 8th hour. The activated charcoal performed similarly with the removal of N during the first hour of measurement, and reached a maximum adsorption of 75% during the 3th and 4th hours of experimentation. The Removal of P was similar during the 1st hour and gradually increased in efficiency to 83.26% during the 4th hour. After this point, an obstruction of effluent flow occurred (Table 6).

**Table 6** The nitrogen and phosphorus removal efficiency of burned blood cockle shell (0.85-2.0mm.) in comparison with the reference adsorbents

| Removal | Adsorbents | Efficiency | Time (Hours) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Nitrogen | BBCS | Concentration (mg/L) | 12.6 | 4.76 | 3.92 | 2.52 | 1.68 | 3.36 | 3.64 | 4.2 | 4.2 |
| | | Efficiency (%) | - | 62.22 | 68.88 | 80.00 | 86.66 | 73.33 | 71.11 | 66.66 | 66.66 |
| | NBCS | Concentration (mg/L) | 11.48 | 10.92 | 10.08 | 9.24 | 7.84 | 7.84 | 7.84 | 8.12 | 9.24 |
| | | Efficiency (%) | - | 4.88 | 12.19 | 19.51 | 31.71 | 31.71 | 31.71 | 29.27 | 19.51 |
| | AC | Concentration (mg/L) | 10.08 | 4.2 | 3.36 | 2.52 | 2.52 | - | - | - | - |
| | | Efficiency (%) | - | 58.33 | 66.66 | 75.00 | 75.00 | - | - | - | - |
| Phosphorus | BBCS | Concentration (mg/L) | 2.21 | 2.17 | 1.87 | 1.7 | 0.27 | 0.28 | 0.32 | 0.81 | 1.54 |
| | | Efficiency (%) | - | 1.81 | 15.38 | 23.08 | 87.78 | 87.33 | 85.52 | 63.35 | 30.31 |
| | NBCS | Concentration (mg/L) | 2.01 | 1.08 | 1.08 | 0.85 | 1.14 | 1.23 | 1.23 | 1.23 | 1.33 |
| | | Efficiency (%) | - | 46.27 | 46.27 | 57.7 | 43.28 | 38.8 | 38.8 | 38.8 | 33.83 |
| | AC | Concentration (mg/L) | 2.21 | 0.46 | 0.44 | 0.41 | 0.37 | - | - | - | - |
| | | Efficiency (%) | - | 79.19 | 80.09 | 81.44 | 83.26 | - | - | - | - |

**Remark:** BBCS = Burned blood cockle shell, NBCS = Blood cockle shell (Natural form),
AC = Activated charcoal A.R.(300 micron)

### *3.5 Adsorption isotherm study*

As well, the constants $Q_m$ and $K_a$ through Langmuir equation and K, 1/n through Freundlich equations were calculated. Then the linearized equation for Langmuir and Freundlich was conducted and the least square fit ($R^2$) in each equation was found, as shown in Table 9.

**Table 7** Efficiency of nitrogen removal by burned blood cockle shell at the determined concentration (1, 5, 10, 15 mg/L) of synthesis effluent

| Time (hours) | Total nitrogen removal | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Concentration (mg/L) | Efficiency (%) | Concentration (mg/L) | Efficiency (%) | Concentration (mg/L) | Efficiency (%) | Concentration (mg/L) | Efficiency (%) |
| 0 | 1 | - | 5 | - | 10 | - | 15 | - |
| 1 | 0.84 | 16 | 4.2 | 16.0 | 7.84 | 21.6 | 1.15 | 92.3 |
| 2 | 0.56 | 44 | 3.64 | 27.2 | 7.56 | 24.4 | 1.14 | 92.4 |
| 3 | 0.28 | 72 | 3.08 | 38.4 | 7.0 | 30.0 | 0.58 | 96.1 |
| 4 | 0.28 | 72 | 2.52 | 49.6 | 6.72 | 32.8 | 0.48 | 96.8 |
| 5 | 0.28 | 72 | 2.24 | 55.2 | 5.32 | 46.8 | 0.12 | 99.2 |
| 6 | 0.56 | 44 | 2.52 | 49.6 | 6.44 | 35.6 | 0.17 | 98.8 |
| 7 | 0.56 | 44 | 4.20 | 16.0 | 7.84 | 21.6 | 0.18 | 98.8 |
| 8 | 0.56 | 16 | 3.64 | 27.2 | 7.56 | 24.4 | 0.24 | 98.4 |

**Table 8** Efficiency of phosphorus removal by burned blood cockle shell at the determined concentration (1, 5, 10, 15 mg/L) of synthesis effluent

| Time (hours) | Total phosphorus removal | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Concentration (mg/L) | Efficiency (%) | Concentration (mg/L) | Efficiency (%) | Concentration (mg/L) | Efficiency (%) | Concentration (mg/L) | Efficiency (%) |
| 0 | 1 | - | 5 | - | 10 | - | 15 | - |
| 1 | 0.91 | 9 | 0.14 | 97.2 | 0.34 | 96.6 | 1.15 | 92.33 |
| 2 | 0.90 | 10 | 0.12 | 97.6 | 0.32 | 96.8 | 1.14 | 92.4 |
| 3 | 0.86 | 14 | 0.12 | 97.6 | 0.16 | 98.4 | 0.58 | 96.13 |
| 4 | 0.16 | 84 | 0.12 | 97.6 | 0.13 | 98.7 | 0.48 | 96.8 |
| 5 | 0.12 | 88 | 0.11 | 97.8 | 0.11 | 98.9 | 0.12 | 99.2 |
| 6 | 0.12 | 88 | 0.12 | 97.6 | 0.11 | 98.9 | 0.17 | 98.86 |
| 7 | 0.12 | 88 | 0.12 | 97.6 | 0.12 | 98.8 | 0.18 | 98.8 |
| 8 | 0.14 | 86 | 0.13 | 97.4 | 0.13 | 98.7 | 0.24 | 98.4 |

**Table 9** The outputs of calculation through Langmuir and Freundlich equations

| | Concentration (mg/L) | Langmuir equation | | | Freundlich equation | | |
|---|---|---|---|---|---|---|---|
| | | $Q_m$ | $K_a$ | $R^2$ | l/n | $K_F$ | $R^2$ |
| Nitrogen | 1 | -1.0712 | -0.1208 | 0.2677 | 0.0391 | 0.1233 | 0.1898 |
| | 5 | -0.8055 | -0.1184 | 0.5537 | 0.058 | 0.3958 | 0.5896 |
| | 10 | -1.8512 | -0.0624 | 0.4073 | 0.024 | 0.8947 | 0.3338 |
| | 15 | -28.2486 | -0.0075 | 0.0116 | 0.002 | 2.0403 | 0.0097 |
| Phosphorus | 1 | -0.2344 | -0.1523 | 0.7606 | 0.167 | 0.0260 | 0.7504 |
| | 5 | -2000 | -0.0071 | 0.0696 | 0.00008 | 1.8047 | 0.0695 |
| | 10 | -112.359 | -0.1 | 0.648 | 0.0014 | 3.5851 | 0.6504 |
| | 15 | -33.333 | -0.1292 | 0.7624 | 0.0049 | 5.0898 | 0.7285 |

Hence, the reaction phenomena of N removal by BBCS followed the Langmuir equation, because the least square ($R^2$) in each concentration adsorption (1, 5, 10 and 15 mg/L and 1, 5, 10) were as high as 0.2677, 0.5537, 0.4073, 0.0116, while the least square ($R^2$) of Freundlich equation was less at 0.1898, 0.5896, 0.3338 and 0.0097 respectively. However, in consideration of P removal, there was no obvious difference of the least square ($R^2$) between Langmuir and

Freundlich equations as 0.7606, 0.0696, 0.648 and 0.7624 for Langmuir and 0.7504, 0.0695, 0.6504 and 0.7285 for Freundlich, respectively.

## 4. Discussion

The study of P and N removals by blood cockle shells, in various sizes of ground shells, flow rates, as well as the modification of adsorption capacity through the increasing pore volume and size by burning performed well, with some details to be discussed as follows.

### *4.1 Efficiency of blood cockle shell*

In consideration the removal efficiency of BNBC and NBC forms with the reference to adsorbents such as activated charcoal (analytical reagent AR grade, free of N and P contents, particle size 300 micron or 0.3 mm.) The activated charcoal started to perform the potential N and P removal as early as in the 1st hour of adsorption. The charcoal reached the maximum adsorption at 75% (N) and 83.6% (P) in the 3rd – 4th hour of experiment. Then, it became obstructed, or the life function was only 3-4 hours, compared with 8 hours of BNBC and NBC.

The study could not conclude whether BBCS had higher N removal efficiency than AC or not. But performed with a longer-life function, and thus it should have more removal capacity than AC. Furthermore, NBCS had a lower efficiency of P removal than AC during the first 3 hours, but after that, it showed the same potential, or the 8 hours of life function. Hence, NBCS should have greater potential than AC (life function only 4 hours).

It can be concluded that BBCS definitely has a higher N & P removal efficiency than NBCS. Therefore, the more BET surface area and bigger average pore size of BBCS created by burning produced greater adsorption efficiency than NBCS (see Table 2 and 6). This agrees with at least 2 studies. First, Delhoménie et al. (2002) stated that for the optimal N-concentration, the maximum elimination capacities decreased with pellet size, but increased with the specific surface area. Second, Kara (2006) emphasized that the adsorption efficiency depended on two parameters: the adsorbent dosage and the particle size (or surface area). The adsorption efficiency was proportional to increasing adsorbent dosage, and was inversely proportional to the particle size (optimal size).

### *4.2 Adsorption isotherm study*

Freundlich and Langmuir adsorption isotherms were used to model the equilibrium adsorption data obtained for adsorption of N and P on BBCS. Adsorption processes were executed by equilibrating various quantities of N and P synthesis effluents (1, 5, 10, 15 mg/L concentration). The Langmuir isotherm parameters $Q_m$ and $K_a$ indicate the monolayer capacity, and the Freundlich isotherm parameters $K_F$ and l/n indicate the extent of adsorption, and were determined from the adsorption equilibrium data of the various concentration. Correlation coefficients were determined to indicate or compare how fit each equation was. In N removal, the equilibrium adsorption data fitted well with Langmuir (see Table 9), it was indicated by the quite high value of $R^2$ in most synthesis effluent concentrations. While there were no obvious differences of correlation coefficients of $R^2$ values in P removal of both adsorption isotherms. P adsorption capacity of BBCS had same fit with both equations. So, the adsorption capacity of BBCS contrasted and confirmed with Okeola and Odebunmi (2010), who found that such activated carbons produced from different agro wastes (coconut shell, orange peels, maize cob), equilibrium of adsorption data of methylene blue (MB) and fitted well on both equations, as was evident from the high value of $R^2$ of 0.99 . In the other aspects, the larger molecule size (MB) of adsorbate had the higher adsorption capacity. Song et al. (2012) suggested that the adsorbent was suitable for adsorption when its critical pore width was 2 times larger than that of the adsorbate molecule diameter.

### *4.3 The potential of N & P removal efficiency of burned cockle shell*

Our findings show that BBCS (by percentage of removal efficiency) had a greater capacity of N and P removal than an aerated lagoon effluent by chemical precipitation (Khonkhaysap, 1998) and sea weed (Thongtong, 1986). Filter sand, antacite and concrete residue showed higher P removal efficiency than BNBC (Taweesup, 1996; Thawornjarernpong, 1998). While BNBC performed the lower efficiency of P removal, in comparison with the iron slag (Wuttiyingyong, 1999) and oyster shell (Kwon et al., 2004).

## 5. Conclusion

Adsorption processes are necessary for water treatment of households, community and production units, etc. Activated carbon is known to be a universal adsorbent for the removal of N & P from waste water. However, it is limited due to its high costs and short-life function. Attempts have been made to develop inexpensive adsorbents with longer life function, utilizing numerous agro-waste materials. In this study, the utilization of agro-wastes such as, blood cockle shell presents many attractive features in comparison with the standard adsorbent material of activated carbon. Although previous studies have shown tremendous results, there are still some issues which need to be considered , such as i) the adsorbent–adsorbate characteristics or the effectiveness of adsorbent and adsorbate, ii) the environmental conditions and variables used for the adsorption process, e.g. pH, temperature, concentration, initial adsorbate/adsorbent concentration etc., iii) the conditions of the surface modification of adsorbents in order to optimize efficiency and cost, iv) the feasibility of the regeneration mechanism of adsorbents, as well as the recovery of adsorbates to be reused. Moreover, studies should not be limited only to lab scale, but also pilot-plant studies to check their feasibility on a real life scale. Lastly, the end use of or environmentally safe disposal of adsorbent-adsorbates should be considered.

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