Fasa 1/2008

BORANG FRGS – P3(R)

FINAL REPORT
FUNDAMENTAL RESEARCH GRANT SCHEME (FRGS)
Laporan Akhir Skim Geran Penyelidikan Asas (FRGS) IPT
Pindaan 1/2010

A	**RESEARCH TITLE** *Tajuk Penyelidikan*	:	Characterization and biodegradation study of prawn-pond wastewater at influent, after oxidation and post filtration by low cost composite media
	PROJECT LEADAER *Ketua Projek*	:	Prof. Hamidi Abdul Aziz
	PROJECT MEMBERS (Including GRA) *Ahli Projek*	:	1. Dr. Kamar Shah Ariffin 2.

PROJECT ACHIEVEMENT *(Prestasi Projek)*

B

ACHIEVEMENT PERCENTAGE			
Project progress according to milestones achieved up to this period	**0 – 50%**	**51 – 75%**	**78- 100%**
Percentage			**100%**

RESEARCH OUTPUT		
Number of articles/manuscripts/ books *(Please attach the First Page of Publication)*	**Indexed Journal**	**Non-Indexed Journal**
	1 (published) 3 (under review)	
Conference Proceeding *(Please attach the First Page of Publication)*	**International**	**National**
Intellectual Property *(Please specify)*		

HUMAN CAPITAL DEVELOPMENT

Human Capital	**Number**				**Others** *(Please specify)*
	On-going		**Graduated**		Post-doc
Citizen	Malaysian	Non Malaysian	Malaysian	Non Malaysian	1 post doctorate has been appointed and unfortunately has resigned as he has been appointed as lecturer
PhD Student					
Master Student			2		
Undergraduate Student			1		
Total					

EXPENDITURE *(Perbelanjaan)*

C

Budget Approved *(Peruntukan diluluskan)* : **RM86,600.00**
Amount Spent *(Jumlah Perbelanjaan)* : **RM86,530.48**

Balance *(Baki)* : **RM2,300.92**
Percentage of Amount Spent *(Peratusan Belanja)* : 99.9 %

ADDITIONAL RESEARCH ACTIVITIES THAT CONTRIBUTE TOWARDS DEVELOPING SOFT AND HARD SKILLS *(Aktiviti Penyelidikan Sampingan yang menyumbang kepada pembangunan kemahiran insaniah)*

D

International

Activity	Date (Month, Year)	Organizer
(e.g. : Cource/Seminar/Symposium/Conference/Workshop/Site Visit)		

National

Activity	Date (Month, Year)	Organizer
(e.g. : Cource/Seminar/Symposium/Conference/Workshop/Site Visit)		

PROBLEMS/CONSTRAINTS IF ANY *(Masalah/Kekangan sekiranya ada)*

E

Has sent at least 5 papers to different journals, however, it is very difficult to get them published.

RECOMMENDATION *(Cadangan Penambahbaikan)*

F

RESEARCH ABSTRACT – Not More Than 200 Words *(Abstrak Penyelidikan – Tidak Melebihi 200 patah perkataan)*

G

The effluent used in this research project was taken from a prawn pond in Tanjong Piandang Fisherman Village, Kuala Kurau, Perak (latitude 5.01N and longitude 100.42E). Prawn pond effluent contains high concentrations of ammonia and COD and high pH value. COD and ammonia are normally removed by biological process and air stripping methods, respectively. However, post treatment is always necessary. The main purpose of this project was to examine the efficiency of composite media which is a mixture of limestone, activated carbon, zeolite and rice husk as post-treatment in the prawn pond effluent treatment. Experiments were conducted at three different conditions. i.e., experiments conducted by sole aeration, with adsorption only and adsorption of pre-aerated (24 hours aeration) sample. Control experiments were conducted without adding any media at different pH to determine whether pH influences the removal. Results indicated that the best removal was achieved in the experiment conducted with pre-aerated sample where 92% of COD, 85% of NH_4-N and 96% of colour removals were achieved. Freundlich and Langmuir adsorption models, which have been successfully applied to many adsorption processes, were used to study the ammonia, COD and colour adsorption behaviour of the composite media. The empirical constant (n) value of Freundlich Isotherm was greater than 1 implying beneficial adsorption for all the parameters tested in this study. Freundlich and Langmuir isotherms offer very good fits for all parameters studied with R^2 values above 0.9.

Date : 03 February 2012 *Tarikh*	**Project Leader's Signature** : *Tandatangan Ketua Projek*

COMMENTS IF ANY/ENDORSEMENT BY RESEARCH MANAGEMENT CENTER (RMC)
(Komen, sekiranya ada/Pengesahan oleh Pusat Pengurusan Penyelidikan)

H

……

……

……

Name :
Nama :

Signature :
Tandatangan :

Date :
Tarikh :

ATTACHMENT

PUBLISHED:

Hussain, S., Aziz, H.A., Isa, M.H., Ahmad, A., Van Leeuwen, J., Zou, L., Beecham, S., Umar, M.. Orthophosphate removal from domestic wastewater using limestone and granular activated carbon. (2011) *Desalination*, 271 (1-3), pp. 265-272.

PAPER UNDER REVIEW:

1) Hamidi Abdul Aziz, Manogari Sundram, Yung-Tse Hung, Ammonia, 'COD and colour removal from prawn pond effluent using composite media', paper under review to be published in International Journal of Environment and Engineering Science.
2) Hamidi Abdul Aziz, Manogari Sundram, Abu Ahmed Mokammel Haque, Mohd. Nordin Adlan, Irvan Dahlan, Mohd. Suffian Yusoff, Mohamed Razip Selamat, Kamar Shah Ariffin, Md Azlin Md Said, Mohammed J.K Bashir, Removal of Ammonia, Chemical Oxygen Demand, and Color From Prawn Pond Wastewater Using Composite Media. Paper under review to be published in Environmental Engineering and Management Journal;
3) Hamidi Abdul Aziz, Hwang Shiang Lin, Abu Ahmed Mokammel Haque, Muhammad Umar, Mohd Nordin Adlan. Treatment of synthetic shrimp farm wastewater by composite adsorbent. Paper under review to be published in Environmental Progress & Sustainable Energy.

GRADUATED M.SC. (MIXED-MODE):

1. Manogari A/P Sundram, Ammonia, COD and colour removal from prawn pond effluent using composite media (completed May 2008)
2. Hwang Shiang Lin, Treatment of synthetic shrimp farm wastewater by composite adsorbent (completed May 2010)

STATEMENT OF ACCOUNT

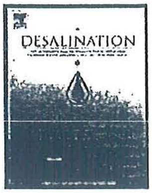
Budget Account Code	Roll over	Budget	Commit	Actual	Available
203.111.0.PAWAM.6071166	-11821.16	0	0	0	-11821.16
203.112.0.PAWAM.6071166	-851.64	0	0	0	-851.64
203.113.0.PAWAM.6071166	-531.25	0	0	0	-531.25
	-13204.05	0	0	0	-13204.05
203.221.0.PAWAM.6071166	10742.8	0	293.2	1938.2	8511.4
203.226.0.PAWAM.6071166	2765.17	0	0	0	2765.17
203.227.0.PAWAM.6071166	5090.1	0	0	0	5090.1
203.228.0.PAWAM.6071166	-2250	0	0	0	-2250
203.229.0.PAWAM.6071166	-843.1	0	0	0	-843.1
	15504.97	0	293.2	1938.2	13273.57
GrandTotal	2300.92	0	293.2	1938.2	69.52

Desalination 271 (2011) 265–272

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal



Orthophosphate removal from domestic wastewater using limestone and granular activated carbon

Sabir Hussain [a,b], Hamidi Abdul Aziz [b,*], Mohamed Hasnain Isa [c], Anees Ahmad [d], John Van Leeuwen [a], Linda Zou [a], Simon Beecham [a], Muhammad Umar [b]

[a] South Australian Centre for Water Management and Reuse, School of Natural and Built Environments, University of South Australia, SA 5095, Australia
[b] School of Civil Engineering, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia
[c] Civil Engineering Department, Universiti Teknologi PETRONAS, 31750 Tronoh, Perak, Malaysia
[d] School of Industrial Technology, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia

ARTICLE INFO

Article history:
Received 15 October 2010
Accepted 19 December 2010
Available online 21 January 2011

Keywords:
Adsorption
Domestic wastewater
Granular activated carbon
Limestone
Orthophosphate

ABSTRACT

The discharge of excessive concentration of orthophosphate (PO_4-P) ions into the receiving water causes environmental problems such as "eutrophication." The aim of the present study was to investigate the adsorption behavior of limestone (LS), granular activated carbon (GAC) and the mixture of both adsorbents for orthophosphate removal from domestic wastewater. The range of initial concentration of PO_4-P throughout the study was between 9 and 25 mg/L. Effects of contact/settling times, pH, adsorbent dosage, initial concentration, adsorption isotherm models and kinetics were studied in batch-scale experiments while for the column experiments, the effects of flow rate, pH and initial concentration were studied. Limestone alone was shown to be an effective adsorbent which has potential to remove over 90% orthophosphate at optimum conditions. The lower initial concentration (2.5 mg PO_4-P/L) yielded the maximum removal (94%) compared to the higher concentration (80% removal at 100 mg PO_4-P/L). Freundlich and Langmuir isotherms provided good correlation coefficient for PO_4-P and the data agreed with the pseudo-second-order kinetics model ($R^2 > 0.95$). In the up-flow column study, higher flow rate, alkaline pH and higher initial concentration yielded shorter column saturation time.

1. Introduction

Fresh water for human needs is a precious natural resource that in many parts of the world is becoming more scarce due to climate change impacts and increased human demands. Its sources and security of supply has become a key concern for communities and more attention is being made on water conservation and use efficiency, new water sources and advanced treatment technologies and water reuse. In recent years water recycling has become an important resource for agricultural and domestic use, including for potable supply in some countries. Since the early 1970s, the presence of phosphorous in domestic wastewaters has received increased attention due to the realization of negative impacts it can have on receiving waters in the environment. In wastewater treatment processing, phosphorus is a vital nutrient for bacteria needed to degrade and biologically stabilize the organic wastes. Phosphorus is also an essential nutrient for plant growth in lakes and streams. Phosphorus is generally present in the form of orthophosphate (condensed phosphate or polyphosphate) in natural and waste waters [1]. It commonly originates from human and animal wastes, agricultural runoff and household detergents. The discharge of excessive amount of phosphate ions from wastewater treatment plants may adversely affect the water quality of a receiving body. Domestic wastewater is an important source of inorganic nutrients such as ammoniacal-nitrogen (NH_4-N) and orthophosphate (PO_4-P). Phosphorus was found between the levels of 3–15 mg/L in domestic wastewater; merely about 3 mg/L was formed by the breakdown of protein wastes while the majority came through the usage of detergents [2].

Many countries around the world including the European Union allow 1–2 mg/L as the limit of total phosphorus (TP) for effluent discharge in wastewater treatment plants. However, some regions followed more strict measures of around 0.5–0.8 mg P/L to control eutrophication [3]. Algal blooms can occur if the concentration of PO_4-P exceeds 0.1–0.5 mg/L which cause "eutrophication" in the receiving water, thus phosphate removal is an essential part of domestic wastewater treatment [4,5].

Phosphorus removal can be brought about by several available wastewater technologies such as biological, coagulation-flocculation, physico-chemical and electrolytic. These include adsorption, ion exchange, chemical precipitation and membrane filtration/reverse osmosis [6]. Some of them are relatively expensive to run due to high

---

* Corresponding author. Tel.: +60 4 5996203; fax: +60 4 5941009.
E-mail address: cehamidi@eng.usm.my (H.A. Aziz).

doi:10.1016/j.desal.2010.12.046

operational and maintenance cost. Biological process is a low-cost operating technology compared to chemical process. But the process could not achieve the required level of phosphorus removal compared to a well-run physico-chemical process [7,8]. In chemical precipitation, alum, lime and iron salts are widely used as effective coagulants for the removal of phosphate and ammonium ions from wastewaters. However, handling of high volumes of sludge, its disposal and neutralization of the effluent are the major disadvantages of this technology [6]. Orthophosphate removal has been accomplished by chemical precipitation as a wastewater treatment technology. However, as a new approach, its removal and recycling technologies have not been widely implemented due to scarcity of advanced scientific knowledge [9].

Pure MgO and low-grade MgO (LG-MgO) were used as a source of magnesium for the removal of ammonium and phosphate ions from wastewater by precipitating in the form of ammonium magnesium phosphate (MAP) $MgNH_4PO_4$ compound, also known as struvite. Pure MgO performed better than LG-MgO but it has substantial cost-effective disadvantages [10]. The recovery of MAP, though, would be beneficial to use it as a source of agricultural fertilizer [9]. Aguilar et al. [11] reported about 100% orthophosphate removal using different coagulants such as aluminium sulphate, ferric sulphate and poly-aluminium chloride with or without coagulant aids such as powdered activated carbon, precipitated calcium carbonate, cationic polyacrylamide, polyacrylic acid, polyvinyl alcohol and anionic polyacrylamide. The addition of these coagulant aids caused reduction of sludge volume of up to 41.6%. Still the high cost of chemicals usage is the main disadvantage.

In order to solve these problems, it is desirable to develop a low-cost and simple treatment alternative. Domestic or municipal wastewater treatment could be achieved by adsorption using various adsorbents. Activated carbons, in granular or powdered forms, are widely used adsorbents due to the availability of their high surface area which enhanced adsorption rate. However, its expensive regeneration and disposal problems are the major disadvantages of this material [6].

The removal of phosphate by adsorption is quite simple and convenient. Successful results were reported by various researchers using different adsorbents such as fly and bottom ashes [12–17], opoka and calcinated opoka [18], $ZnCl_2$-activated coir pith [19], natural indigenous rocks and waste materials [20–22], red mud and sand [23,24] and calcium hydroxide, iron oxide, mesoporous alumina [25–27] from wastewater. Limestone and zeolite were used as filter media to adsorb anions and cations from rainfall runoff [22]. Phosphate ion can be removed by ion exchange or physical adsorption [20]. Tanik and Comakoglu [28] evaluated effective phosphorus removal efficiency from domestic wastewater by rapid infiltration system through porous media (sand and gravel from crushed stone). The range of phosphorus removal achieved in the system was about 46–93%. The removal efficiency increased with decreasing effective size of soil media. The system was considered to be suitable because of low-cost media and energy saving.

Rahman et al. [21] investigated wastewater treatment with multilayer media consisting of natural indigenous rocks (andesite, granite, limestone and nitrolite) and waste materials (refuse concrete, waste paper and charcoal). In the multilayer media system, the removal of phosphate ion from wastewater, the combinations of andesite and nitrolite with charcoal and refuse concrete showed relatively higher efficiencies. In the single medium treatment, the removal efficiencies using andesite, nitrolite, refuse concrete and charcoal were 18%, 36–66%, 55–91% and 11–17%, respectively. Therefore, the addition of refuse concrete in the multilayer system resulted in higher potential to remove phosphate ion.

Kietlinska [18] stated that treatment of landfill leachate is difficult because of its complex composition. He performed a short-term column experiment to study the effect of opoka adsorbent for the removal of orthophosphate from landfill leachate. Columns I, II, III and IV were filled with opoka (Polonite) (<1 mm grain size), sand (2 mm), calcinated opoka (<2 mm) mixed with zeolite (2 mm) in the ratio 1:1 and peat mixed with calcinated opoka, respectively. Columns I and II removed about 42% and 39% ortho-P, respectively while columns III and IV removed more than 90% of ortho-P. Kirk et al. [16] investigated the removal of soluble phosphorus from wastewater using coal bottom ashes. The lignite bottom ashes had higher adsorption capacity (80–600 mg P/kg_{ash}) as compared to bituminous (14–1000.002 for flowrate = 10 mL/min mg P/kg_{ash}). The bituminous and lignite coal bottom ashes removed about 73% and 82% phosphorus, respectively.

Namasivayam and Sangeetha [19] studied the sorption capacity of phosphate from aqueous solution using $ZnCl_2$-activated coir pith. The results suggested the possible monolayer coverage of phosphate on the surface of $ZnCl_2$-activated coir pith. The adsorption kinetics showed a clear idea about pseudo-first-order and pseudo-second-order kinetics. It was concluded that the calculated q_e values of second-order-kinetic were in agreement with the experimental values compared to the pseudo-first-order kinetics. The correlation coefficient R^2 values of the second-order kinetics were greater than 0.99. Therefore, the study was represented by the second-order-kinetic model. The percentage removal increased from 20% to 95% with increased adsorbent dosage from 25 to 600 mg, respectively.

Limestone is a low-priced material "US$ 12/ton" compared to the cost of activated carbon "US$ 2.7/kg" [29]. It has shown good adsorption potential in several studies [22,29–32]. The main purpose of the present study was to investigate the effect and adsorption behavior of limestone, activated carbon and mixture of both materials as filtering media for PO_4-P removal from domestic wastewater. This study was focused on the establishment of essential parameters for the design of limestone or mixture of limestone and activated carbon filter as a post-treatment of domestic wastewater before releasing it into the receiving water.

2. Materials and methods

2.1. Wastewater analysis and adsorbents

Wastewater samples were collected from the influent point of the oxidation pond at Engineering Campus, Universiti Sains Malaysia, Penang, Malaysia. The oxidation pond receives a mixture of domestic wastewater from hostels, administrative blocks, schools and cafeterias. Characterization of the wastewater involved the determination of NH_4-N, PO_4-P, COD, BOD, turbidity and suspended solids (SS) using HACH DR2500 spectrophotometer. The pH of wastewater samples was analyzed onsite, immediately after sample collection. The samples were collected in plastic containers and stored at 4 °C before analysis. Domestic and synthetic wastewater samples were used in batch and column experiments, respectively. The pH was adjusted by the addition of 0.1 M H_2SO_4 or NaOH solutions. All parameters were analyzed in accordance with the Standard Methods for the Examination of Water and Wastewater [1]. Ammoniacal nitrogen (NH_4-N) was determined using Nesslerization method (4500-NH_3). Orthophosphate (PO_4-P) was determined using Molybdovanadate Method (4500-P). Chemical oxygen demand (COD) was determined using Colorimetric Method (5220-D). BOD was determined using 5-Day BOD Test (5210-B). Turbidity and suspended solids were determined using 2130 and 2540 Methods, respectively.

The properties of adsorbents, limestone (LS) and granular activated carbon (GAC), used in the experiments were obtained commercially from the industries as discussed by Hussain et al. [29].

2.2. Batch study

The batch study was conducted to establish the removal pattern of PO_4-P using limestone (LS), granular activated carbon (GAC) and the mixture of both adsorbents. The effects of contact and settling times were determined prior to the main experiment. Settling was allowed in order to examine the effect of particle sedimentation after shaking. The total volume of adsorbent mixture (LS:GAC) and contact speed were adopted as 40 mL and 350 rpm, respectively [29]. The LS and GAC combinations (v/v) were 0:0, 40:0, 35:5, 30:10, 25:15, 20:20, 15:25, 10:30, 5:35 and 0:40 corresponding to 0:0, 104:0, 91:7, 78:13, 65:20, 52:26, 39:33, 26:40, 13:46 and 0:53 on mass (g) basis. The range of initial concentration of PO_4-P was 6–25 mg/L throughout the study, except for the experiment on the effect of initial concentration. To determine the optimum contact time, 250 mL conical flasks containing 120 mL of domestic wastewater with 40 mL of media mixture (LS:GAC) ratios of 0:0, 40:0, 35:5, 30:10, 25:15 and 15:25 were agitated on an orbital shaker at uniform shaking speed. The conical flasks were removed from the shaker one by one after 30, 60, 90, 120, 150, 180, 210, 240 and 270 min. A settling period of 120 min was allowed prior to withdrawing the supernatant for PO_4-P analysis. The optimum settling time was determined in a similar fashion as the optimum shaking time and the supernatant withdrawn after 30, 60, 90, 120, 150, 180, 210, 240 and 270 min for analysis. Samples were adjusted to pH 2, 5, 7, 11 and 13 (with 0.1 M HCl or NaOH) to determine the effect of pH on PO_4-P removal at different mixture ratios of LS:GAC i.e. 0:0, 40:0, 25:15, 20:20 and 0:40. Three ranges of particle size of both adsorbents were used, i.e., 0.65–1.14 mm, 1.14–2.0 mm and 2.36–4.75 mm. The effect of initial concentration ranging from 2.5 to 100 mg PO_4-P/L was studied. Data for Freundlich and Langmuir isotherms generation were obtained by varying the amount of adsorbent mixture from 5 to 40 mL. The isotherm constants and least squares correlation coefficients (R^2) of both models were compared to determine the best-fit isotherm model. Adsorption kinetics was studied based on pseudo-first-order and pseudo-second-order models. All experiments were conducted at room temperature (25 ± 2 °C).

2.3. Column study

A column, 7.5 cm diameter and 17.5 cm bed height, filled with a mixture ratio of LS and GAC 25:15 was employed for this study. The column was operated in up-flow mode without effluent recycle. The particle size of both adsorbents (LS and GAC) used was 2.36–4.75 mm. The operational conditions of this column experiment are shown in Table 1. The column was cleaned with diluted nitric acid and rinsed with distilled water before the experiments. The limestone and granular activated carbon mixture was air-dried at room temperature (25 ± 2 °C) for 24 h prior to filling the column. The mixture in the column was cleaned with distilled water for 24 h in an up-flow mode to remove any trapped air and unwanted impurities from the bed. The effects of flow rate, pH and initial concentration on column performance were investigated.

Table 1
Adsorbent characteristics and operational parameters of the experimental set up.

Flow rate (mL/min)	10 and 30
Column height (cm)	20
Internal diameter (cm)	7.5
Area of column (cm^2)	44.18
Column material	Glass fiber (plastic)
Bed height (cm)	17.5
Bed volume (cm^3)	773.13
Adsorbents, ratio	Limestone and granular activated carbon (LS:GAC, 25:15)
Bulk density of LS:GAC (25:15) (kg/m^3)	1769
Mass of adsorbent (g)	741
Particle size range (mm)	2.36–4.75
Void (%)	46.2
Type of pump	Master flex/peristaltic pump
Empty bed contact time EBCT (min)	12.9
Retention time (min)	13.86 for flowrate = 30 mL/min 41.59 for flowrate = 10 mL/min
Filtration rate (m^3/m^2 min)	0.007 for flowrate = 30 mL/min 0.002 for flowrate = 10 mL/min
Mode of flow	Up flow (without effluent recycling)

3. Results and discussion

Characterization of domestic wastewater: The composition of raw domestic wastewater collected from the influent point of oxidation pond is shown in Table 2. The measured average density of limestone and granular activated carbon were 2598 kg/m^3 and 1265 kg/m^3, respectively.

3.1. Batch study

3.1.1. Preliminary experiments

Effects of contact and settling times and shaking speed. The effects of contact and settling times at different ratios of LS:GAC were evaluated at constant settling time and contact speed as shown in Figs. 1 and 2. Here 0:0 means there was no adsorbent, which confirmed negligible removal of PO_4-P. It was observed that PO_4-P removal which was ≥ 90% (as the initial concentration decreased from 16 mg/L to 0.50 mg/L) at contact times ranging from 30 to 270 min. The contact times between 150 and 180 min showed good performance with about 95%, 89–94% and 65–70% removals using LS:GAC ratios of 35:5, 25:15 and 15:25, respectively. The results indicated that increased dosage of GAC in all ratios showed significant decrease in removal. This may be due to higher physico-chemical sorption capacity of LS for PO_4-P compared to GAC which generally represents physical sorption. Fig. 2 shows the effect of settling time in simulated sedimentation after shaking of the adsorbent mixtures on sorption capacity. It was observed that increase in settling time showed a little enhanced removal. Settling times of 120–150 min showed better removals of about 91–94%, 92%, 89–92%, 85–87% and 72% for ratios 40:0, 35:5, 30:10, 25:15 and 10:30, respectively at optimum contact time of 150 min and shaking speed of 350 rpm. The optimum contact and settling times were adopted as 150 and 120 min for the rest of the experiments.

Fig. 3 shows that limestone has potential to remove approximately 90% orthophosphate at higher shaking speed ranging between 300 and 400 rpm. The initial PO_4-P concentration of 20 mg/L was reduced to a final concentration of 2 mg/L. Increase in shaking speed causes better surface contact between the adsorbent and the aqueous solution, thus enhanced the sorption rate.

3.1.2. Effect of pH

Fig. 4 shows the effect of various pH values, i.e. 2, 5, 7, 11 and 13 on the sorption of PO_4-P at the mixture of LS:GAC taken in different ratios. The agitation of the aqueous solution without adsorbent confirmed almost negligible removal over the entire range of pH values. However, it is clearly observed that limestone alone showed

Table 2
Domestic wastewater characteristics.

Parameter	Units	Range	Average
Ammoniacal nitrogen, NH_4-N	mg/L	6–25	15
Orthophosphate, PO_4-P	mg/L	11–20	16
COD	mg/L	98–123	111
BOD_5	mg/L	30–43	37
SS	mg/L	25–65	45
Turbidity	NTU	62–77	70
pH		6.45–6.95	6.70

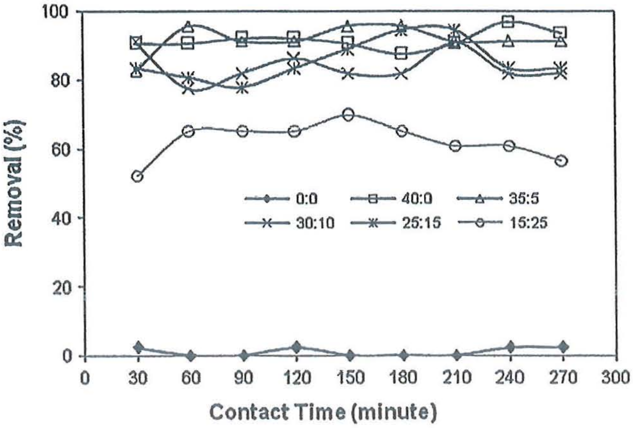


Fig. 1. The effect of contact time versus PO_4-P removal (conditions: LS, 2.36–4.75 mm; GAC, 0.65–2.36 mm; shaking speed, 350 rpm).

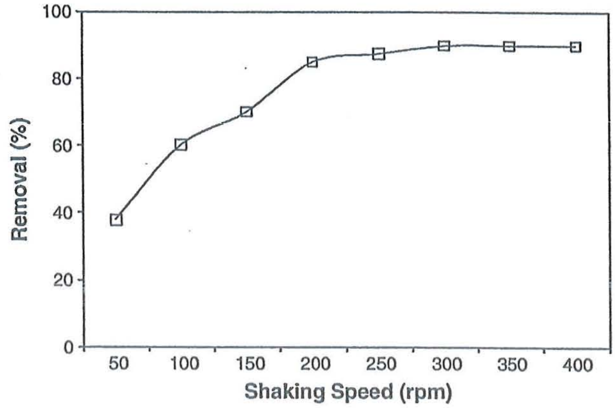


Fig. 3. The effect of shaking speed on the sorption capacity of PO_4-P (conditions: PO_4-P, 20.10 mg/L; LS, 2.36–4.75 mm; GAC, 0.65–2.36 mm; pH, 6.84).

uniform removal (>94%) over the entire range of pH "2–13" which means that the removal was unaffected by the initial pH of the wastewater. The LS:GAC ratios 25:15 and 20:20 attained about 87% and 82% PO_4-P removal at neutral pH (7), respectively. For the mixture ratios of LS:GAC 25:15, 20:20 and 0:40, sorption capacity was slightly decreased at alkaline pH. GAC alone removed about 94% at pH 5 but this was reduced to 67% under alkaline conditions (pH 13). The results indicated that the phosphate sorption capacity tends to decrease with the increase of initial pH of the solution which is in agreement with Zeng et al. [26], who stated that phosphate removal decreased by increasing the initial pH of the aqueous solution from 3.2 to 9.5. Srinivasan et al. [22] investigated the ability of limestone to remove anions from rainfall runoff. As LS alone achieved significant removal of phosphate (>94%) over the pH range of 2–13, subsequent experiments were conducted at neutral pH.

3.1.3. *Effect of adsorbent mixture ratio (LS:GAC) and particle size*

Fig. 5 shows the effect of varying the LS:GAC ratio on the sorption capacity of PO_4-P. The results indicated that the LS alone, ratio 40:0, has potential to adsorb about 98% PO_4-P from aqueous solution at optimum experimental conditions; the initial PO_4-P concentration of 20 mg/L was reduced to 0.5 mg/L. While the ratio 25:15 yielded about 93% removal, it is clearly observed that the ratios 40:0, 35:5 and 30:10 achieved over 90% removal. However, the sorption capacity was reduced to about 70% when ratio 0:40 (GAC only) was used. This was probably due to the fact that the physio-chemical/adsorption/anion exchange or calcium phosphate precipitation/ capacity of limestone was much higher than the physical sorption of granular activated carbon. Increase in pH after certain agitation was attributed to increased dosage of GAC (initial pH of GAC was around 9–10) at various LS:GAC ratios. Limestone increased the influent pH of 6.79 to the final effluent pH of 8.5. In the present study, the ratio 25:15 was adopted as optimum mixture ratio as it not only has ability to remove PO_4-P (about 93%) but also yielded substantial removal around 58% of NH_4-N [29], which could reduce the cost of expensive adsorbent (GAC).

Fig. 6 shows the effect of various particle size ranges i.e. 0.65–1.14 mm, 1.14–2.0 mm and 2.36–4.75 mm on the sorption capacity of orthophosphate. The adsorption capacity was not significantly affected by these different particle sizes when 40:0 and 35:5 ratios were used which showed consistent removal of about 97–99%. As the dosage of GAC increased, PO_4-P sorption capacity decreased to some extent for 30:10, 25:15 and 15:25 ratios.

3.1.4. *Effect of initial concentration and adsorbent dosage*

Fig. 7 shows the effect of varying initial PO_4-P concentration from 2.5 to 100 mg/L on the sorption capacity of the sorbent mixture of LS:GAC, 25:15. It was observed that lower initial concentration (2.5 mg PO_4-P/L) resulted in higher removal efficiency (94%) compared to the higher concentration (80% at 100 mg PO_4-P/L). This is due to the greater relative availability of sorption sites on the sorbent mixture for

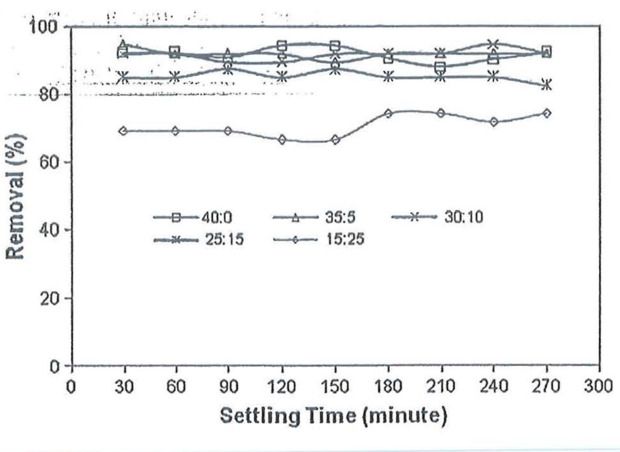


Fig. 2. The effect of settling time versus PO_4-P removal (conditions: LS, 2.36–4.75 mm; GAC, 0.65–2.36 mm; contact time, 150 min; shaking speed, 350 rpm).

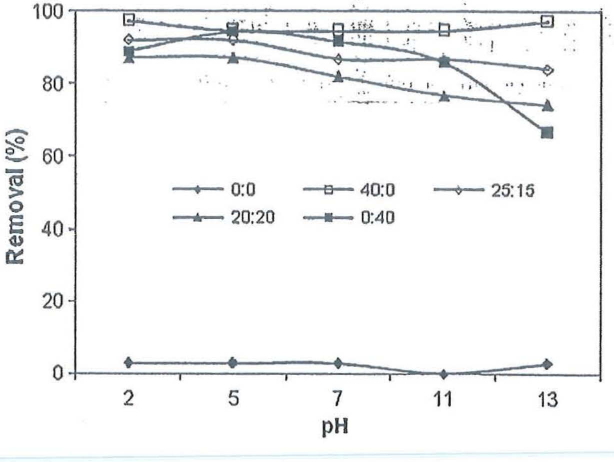


Fig. 4. Effect of pH on PO_4-P removal at different ratios of LS:GAC (conditions: shaking speed, 350 rpm; contact time, 150 min; settling time, 120 min).

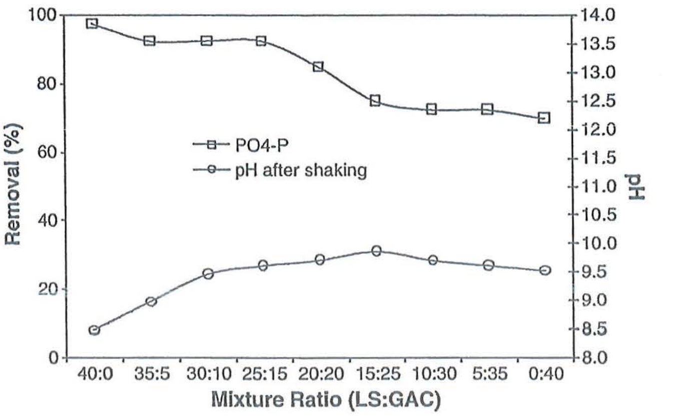


Fig. 5. The effect of mixture ratio LS:GAC versus removal (%) (conditions: PO_4-P, 20.0 mg/L; shaking speed, 350 rpm; contact time, 150 min; settling time, 120 min; pH, 6.79).

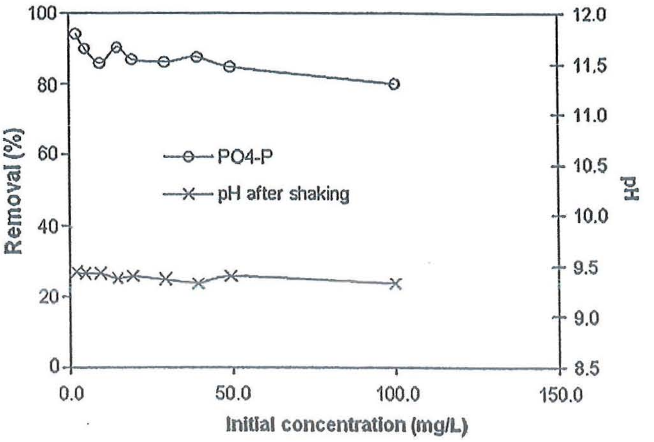


Fig. 7. Initial concentration versus removal (%) (conditions: shaking speed, 350 rpm; contact time, 150 min; settling time, 120 min; LS:GAC, 25:15; pH, 6.91).

PO_4-P removal. In the case of higher initial PO_4-P concentration, the total number of available sorption sites was exceeded by the moles of PO_4-P which caused the decrease in the phosphate adsorption rate.

Fig. 8 shows PO_4-P removal as a function of adsorbent dosage using the optimum ratio 25:15. It was observed that the increase in adsorbent dosage increased the percentage removal of PO_4-P. The 5 mL dosage resulted in about 66% removal while the maximum removal of 91% was achieved with both 35 mL and 40 mL dosages. Higher dosages increased the available surface area and lead to greater adsorption.

3.1.5. Adsorption isotherm

Freundlich and Langmuir adsorption isotherm models were applied to study the adsorption capacity of limestone and granular activated carbon for the removal of orthophosphate at optimum conditions from wastewater.

The Freundlich model is expressed as follows [6]:

$$\frac{x}{m} = K_f C_e^{1/n} \tag{1}$$

where x/m is the amount of PO_4-P adsorbed per unit mass of adsorbent (mg/g), C_e is the equilibrium concentration (mg/L) and, K_f and $1/n$ are the Freundlich isotherm constant (L/mg) and intensity of adsorption, respectively. Large K_f value shows that the adsorbent has a high adsorption capacity for the adsorbate and small value of $1/n$ means that adsorption bond is strong. A linear plot of log x/m versus log C_e yielded the following values of Freundlich isotherm constants as shown in Fig. 9.

$$K_f = 27.18, 1/n = 1.06 \text{ and } R^2 = 0.94$$

The Langmuir isotherm model is expressed as follows:

$$\frac{x}{m} = \frac{abC_e}{1+aC_e} \text{ or } \frac{1}{x/m} = \frac{1}{abC_e} + \frac{1}{b} \tag{2}$$

The values of a, b and corresponding correlation coefficients (R^2) are 0.0063 L/mg, 3.0193 mg/g, and 0.94, respectively. Fig. 9 shows that the correlation coefficient (R^2) values for Freundlich and Langmuir isotherms are same. Thus, the experimental data fits both, Freundlich as well Langmuir adsorption isotherm. Langmuir model assumes the formation of a mono layer of the adsorbate on the adsorbate where as Freundlich model explains the multi layer formation. The former hints towards surface homogeneity where as the later towards surface heterogeneity. The fitting of both models can be interpreted in terms of surface nature of the two substances involved in the adsorption process especially the adsorbent. Probably the surface of the adsorbent contains the uniformly distributed patches of similar functional groups. Thus the surface becomes a uniform system of

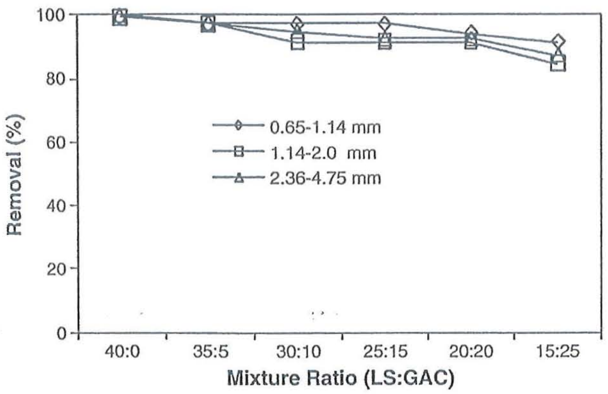


Fig. 6. The effect of media size for PO_4-P removal at different mixture ratios (conditions: shaking speed, 350 rpm; contact time, 150 min; settling time, 120 min; LS:GAC, 25:15; pH, 6.87).

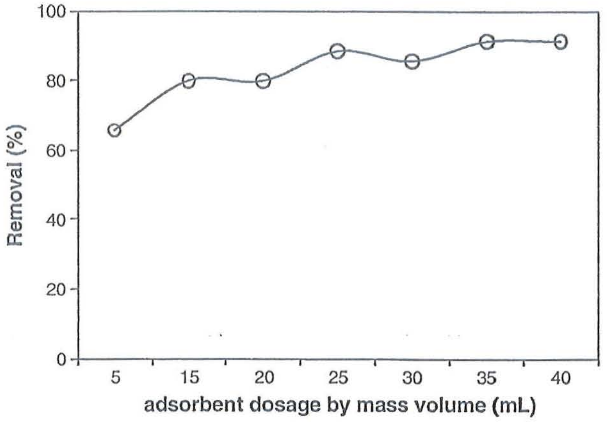


Fig. 8. Effect of adsorbent dosage versus removal (%) (conditions: PO_4-P, 17.50 mg/L; LS:GAC, 25:15; shaking speed, 350 rpm; contact time, 150 min; settling time, 120 min; pH, 6.78).

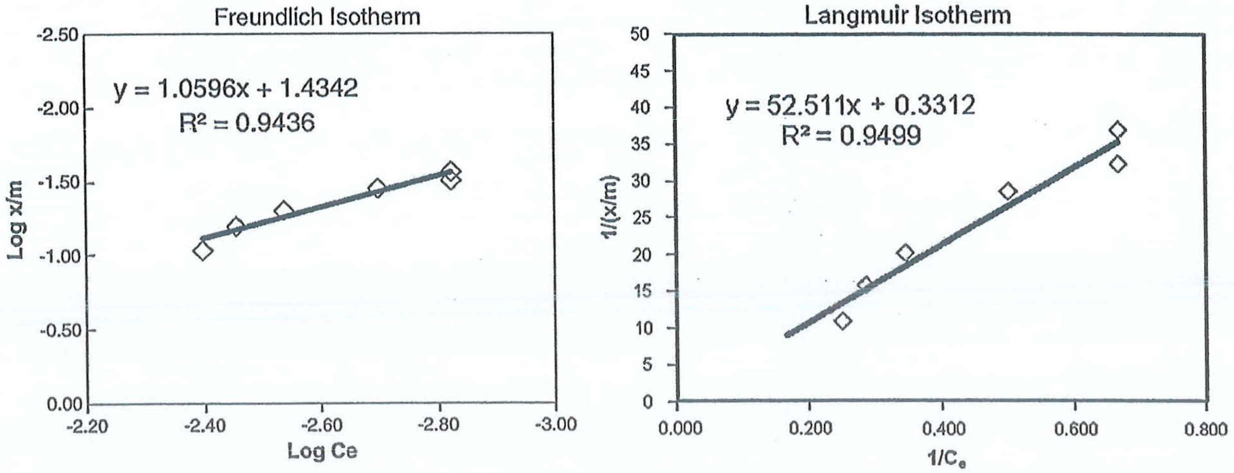


Fig. 9. Freundlich and Langmuir Isotherms (conditions: LS:GAC, 25:15; shaking speed, 350 rpm; contact time, 150 min; settling time, 120 min; pH, 6.78).

heterogeneous moieties. This uniformity in homogeneity brings a conformity to fit both the models up to similar extents.

3.1.6. Adsorption kinetics

3.1.6.1. Comparison of pseudo-first-order and pseudo-second-order kinetics. Fig. 10 shows the adsorption kinetics of orthophosphate. The experimental data was applied to the selected adsorption kinetic models viz., pseudo-first-order and pseudo-second-order.

The adsorption kinetics data was analyzed using linear form of the pseudo-first-order (Lagergren first-order) rate equation as follows:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \tag{3}$$

where q_e and q_t are the amount of PO$_4$-P adsorbed per mass of adsorbent (μg/g) at equilibrium and time t (min), respectively and k_1 is the equilibrium rate constant of pseudo-first-order adsorption, (g/μg min). The values of k_1 and q_e were calculated from the intercept and the slope of the plots of log($q_e - q_t$) versus t. It was observed that the calculated q_e values of PO$_4$-P did not agree with the experimental q_e values for most LS:GAC ratios (Table 3). Moreover, the correlation coefficient (R^2) values of the pseudo-first-order kinetics were also very low.

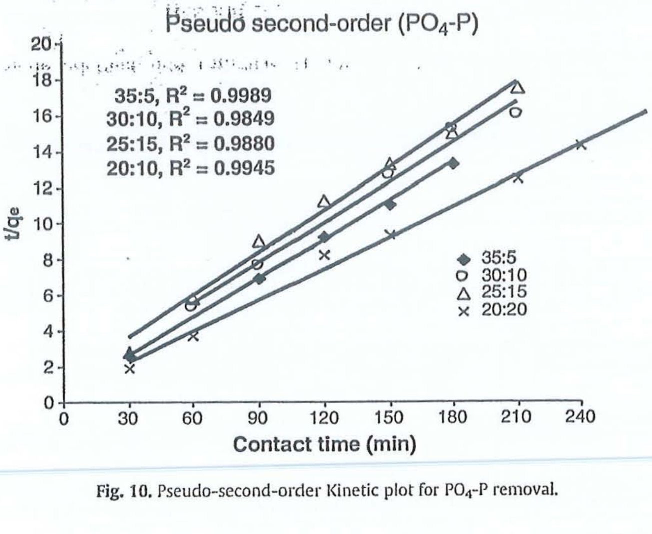


Fig. 10. Pseudo-second-order Kinetic plot for PO$_4$-P removal.

The pseudo-second-order kinetics equation can be written in the linear form as follows [33]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{4}$$

where k_2 is the equilibrium rate constant of pseudo-second-order adsorption (g/μg min). The calculated values of k_2 and q_e, obtained from the plot of t/q_e versus t were in good agreement with the experimental values of q_e (Table 3). The data showed good compliance with the pseudo-second-order kinetics (R^2>0.98). The values of the rate constants (k_2) were found in the range of 5.2×10^{-3}–9.9×10^{-3} g/μg min and the amount of PO$_4$-P adsorbed at equilibrium condition was in the range of 12.69–17.24 μg/g, respectively.

3.2. Column studies

This study was carried out to investigate the effect of flow rates, initial concentration and pH on the breakthrough curve of orthophosphate from synthetic wastewater using optimum mixture ratio of LS:GAC (25:15) at a constant bed depth of 17.5 cm.

3.2.1. Effect of flow rate

The experimental data (Fig. 11) shows that higher flow rate resulted in shorter column saturation/exhaustion time. When the flow rate increases, the residence time in the bed decreases which results in lower bed utilization. Thus, the column saturation time and the bed capacity decreased with increased flow rate. The exhaustion time at initial concentration of 24 and 22.2 mg PO$_4$-P/L for flow rates 10 and 30 mL/min were about 16.5 and 7 h, respectively. The lower flow rate 10 mL/min also yielded higher initial percentage removal (about 77%) compared to the higher flow rate 30 mL/min (about 67%).

Table 3
Pseudo-first-order and pseudo-second-order kinetics data.

Ratio (LS:GAC)	Experimental q_e (μg/g)	Pseudo-first-order kinetics			Pseudo-second-order kinetics		
		q_e (cal), (μg/g)	R^2	k_1	q_e (cal), (μg/g)	R^2	k_2
35:5	13.54	2.526	0.8929	0.0131	14.025	0.9989	0.0099
30:10	13.17	2.017	0.5333	0.0028	13.405	0.9849	0.0053
25:15	12.04	2.267	0.3733	0.0053	12.690	0.9880	0.0052
20:20	16.86	0.725	0.1333	−0.0037	17.241	0.9945	0.0072

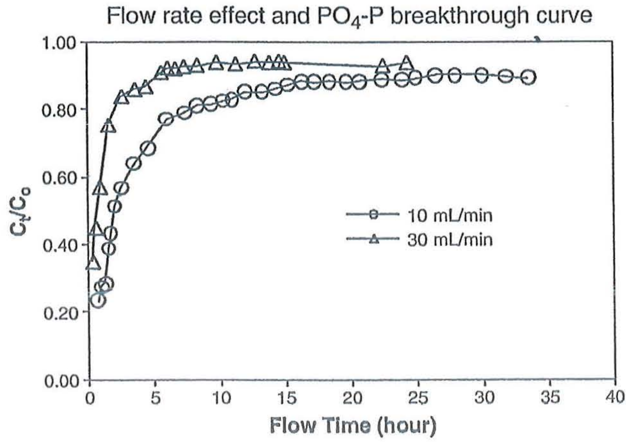


Fig. 11. The effect of different flow rates on PO_4-P breakthrough curve (conditions: PO_4-P, 24.0 and 22.2 mg/L; particle size, 2.36–4.75 mm; pH = 7.05).

3.2.2. Effect of pH

The effect of varying initial pH of the solution on the breakthrough curve of orthophosphate removal is described by Fig. 12. It was observed that column saturation time for PO_4-P at pH 11 (alkaline solution) was much quicker than at pHs 4 and 7 for a flow rate of 10 mL/min (filtration rate, 0.002 m^3/m^2 min). The column saturation times at pHs 11, 7 and 4 were approximately 2.75, 19.5 and 11 h, respectively.

During the pH experiment, it was observed that limestone behaved as an acid neutralizing material and raised the influent pH from 4 to the final effluent pH of 8.24–8.41 which complies with the Malaysian Environmental Quality Act 1974 Standards [34]. Due to dissolution of LS, the net wastewater acidity decreased when it passed through the mixture of LS and GAC filter bed. Limestone particles (added to the acidic aqueous solution) could dissolve neutralizing acids and increase dissolved calcium concentration. The phenomena can be described by the following chemical reactions:

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- \quad (5)$$

$$CaCO_3 + H_2O \rightarrow Ca^{2+} + HCO_3^- + OH^- \quad (6)$$

3.2.3. Effect of initial concentration

The results for initial PO_4-P concentrations of 5.20, 10.20 and 22.20 mg/L (filtration rate, 0.002 m^3/m^2.min) were studies (plot in not given). The experimental results were not so clear to analyze the significant difference among the selected initial concentrations. However, from the data, it is observed that the column saturation time at 22.20 mg/L was slightly shorter than the initial concentrations of 5.20 mg/L and 10.20 mg/L. It was concluded that the higher initial concentration of phosphate ions resulted in quicker column saturation time compared to the lower concentration.

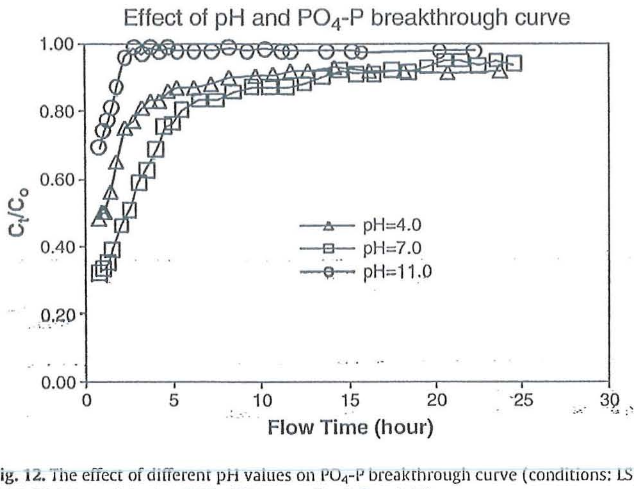


Fig. 12. The effect of different pH values on PO_4-P breakthrough curve (conditions: LS:GAC, 25:15; particle size, 2.36–4.75 mm; pHs, 4, 7 and 11).

4. Conclusions

The present study aimed to investigate the adsorption of PO_4-P using two media; one being the commonly studied granular activated carbon (GAC) and the other being limestone (LS) as low-cost material. In the batch study, optimum contact and settling times were obtained as 150 min and 120 min, respectively. Limestone alone has the potential to adsorb about 98% PO_4-P from aqueous solution at optimum experimental conditions; the initial concentration of 20 mg/L dropped to the final level of 0.5 mg/L. The LS:GAC ratio 25:15 was adopted as optimum mixture ratio as it not only removed PO_4-P (about 93%) but also yielded substantial removal of NH_4-N around 58% [29] which could reduce the cost of expensive adsorbent GAC. Increase in adsorbent dosage increased the percentage removal of orthophosphate. Freundlich and Langmuir isotherms both provided good correlation coefficient ($R^2 > 0.94$). The data fitted well with pseudo-second-order kinetics model ($R^2 > 0.98$) which indicates that the adsorption was chemisorption. Results from the column study showed that higher flow rate and initial concentration resulted in shorter column saturation time. It is recommended that the high-cost GAC adsorbent can be reduced by combining it with low-cost natural LS at optimum ratio (LS:GAC) 25:15.

Acknowledgements

The authors would like to acknowledge the financial support provided by the Ministry of Science, Technology and Innovation, Malaysia for the IRPA research grant that has resulted in this article.

References

[1] A.W.W.A. APHA, WPCF, Standard Methods for the Examination of Water and Wastewater, 20th Ed.American Public Health Association, Washington DC, 2005.
[2] B.A. Hauser, Practical Manual of Wastewater Chemistry, Ann Arbor Press Inc, Michigan, 1996.
[3] E. Galarneau, R. Gehr, Phosphorus removal from wastewater experimental and theoretical support for alternative mechanisms, Water Res. 31 (1996) 328–338.
[4] AWWA, Water Quality and Treatment: A Handbook of Public Water Supplies, 4th Ed, 1990, McGraw-Hill, New York,.
[5] M.J. Hammer, M.J. Hammer (Jr), \Water and Wastewater Technology, 4th Ed, 2001, Prentice-Hall, New Jersey, Ohio.
[6] Eddy Metcalf, Wastewater Engineering: Treatment, Disposal and Reuse, 4th Ed, 2004, McGraw-Hill, New York.
[7] E. Levlin, B. Hultman, Phosphorus recovery from phosphate rich Side streams in wastewater treatments, Proceedings of a Polish-Swedish seminar, Report No.10, Joint Polish-Swedish Reports, 2003, Gdansk Poland.
[8] B. Gullet, J. McLelland, D. Padgett, System-wide planning for phosphorus reduction at Charlotte's three largest wastewater treatment plants, Proceedings of South Carolina Environmental Conference, Columbia, South Carolina, 2003.
[9] L.E. de-Bashan, Y. Bashan, Recent advances in removing phosphorus from wastewater and its future use as fertilizer, Water Res. 38 (2004) 4222–4246, (1997–2003.
[10] J.M. Chimenos, A.I. Fernandez, G. Villalba, M. Segarra, A. Urruticoechea, B. Artaza, F. Espiella, Removal of ammonium and phosphates from wastewater resulting from the process of cochineal extraction using MgO-containing by-product, Water Res. 37 (2003) 1601–1607.
[11] M.I. Aguilar, J. Saez, M. Llorens, A. Soler, J.F. Ortuno, Nutrient removal and sludge production in the coagulation-flocculation process, Water Res. 36 (2002) 2910–2919.
[12] N.M. Agyei, C.A. Strydom, J.H. Potgieter, An investigation of phosphate ion adsorption from aqueous solution by fly ash and slag, Cem. Concr. Res. 30 (2000) 823–826.
[13] D.G. Grubb, M.S. Guimaraes, R. Valencia, Phosphate immobilization using an acidic type F fly ash, J. Hazard. Mater. 76 (2000) 217–236.
[14] K.C. Cheung, T.H. Venkitachalam, Improving phosphate removal of sand infiltration system using alkaline fly ash, Chemosphere 41 (2000) 243–249.