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Wasted cockle shell (*Anadara granosa*) as a natural adsorbent for treating polluted river water in the fabricated column model (FCM)

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ABSTRACT

The potential use of crushed cockle shells (*Anadara granosa*) for treating polluted river water in the fabricated column model was investigated along with the determination of the optimum amount of *A. granosa* used in the fabricated column model based on the results obtained from the series of jar test experiments performed during the study. The result shows that the crushed cockle shell could reduce chemical oxygen demand with the adsorption capacity of 5.3191 mg g^{-1}. Moreover, based on adsorption isotherm, it is shown that the adsorption data best fitted for Freundlich ($R^2 = 0.9798$) when compared to Langmuir isotherm ($R^2 = 0.5737$). The breakthrough curves plotted based on the data obtained from fabricated column model experiment indicates that the exhaustion time of crushed cockle shell was on the third day. The linearization of breakthrough curves based on Thomas model, Yoon–Nelson model, and Adam–Bohart model, shows that the curves best fitted with Adam–Bohart model, since the value of R^2 was higher compared to the other models tested during the experiment.

Keywords: Crushed cockle shells; Adsorption kinetics; Breakthrough curve; Dynamic column; Fabricated column model

1. Introduction

The accumulation of nutrients in waterbody led to eutrophication due to the abundant growth of algae [1]. Several physical, chemical, and biological treatments have been introduced like ion exchange [2,3], coagulation/flocculation [4,5], precipitation [6], membrane filtration [7], and biological treatment [8] for treating wastewater. But the majority of them are

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costly, time-consuming, and generates high amount of sludge [9]. Adsorption is a physicochemical process and widely used in many studies due to its special characteristic of having porous and high surface area. Other features that evaluate the overall behavior of adsorption are adsorption efficiency and adsorption capacity in the removal of organic and inorganic pollutant [10].

The development of low-cost adsorbent is nowadays getting the attention of many researchers. The abandoned waste generated from power plants, agricultural and fishery industries is at a crucial stage because of this issue; re-utilization of these waste materials needs to be expanded. The utilization of industrially generated waste ash as one of promising adsorbent for the removal of organic and inorganic pollutant has been introduced and studied recently [11–13]. Agricultural waste has also been reported as a low-cost adsorbent for the removal of organic matter present in the polluted water [14–17]. Wastes produced from fishery industries such as mussel shells, oyster shells, and mollusk shells [18–21] are extensively used as adsorbent and they show high performance for the removal of organic and inorganic pollutants. Apart from that, cockle shell or *Anadara granosa* can be potentially used for the wastewater treatment by adsorption process. Budin et al. [22] studied the ability of crab and cockle shell to adsorb lead and chromium from industrial effluent, and from their study, it was found that the removal of lead and chromium using cockle shell was due to the presence of $CaCO_3$ in the cockle shell.

In Malaysia Ninth Plan, the cockle production is expected to be around 13,000 metric tons [23] and this has provided the indication that the generation of waste cockle shell will also increase simultaneously. Due to this reason, the pressing need for the preservation of nature and re-utilization of waste have fueled the search for developing alternative solutions in creating a sustainable environment.

This study observed the ability of natural adsorbent such as the cockle shell (*A. granosa*), collected from marine waste, for the treatment of polluted river water using a jar test and also for its application in the fabricated column model system. In order to determine its static adsorption in jar test, Freundlich and Langmuir isotherms were applied and for the investigation of dynamic adsorption in the fabricated column model, mathematical models such as Thomas, Yoon–Nelson, and Adam–Bohart models were used. The value of R^2 obtained from the linear regression plot determined the best model for describing the adsorption process.

2. Materials and methods

2.1. Preparation of adsorbent

The cockle shell or *A. granosa* was collected from the Fisheries Research Institute, Gelang Patah, Johor, Malaysia. Initially, the shells were washed thoroughly with tap water and rinsed with deionized water in order to remove sand and other impurities. Then, the shells were dried naturally under sunlight for 3 d and later with oven drying at 105˚C for 24 h. Next, the shells were crushed and sieved to approximate size of 1 mm and stored in polyethylene bag as to prevent the addition of moisture until further use.

2.2. Experimental procedure

2.2.1. Static adsorption experiment

The static adsorption experiment was carried out using the jar test experimental method. The effect of adsorbent amount and saturation time were studied. The water sample collected from the Desa Bakti River, located in Universiti Teknologi Malaysia was treated with a constant volume of 1 liter for seven consecutive days.

In order to study the effect of adsorbent amount in reducing the chemical oxygen demand (COD) level present in water sample, the range of adsorbent applied was 1–4 g/L. In order to minimize the experimental errors, a control sample was prepared. Now, all the beakers were placed in the jar test machine (SAS-TEC) by lowering the paddle as to stir (100 rpm/min) the water sample in order to provide a constant concentration in all of the beakers. Finally, the water was allowed to settle for about 30 min. 10 ml of the wastewater sample was mixed with COD reagent as to determine the COD value in each of the beakers. A, HACH DR-5000 spectrophotometer was used to examine the value of COD.

The total removal of COD is calculated based on the equation shown below:

$$\text{Removal}(\%) = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 \tag{1}$$

where C_0 is the initial concentration of the river water sample (mg/L) and C_e is the final concentration (mg/L). The amount of COD adsorbed per unit of cockle shell at equilibrium was calculated according to the following equation (Eq. (2)):

$$q_e = \left(\frac{C_0 - C_e}{m}\right) \times \text{Volume of water sample (L)} \tag{2}$$

2.2.2. Method of analysis for static adsorption using adsorption isotherm study (Langmuir and Freundlich kinetic isotherms)

Generally, the mechanism of adsorption shows faster progression of physical and chemical processes, and it is generally known as the accumulation process. Appropriate analysis and design requires suitable isotherm to analyze and provide essential information. Equilibrium modeling based on specific isotherm is practiced in order to describe the adsorption data and parameters that are obtained from different models. Langmuir and Freundlich isotherms [23–25] are applied in this study in order to analyze the adsorption equilibrium data.

Langmuir sorption isotherm portrays the uptake that happens on a homogeneous surface and is expressed as shown below:

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

where q_e (mg/g) is the solid phase concentration and C_e (mg/L) is the liquid phase concentration of adsorbate at equilibrium. While q_m (mg/g) is the maximum adsorption capacity and K_L (L/mg) is the adsorption equilibrium constant. The value of K_L and q_m is obtained from the interception of the graph C_e/q_e and C_e.

Freundlich is the widely used isotherm to describe the adsorption equilibrium and it is an empirical equation which is capable of describing the adsorption of organic and inorganic compounds, and it is expressed as:

$$q_e = K_F C_e \tag{4}$$

This equation (Eq. (4)) also can be represented in the linear form (see Eq. (5))

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{5}$$

From the graph of log q_e vs. log C_e, the value of $1/n$ is obtained from the slope and the intercept magnitude shows the value of log K_F.

2.2.3. Design of fabricated column model

Fig. 1 illustrates the schematic diagram of the fabricated column model. The column model was designed to the height of 7.5 inch, diameter of 2.0 inch in a close loop with three columns arranged in series. This design is capable of monitoring the efficiency of adsorbent in reducing the level of total phosphorus (TP), total nitrogen (TN), COD, and biological oxygen demand (BOD) in river water that is being pumped into the collection tank. Water sample in the collection tank was continuously circulated in FCM in the presence of adsorbents up to the optimum day, as per the jar test experiments conducted earlier. The efficiency rate of the adsorbent was obtained by comparing the initial concentration of water sample at day 0 and day 3, after it has undergone the treatment with the adsorbents present in the column series.

The operation of FCM started by pumping the water from the Desa Bakti River into the collection

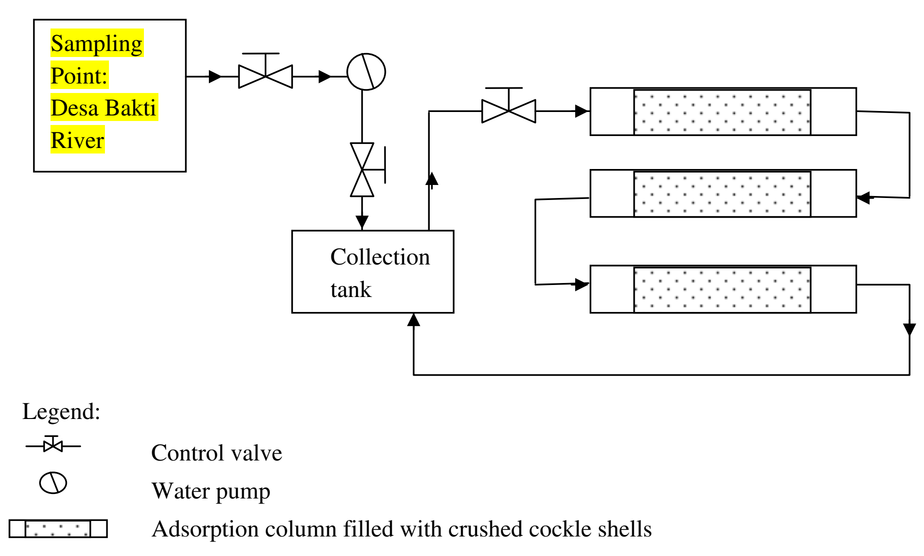

Fig. 1. Schematic diagram of fabricated column model.

tank up to 200 L and the total amount of adsorbent used was 600 g per treatment. The water was consecutively circulated from day 0 until day 3 as to prove the saturation attained by the crushed cockle shells and, at the same time, to determine the efficiency of adsorbent in reducing the level of nutrient present in the Desa Bakti River. This was done by taking water every day from the outlet, checking the value of each of the parameters obtained after analyzing in the laboratory. Finally, the data were evaluated by plotting the breakthrough curves. This experiment was mainly focused as to investigate the applicability, practical approach, and the ability of the crushed cockle shell in reducing the amount of nutrient present in the river water sample.

2.2.4. Breakthrough curve analysis for the determination of dynamic adsorption process

According to Chowdury and Saha [26], the plotting of breakthrough curve is essential when the adsorption experiment is conducted in a column model for analyzing the dynamic of adsorption process. Breakthrough curve was obtained by plotting the graph of C_t/C_0 vs. time, where C_t is the concentration of nutrient present in the river water sample at any time t (mg/L) and C_0 is the inlet concentration of the river water sample (mg/L).

Breakthrough time, t_b, is the time where the nutrient concentration reached 1 mg/L and adsorbent exhaustion time, t_e, is the time where the concentration of effluent attained is 99.5% of its initial concentration. The area above the breakthrough multiplied with flow (F) is representing the total amount of nutrient adsorbed by the crushed cockle shell, m_{ad}.

Following Chowdury and Saha [26], the effluent volume (V_{eff}), the total amount passing through the column model (m_{total}), and total nutrient removal determining the performance of crushed cockle shell as adsorbent material were calculated as follows:

$$V_{eff} = Ft_e \quad (6)$$

$$m_{total} = C_0(V_{eff}) \quad (7)$$

$$\text{Total removal } (\%) = (m_{ad}/m_{total}) \times 100 \quad (8)$$

3. Results and discussion

3.1. Determination of the optimal amount and contact time of crushed cockle shell in jar test experiment

The total amount of adsorbent used provided greater consequences toward the static and dynamic adsorption process. It shows the ability of adsorbent in removing excessive nutrient or pollutant present in the water sample [27]. The effect of the amount of crushed cockle shell used in treating 1 liter of polluted river water sample was investigated in the jar test experiment by varying the amount of crushed cockle shells ranging from 1 to 4 g.

The percentage of COD reduction using crushed cockle shell was calculated according to the mass balance equation. It is seen from Fig. 2 that the percentage of reduction increased along with the increasing of the crushed cockle shell. The maximum COD reduction of 38.8% was found with 3 g/L of crushed cockle shell and the increasing amount of crushed cockle shell did not show significant levels of reduction, which clearly indicates that the adsorption yield is due to the binding of all the nutrients onto the adsorbent surface [9,28].

It was observed that with the increasing amount of crushed cockle shell the equilibrium adsorption capacity (q_e) was found to be decreased, thus, resulting in lesser COD reduction. This is because of the reduction in the total adsorption surface area available for the molecules, which results from the overlapping of the aggregation of adsorption sites [29,30]. Thus, from Fig. 2, it can be seen that the optimal amount of crushed cockle shells obtained from jar test experiment was 3 g/L. In addition, the potential use of *A. granosa* as an adsorbent with the optimal amount of 3 g/L was also monitored from day 0 to day 4. Fig. 3 shows that the percentage of COD removal increased up to 24.39% at day 1 and the maximum removal efficiency of 37.25% was found at day 3. The rapid COD removal at the early stage is due to the reason of having a high number of active binding sites on the surface of cockle shell which provided more availability

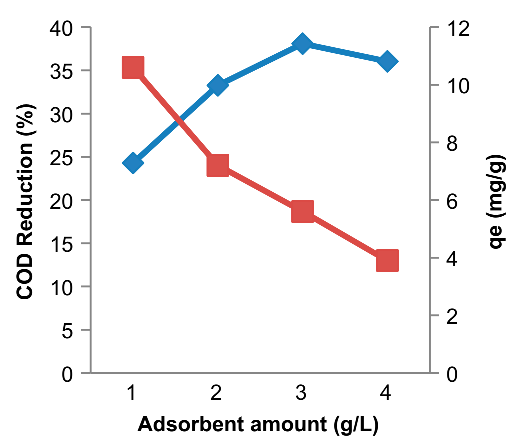

Fig. 2. Effect of adsorbent amount in COD reduction using crushed cockle shells.

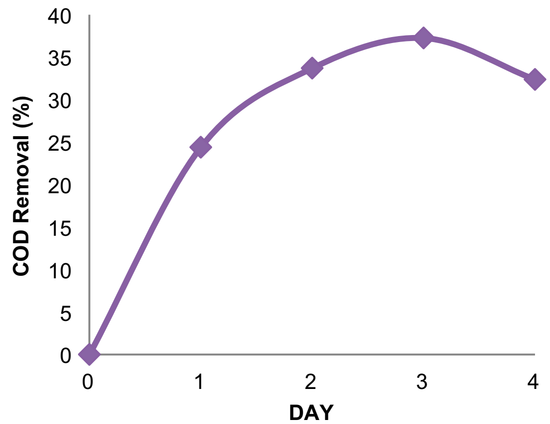

Fig. 3. Effect of contact time in COD reduction using the crushed cockle shell.

for the adsorption process to occur [31,32]. However, during the later stages, the removal rate of COD decreased to 32.37% at day 4. The decreasing of COD removal is due to the reduction of active binding sites, which also indicates the saturation point of the cockle shell during the adsorption process [11,31–33].

3.2. *Analysis of jar test experiment using Freundlich and Langmuir isotherms*

Adsorption isotherm is a vital analysis for wastewater treatment, as it defines the estimation of absorption capacity of the adsorbent materials. Fig. 4 represents Langmuir and Freundlich isotherms of COD reduction using crushed cockle shells with the optimum amount of adsorbent as 3 g/L.

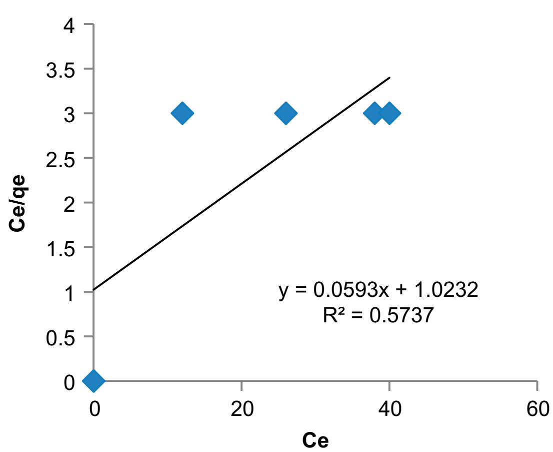

Fig. 4. Langmuir isotherm plot for the reduction of COD in water sample (Condition: pH 6.5, adsorbent amount: 3 g/L).

Table 1
Coefficients of Langmuir and Freundlich isotherm models for COD uptake using the crushed cockle shell

	Langmuir constant			Freundlich constant		
Parameter	q_{max}	K_L	R^2	$1/n$	$\log K_F$	R^2
COD	0.0593	1.0232	0.5737	1.4064	0.0754	0.9798

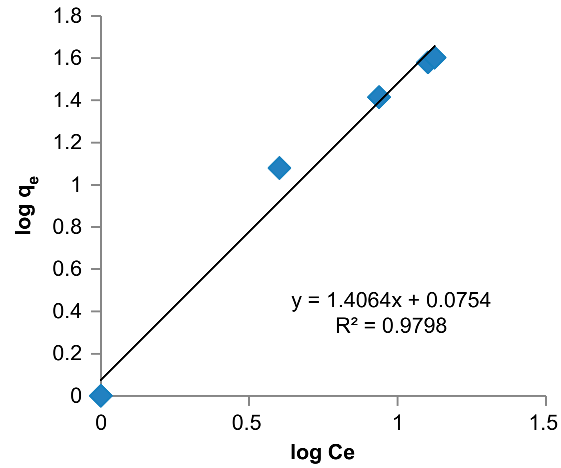

Fig. 5. Freundlich isotherm plot for the reduction of COD in water sample (Condition: pH 6.5, adsorbent amount: 3 g/L).

The correlation coefficient and constant from Eqs. (3)–(5) are presented in Table 1. The correlation value obtained from the Langmuir equation shows that the value of R^2 is 0.5737, which is found to be lower than the Freundlich equation with the R^2 value of 0.9798. This shows that the Freundlich isotherm model is more suitable for determining the adsorption equilibrium required for COD uptake using crushed cockle shell [34–36] (Fig. 5).

3.3. *Determination of saturation point and performance of crushed cockle shell as adsorbent in the fabricated column model*

The optimum amount of crushed cockle shell used in the fabricated column model was 600 g for 200 L of working volume, which was determined based on the preliminary experiment carried out during the jar test and the same was used in the further experiments. Now, the performance of crushed cockle shell in the fabricated column model was evaluated using breakthrough curve plots as shown in Fig. 6.

At the beginning of the experiment, it was found that the breakthrough point of total phosphorus (TP)

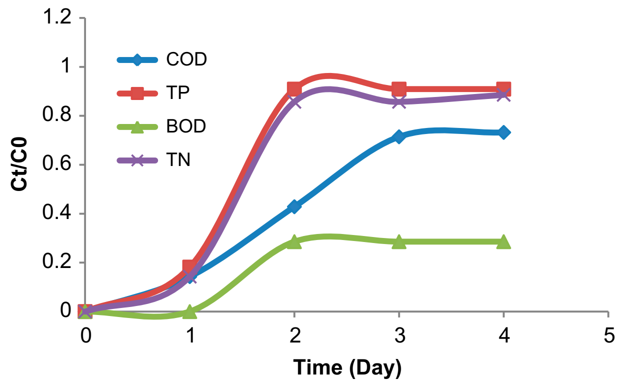

Fig. 6. Breakthrough curve plot based on the fabricated column model using cockle shell.

and total nitrogen (TN) reached earlier, when compared to COD and BOD. Table 2 shows that the removal of TP is high when compared to other nutrients that are present in the polluted river water sample. This shows that the main element present in the cockle shell might be calcium carbonate ($CaCO_3$), which resembles oyster shell in providing higher absorption rate for phosphorous [37,38].

The exhaustion time or saturation time, t, of crushed cockle shells was found to be on day 3 as seen from the plots in Fig. 6 and indicates that at day 3, the active binding sites for crushed cockle shell has saturated.

3.4. Breakthrough curve testing using mathematical empirical models: Thomas, Yoon–Nelson, and Adam–Bohart models

3.4.1. Thomas model

In the Thomas model study, the velocity of the fluid is assumed to be constant across the column pipe or used to be known as plug flow behavior. The linear equation of Thomas model is described as below:

$$\ln\frac{C_0}{C_t} - 1 = \frac{k_{TH} q_0 m}{Q} - \frac{k_{TH} q_0 V_{eff}}{Q} \quad (9)$$

where k_{TH} (mg d/m^3) is the Thomas rate constant, q_0 (mg/g) is the equilibrium adsorbate uptake, and m is the amount of adsorbent in the column (g). The value of k_{TH} and q_0 was determined from the slope and interception of $\ln C_0/C_t - 1$ vs. t [39,40].

Table 3 shows the Thomas model parameters for the fabricated column model using linear regression analysis.

Table 2
The determination of nutrient removal using cockle shell through breakthrough curve analysis

Volume influent (L)	Flow (m^3/d)	Initial conentration (mg/L)		Exhaustion time, t_e (d)	Volume effluent, V_{eff} (L)	Total amount of nutrient adsorbed, m_{ad}	Total amount of nutrient passing through, m_{total}	Total removal of nutrient (%)
200	11.49	COD	56	3	34.47	1.992	1930.32	0.10
200	11.49	BOD	14	3	34.47	0.725	482.58	0.15
200	11.49	TP	0.44	3	34.47	2.005	15.17	13.2
200	11.49	TN	7	3	34.47	2.145	241.29	0.89

Table 3
Thomas model parameters for the fabricated column model using linear regression analysis

Parameter	Initial concentration (mg/L)	Bed height (inch)	Flow rate (m^3/d)	k_{TH} (mg d/m^3)	q_0 (mg/g)	R^2
COD	56	4.5	11.49	0.4719	0.9753	0.4334
TP	0.44	4.5	11.49	0.8412	0.6016	0.5740
BOD	14	4.5	11.49	0.2749	3×10^{-16}	0.75
TN	7	4.5	11.49	0.7679	0.7679	0.5422

As seen from Table 3, R^2 value is not found to be significantly high; this may be due to the reason that the Thomas model is only applicable for the adsorption process that follows the Langmuir kinetic isotherm [41]. It is supported by the result of jar test experiments and shows that the adsorption of nutrient, especially COD follows the kinetic isotherm of Freundlich.

3.4.2. Yoon–Nelson model

The Yoon–Nelson model provides the assumption that the decrease in probability of each adsorbate to be adsorbed is proportional to the probability of its adsorption and breakthrough on the adsorbent [42]. The linearized model of Yoon–Nelson is shown below:

$$\ln\left[\frac{C_t}{C_0 - C_t}\right] = k_{YN}t - \tau k_{YN} \quad 10$$

where k_{YN} and τ are estimated from the slope and intercepts of linear graph between $\ln[C_t/C_0 - C_t]$ vs. t.

Table 4 shows that the value of τ is inversely proportional to R^2, and this trend is similar to the one as achieved by Sotelo et al. [43]. The initial concentration of each parameter does not provide any significance to the value of k_{YN}, τ, and R^2, since Yoon–Nelson model is limited through its rough and simple form. Due to this reason, Yoon–Nelson model is considered to be less valuable for the prediction of adsorption under various conditions [44].

3.4.3. Adam–Bohart model

Adam–Bohart model came up with the hypothesis that the uptake rate of adsorbate is proportional to the concentration of contaminant/pollutant/nutrient in the bulk fluid and the residual absorptive capacity of the adsorbent [44]. This model is commonly applied to describe the relationship between bed depth and service time at the column adsorption experiment [45]. The linear form of the Adam–Bohart model is expressed as follows:

$$\ln\frac{C_0}{C_t} - 1 = k_{AB}N_0\frac{Z}{F} - k_{AB}C_0t \quad (11)$$

where k_{AB} and N_0 are obtained from the plot of $\ln C_0/C_t$ vs. t. The interception and slope represent the value of k_{AB} and N_0, respectively.

Table 4
Yoon–Nelson model parameters for the fabricated column model using linear regression analysis

Parameter	Initial concentration (mg/L)	Bed height (inch)	Flow rate (m^3/d)	k_{YN} (mg d/m^3)	τ	R^2
COD	56	4.5	11.49	0.4719	2.0661	0.4334
TP	0.44	4.5	11.49	0.8412	0.7152	0.5740
BOD	14	4.5	11.49	0.2749	0	0.75
TN	7	4.5	11.49	0.7679	1.0000	0.5422

Table 5
Adam–Bohart model parameters for the fabricated column model using linear regression analysis

Parameter	Initial concentration (mg/L)	Bed height (inch)	Flow rate (m^3/d)	k_{AB} (mg d/m^3)	N_0 (mg/L)	R^2
COD	56	4.5	11.49	0.3733	0.0899	0.9385
TP	0.44	4.5	11.49	0.6933	0.0803	0.7696
BOD	14	4.5	11.49	0.1010	0	0.750
TN	7	4.5	11.49	0.6130	0.0171	0.8211

Based on Table 5, the overall value of R^2 is found to be higher compared to other models which are Thomas and Yoon–Nelson model. This shows that the breakthrough curve obtained from the fabricated column model follows Adam–Bohart model and the adsorption process is likely affected by the initial concentration of nutrient present in the water sample, and is proving that Adam–Bohart model is more suitable in expecting breakthrough curves and optimizing the parameters.

4. Conclusion

From the jar test experiments, the optimum adsorbent amount and contact time were found to be as 3 g/L in 3 d of continuous operation. These results were based on the maximum removal of COD and with the equilibrium study of crushed cockle shell, it showed that Freundlich isotherm model provided the best fit to the experimental data. A continuous adsorption process with crushed cockle shell was carried out on the fabricated column model. The breakthrough curves were plotted separately according to the type of nutrient present in the river water sample and the curves showed that the exhaustion time of crushed cockle shell was determined to be on day 3. The presence of higher amount of $CaCO_3$ in the shell helped the removal rate of P to increase. The column study showed that the Adam–Bohart model best fitted to the experimental data because of its higher R^2 value and is considered suitable for expecting the breakthrough curves and also for optimizing the parameters for treating polluted river water.

Acknowledgments

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References

[1] O. Khelifi, Y. Kozuki, H. Murakami, K. Kurata, M. Nishioka, Nutrients adsorption from seawater by new porous carrier made from zeolitized fly ash and slag, Mar. Pollut. Bull. 45 (2002) 311–315.

[2] A. Grefte, M. Dignum, E.R. Cornelissen, L.C. Rietveld, Natural organic matter removal by ion exchange at different positions in the drinking water treatment lane, Drink. Water Eng. Sci. 6 (2013) 1–10.

[3] J. Charles, C. Bradu, M.C. Nadia, B. Sancey, P. Winterton, G. Torri, P.M. Badot, G. Crini, Pollutant removal from industrial discharge water using individual and combined effects of adsorption and ion exchange process: Chemial abatement, J. Saudi Chem. Soc. (2013) 1–10, doi: 10.1016/j.jscs.2013.03.007.

[4] M. Riera-Torres, C. Gutiérrez-Bouzán, M. Crespi, Combination of coagulation-flocculation and nanofiltration techniques for dye removal and water reuse in textile effluents, Desalination 252 (2010) 53–59.

[5] A.K. Verma, R.R. Dash, P. Bhunia, A review on chemical/flocculation technologies for removal of colour from textile wastewater, J. Environ. Manage. 93 (2012) 154–168.

[6] J.W. Choi, H.K. Song, K.K. Koo, C. Han, B.K. Na, Reduction of COD and color of acid and reactive dyestuff wastewater using ozone, Korean J. Chem. Eng. 21(2) (2004) 398–403.

[7] S. Chakraborty, M.K. Purkait, S. DasGupta, S. De, J.K. Basu, Nanofiltration of textile plant effluent for color removal and reduction in COD, Sep. Purif. Technol. 31 (2) (2003) 141–151.

[8] G. Sudarjanto, B.K. Keller-Lehmann, J. Keller, Optimization of integrated chemical-biological degradation of a reactive azo dye using response surface methodology, J. Hazard. Mater. B138 (2006) 160–168.

[9] D. Suteu, D. Bilba, M. Aflori, F. Doroftei, G. Lisa, M. Badeanu, T. Malutan, The seashell wastes as biosorbent for reactive dye removal from textile effluents, Clean-Soil Air Water 40(2) (2012) 198–205.

[10] H.M. El Naas, S. Al-Zuhair, M.A. Alhaija, Reduction of COD in refinery wastewater through adsorption on date-pit activated carbon, J. Hazard. Mater. 173 (2010) 750–757.

[11] R. Devi, V. Singh, A. Kumar, COD and BOD reduction from coffee processing wastewater using avocado peel carbon, Bioresour. Technol. 99 (2008) 1853–1860.

[12] M. Rachakornkij, S. Ruangchuay, S. Teachakulwiroj, Removal of reactive dyes from aqueous solution using bagasse fly ash, Songklanakarin. J. Sci. Technol. 26(1) (2004) 13–24.

[13] S. Wang, H. Wu, Environmental-benign utilization of fly ash as low-cost adsorbents, J. Hazard. Mater. 136 (2006) 482–501.

[14] R.R. Bansode, J.N. Losso, W.E. Marshall, R.M. Rao, R.J. Portier, Pecan shell-based granular activated carbon for treatment of chemical oxygen demand (COD) in municipal wastewater, Bioresour. Technol. 94 (2004) 129–135.

[15] R. Chand, T. Watari, K. Inoue, H. Kawakita, H.N. Luitel, D. Parajuli, T. Torikai, M. Yada, Selective adsorption of precious metals from hydrochloric acid solutions using porous carbon prepared from barley straw and rice husk, Miner. Eng. 22 (2009) 1277–1282.

[16] M.A.M. Salleh, K.D. Mahmoud, A.W.W.A. Karim, A. Idris, Cationic and anionic dye adsorption by agricultural solid wastes: A comprehensive review, Des. 280 (2011) 1–13.

[17] J. Anwar, U. Shafique, Waheed-uz-Zaman, M. Salman, A. Dar, S. Anwar, Removal of Pb(II) and Cd(II) from water by adsorption on peels of banana, Bioresour. Technol. 101 (2010) 1752–1755.

[18] A. Abeynaike, L. Wang, M.I. Jones, D.A. Patterson, Pyrolysed powdered mussel shells for eutrophication

control: Effect of particle size and powder concentration on mechanism and extent of phosphate removal, Asia-Pac. J. Chem. Eng. 6 (2011) 231–243.

[19] H. Ting-Chu, Experimental assessment of adsorption of Cu^{2+} and Ni^{2+} from aqueous solution by oyster shell powder, J. Hazard. Mater. 171 (2009) 995–1000.

[20] Y. Du, L. Zhu, G. Shan, Removal of Cd^{2+} from contaminated water by nano-sized aragonite mollusk shell and the competition of coexisting metal ions, J. Colloid Interface Sci. 367 (2012) 378–382.

[21] I. Ali, M. Asim, T.A. Khan, Low cost adsorbents for removal of organic pollutants from wastewater, J. Environ. Manag. 113 (2012) 170–183.

[22] K. Budin, Y. Subramanian, R. Tair, S.A. Mohd Ali, The ability of crab and cockle shell to adsorb lead and chromium from industrial effluent, IOSR J. Environ. Sci. Toxicol. Food Technol. 8 (2014) 4–6.

[23] M. Mohamed, S. Yusup, S. Maitra, Decomposition study of calcium carbonate in cockle shell, J. Eng. Sci. Technol. 7(1) (2012) 1–10.

[24] Z. Zhang, Z. Zhang, Y. Fernández, J.A. Menéndez, H. Niu, J. Peng, L. Zhang, S. Guo, Adsorption isotherms and kinetics of methylene blue on low-cost adsorbent recovered from a spent catalyst of vinyl acetate synthesis, Appl. Surf. Sci. 256 (2010) 2569–2576.

[25] S. Dahiya, R.M. Tripathi, A.G. Hegde, Biosorption of heavy metals and radionuclide from aqueous solutions by pre-treated arca shell biomass, J. Hazard. Mater. 150 (2008) 376–386.

[26] S. Chowdhury, P.D. Saha, Fixed-bed adsorption of Malachite Green onto binary solid mixture of adsorbents: Seashells and eggshells, Toxicol. Environ. Chem. 94(7) (2012) 1272–1282.

[27] G.Z. Memon, M.I. Bhanger, M. Akhtar, Peach-nut shells-and effective and low cost adsorbent for the removal of endosulfan from aqueous solutions, Pak. J. Anal. Environ. Chem. 10(1–2) (2009) 14–18.

[28] A.A. Jalil, S. Triwahyono, M.R. Yaakob, Z.Z.A. Azmi, N. Sapawe, N.H.N. Kamarudin, H.D. Setiabudi, N.F. Jaafar, S.M. Sidik, S.H. Adam, B.H. Hameed, Utilization of bivalve shell-treatment *Zea mays*.L (maize) husk leaf as a low-cost biosorbent for enhanced adsorption of malachite green, Bioresour. Technol. 120 (2012) 218–224.

[29] S. Chowdhury, P. Saha, Sea shell powder a new adsorbent to remove Basic Green 4 (Malachite Green) from aqueous solutions: Equilibrium, kinetic and thermodynamic studies, Chem. Eng. J. 164 (2010) 168–177.

[30] S. Montalvo, F. Díaz, L. Guerrero, E. Sánchez, R. Borja, Effect of particle size and doses of zeolite addition on anaerobic digestion processes of synthetic and piggery wastes, Process Biochem. 40 (2005) 1475–1481.

[31] A.A. Ahmad, B.H. Hameed, Reduction of COD and color of dyeing effluent from a cotton textile mill by adsorption onto bamboo-based activated carbon. J. Hazard. Mater. 172(2–3) (2009) 1538–1543.

[32] A.K. Parande, A. Sivashanmugam, H. Beulah, N. Palaniswamy, Performance evaluation of low cost adsorbents in reduction of COD in sugar industrial effluent, J. Hazard. Mater. 168 (2009) 800–805.

[33] S. Bellebia, S. Kacha, A.Z. Bouyakoub, Z. derriche, Experimental investigation of chemical oxygen demand and turbidity removal from cardboard paper mill effluents using combined electrocoagulation and adsorption processes, Environ. Prog. Sustain. Energy 31(3) (2012) 361–370.

[34] S. Qi, L.C. Schideman, An overall isotherm for activated carbon adsorption of dissolved natural organic matter in water, Water Res. 42 (2008) 3353–3360.

[35] B.H. Hameed, I.A.W. Tan, A.L. Ahmad, Adsorption isotherm, kinetic modeling and mechanism of 2,4,6-trichlorophenol on coconut husk-based activated carbon, Chem. Eng. J. 144 (2008) 235–244.

[36] V. Vimonses, S. Lei, B. Jin, C.W.K. Chow, C. Saint, Kinetic study and equilibrium isotherm analysis of Congo Red adsorption by clay materials, Chem. Eng. J. 148 (2009) 354–364.

[37] H. Kwon, C. Lee, B. Jun, J. Yun, S. Weon, B. Koopman, Recycling waste oyster shells for eutrophication control, Resour. Conserv. Recycl. 41(1) (2004) 75–82.

[38] J. Xiong, Y. Qin, E. Islam, M. Yue, W. Wang, Phosphate removal from solution using powdered freshwater mussel shells, Desalination 276 (2011) 317–321.

[39] B. Zhao, Y. Shang, W. Xiao, C. Dou, R. Han, Adsorption of Congo red from solution using cationic surfactant modified wheat straw in column model, J. Environ. Chem. Eng. 2 (2014) 40–45.

[40] J.L. Sotelo, G. Ovejero, A. Rodríguez, S. Álvarez, J. García, Adsorption of carbamazepine in fixed bed columns: Experimental and modeling studies, Sep. Sci. Technol. 48(17) (2013) 2626–2637.

[41] M. Trgo, N.V. Medvidović, J. Perić, Application of mathematical empirica models to dynamic removal of lead on natural zeolite clinoptilolite in a fixed bed column, Indian J. Chem. Technol. 18 (2011) 123–131.

[42] Y.H. Yoon, H.N. James, Application of gas adsorption kinetics I. A theoretical model for respirator cartridge service life. Am. Ind. Hyg. Assoc. J. 45(8) (1984) 509–516.

[43] J.L. Sotelo, G.M. Ovejero, A. Rodríguez, S. Álvarez, J. García, Adsorption of carbamazepine in fixed bed columns: Experimental and modeling studies, Sep. Sci. Technol. 48(17) (2013) 2626–2637.

[44] Z. Xu, J.G. Cai, B.C. Pan, Review: Mathematically modeling fixed-bed adsorption in aqueous systems, J. Zhejiang. Univ. Sci. A, 14(3) (2013) 155–176.

[45] N. Li, J. Ren, L. Zhao, Z.L. Wang, Fixed bed adsorption study on phosphate removal using nanosized FeOOH-modified anion resin, J. Nano. 2013 (2013) 1–5, doi: 10.1155/2013/736275.