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Application of used cement blocks for the removal of phosphate from aqueous solution under low temperature conditions

Yueyao Pu[a], Jianghua Yu[a,*], Tao Tao[a,b], Lin Zhu[a]

[a]*Jiangsu Collaborative Innovation Center of Atmospheric Environment and Equipment Technology, School of Environmental Science and Engineering, Nanjing University of Information Science & Technology, Nanjing 210044, China, Tel. +86-25-58695677; Fax +86-25-58731090; email: yujh@nuist.edu.cn (J. Yu)*

[b]*Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control, Jiangsu Joint Laboratory of Atmospheric Pollution Control, Nanjing 210044, China*

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ABSTRACT

The phosphate adsorption characteristics of used cement block powder were evaluated. Batch adsorption was conducted under low temperature conditions to study the effects of various parameters, such as initial concentration, contact time, and solution pH, on phosphate adsorption. The brick powder showed better phosphate adsorption performance under neutral conditions at low temperatures. Adsorption kinetics data were tested using pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. The results showed that the adsorption process followed the pseudo-second-order reaction better, and the mechanism of the adsorption process was determined from the intraparticle diffusion model. The outcome indicated that the used cement blocks were a promising material for the removal of phosphate from stormwater infiltration systems, which provided a win–win approach for both construction solid waste disposal and wastewater control.

Keywords: Adsorption kinetics; Cement blocks; Low temperature conditions; Phosphate

1. Introduction

Phosphorous has been identified as the crucial factor that causes eutrophication in water bodies [1]. Studies have shown that the pollution of water bodies with phosphates is significantly increasing the growth rate of plants and aqueous life, which has resulted in less dissolved oxygen for aquatic organisms [2]. It is worth noting that phosphate is naturally present in water bodies, but its quantity is increased by human activities, such as from domestic waste, industrial waste, and stormwater rainfall [3–4].

Therefore, a large number of studies have focused on the removal of phosphorus from aquatic systems [1,2,4]. In addition, many methods have been implemented, such as biological, physical, and chemical methods, to remove phosphate from water bodies [5]. Due to advantages such as low cost, easy availability, and simple operation, adsorption has been widely applied in the removal of phosphate.

Papers have been published about phosphate removal using the absorption method where natural materials are used to adsorb phosphate; for example, many adsorbents have been experimented with, such as red mud [6], peat [7], fly ash [8], blast furnace slag, eggshells, giant reeds, and sugarcane [9]. Synthetic materials and industrial waste have also been used to adsorb phosphorus from aqueous solutions [10].

Many studies have paid more attention to various parameters that affect adsorption at normal temperature levels [2,6,11]. However, the temperature of many northern cities in winter is low and accompanied by snow or rainfall, so it is necessary to study the characteristics of adsorption at low temperature levels and not just as a factor that affects the results of adsorption.

Used bricks from demolished construction sites are easily accessible and very cheap [11]. Among many existing

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* Corresponding author.

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industries that have emerged in the present few decades, the construction industry is among the leading waste generators worldwide. The composition of this waste differs depending on the construction or demolition of buildings and infrastructures. The content mostly includes concrete, bricks, wood, gypsum, metals, plastics, glass, asbestos, and soil, and some of these materials can be recycled [12]. Construction and demolition waste have a high potential for recycling and reuse because some of their contents display high resource value [13], such as the cement blocks used in this study. Some studies have recycled used bricks, such as by making concrete with recycled ceramic coarse aggregates from industrial brick waste [14] and encasing recycled aggregate concrete and recycled clay brick aggregates with polyester FRP tubes [15]. Bricks are made using a type of soil that has advantageous properties, which can be enhanced in order to adsorb phosphate from aqueous solutions.

Stormwater infiltration systems have the capability to remove contaminants from aqueous solutions. Few studies have reviewed these systems to understand the extent of removal [16]. In this study, we examined the physicochemical properties and adsorption characteristics of used cement bricks with the goal of applying the used bricks to remove phosphate from stormwater under low temperature conditions.

2. Materials and methods

2.1. Preparation and characterization of adsorbent

The used cement blocks applied in our experiments were collected from a housing demolition project in Nanjing, China. The blocks were crushed into coarse grains, which were separated using stainless-steel sieves into three particle size ranges of <1 mm, 1–3 mm, and 3–5 mm.

The mineral composition of the bricks was determined using X-ray diffraction (XRD-6100). XRD analysis was conducted using an analytical D/Max-2500 X-ray diffractometer equipped with Cu-K radiation (1.5406 Å) operating at 40 kV and 50 mA, and the scanning rate was set at 0.02 s^{-1}. Scanning electron microscopy (SEM) analysis was also applied to investigate the surface morphology of the cement blocks. The multi-point BET specific surface area of the sample was measured using a fully automatic gas adsorption instrument (Autosorb-iQ-AG-MP).

2.2. Experimental methods

In the present study, a phosphate solution was prepared by dissolving potassium dihydrogen orthophosphate (KH_2PO_4) in deionized water. Adsorption experiments were conducted in beakers using different sized brick particles at a dosage of 50 g L^{-1} and shaken at 120 rpm [11]. The experimental temperature was set at 5°C, which is the normal, lowest possible non-freezing temperature in the cold season. Considering the practical chemical properties of stormwater, the solution pH was controlled in the range of 5–9. The contact time was controlled in the range of 30–40 h depending on the time to reach adsorption equilibrium. After adsorption, the solution was filtered through a 0.45 μm microporous fiber membrane, and the phosphorus concentration in the filtrate was determined using the ascorbic acid method.

2.3. Adsorption kinetics

Three kinetic models, namely the pseudo-first-order model, pseudo-second-order model, and intraparticle diffusion model [2], were evaluated in order to investigate the kinetics of phosphate removal by cement blocks using the experimental data above, which are described as follows:

Pseudo-first-order equation:

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{1}$$

Pseudo-second-order equation:

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

Intraparticle diffusion equation:

$$q_t = kt^{0.5} + C \tag{3}$$

where q_e and q_t are the amounts of phosphate removed at equilibrium and at time t (mg g^{-1}), respectively; t is the contact time (min); k_1 is the equilibrium rate constant of pseudo-first-order kinetics (min^{-1}); k_2 is the equilibrium rate constant of pseudo-second-order kinetics (g mg^{-1} min^{-1}); k is the intraparticle diffusion rate constant (mg g^{-1} $min^{-0.5}$); and C is the constant that is proportional to the boundary layer thickness.

3. Results and discussion

3.1. Characterization of the used blocks

A SEM micrograph is shown in Fig. 1. The results showed that the cement blocks have a rough surface with some particles adhered unevenly on the main structure. This multiple site-surface was favorable for the adsorption reaction [17].

The specific surface area of the used bricks was 20, 12, and 10 for <1, 1–3, and 3–5 mm grains, respectively (Table 1). Compared with other media, the three particle sizes of the

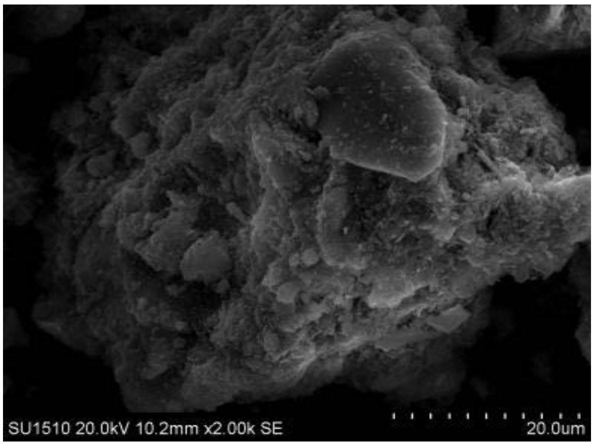

Fig. 1. Scanning electron microscopy micrograph of the cement blocks.

Table 1
Physical and chemical properties of the cement blocks

Particle size (mm)	Specific surface area (m^2 g^{-1})	Mineral composition (%)					Hydraulic conductivity (cm s^{-1})
		SiO_2	$AlPO_4$	Calcite			
				$Ca(CO_3)$	$Mg_{0.03}Ca_{0.97}CO_3$	$Mg_{0.06}Ca_{0.94}CO_3$	
<1	20.284	36.88	25.40	9.80	10.10	9.90	0.0381 ± 0.03
1–3	12.976						1.7225 ± 1.72
3–5	10.664						2.8345 ± 2.83

cement blocks had larger surface areas, thereby indicating that they have larger phosphorus adsorption capacities [18].

Hydraulic conductivity is one of the most fundamental factors in the design, manufacturing, and operation of stormwater infiltration systems. The values of hydraulic conductivity increased with the increase in particle size of the cement blocks. Permeability values of filling affect the purification capability of rainwater biofilters [19]. Small values of permeability tend to cause problems such as clogging of the system and low decontamination efficiency [20]. According to the infiltration capacity requirements of marsh biofiltration systems in the range of 0.00069–0.0027 cm s^{-1} [21], the hydraulic conductivity of the three sizes of cement block particles in this experiment met the requirements.

The mineral components of the used bricks were determined. The results indicated that they contain SiO_2 (36.88%), $AlPO_4$ (25.4%), and calcite (37.72%), as well as aluminum, calcium, and magnesium. When bricks are used as the media of stormwater infiltration systems, these metal ions and their hydrates and oxides can form hardly soluble compounds with phosphate precipitation, or calcium and magnesium ions on the brick surface can exchange ions with phosphate and be incorporated into the filler nuclei. Previous studies have also shown that the presence of metal ions in the media favors phosphorus removal [22].

3.2. Effect of contact time

In order to investigate the influence of contact time on the phosphate removal by cement blocks, experiments were conducted with a contact time of 40 h, solution pH of 7, and initial phosphate concentration of 5 mg L^{-1}.

Overall, the concentration of phosphate in the solution decreased with contact time. In particular, it decreased to around 40% of the initial concentration (2 mg L^{-1}) during the first 5 h. Then, the adsorption progressed relatively slowly and reached a stable stage at around 20 h. It has been reported that the surface of cement powder has a large number of active adsorption sites and that the adsorption rate decreases, at which point the surface adsorption is essentially saturated [2]. In addition, the adsorption was also influenced by the grain size of the cement bricks. The smaller brick grains showed a higher adsorption rate. The phosphate concentration decreased to around 1.2 mg L^{-1} for the <1 mm grains at 10 h, while it was around 2.3 mg L^{-1} for the 3–5 mm grains due to the different contact surface. The possible reason for this was that the smaller brick grains might have had more active adsorption sites [2] (Fig. 2).

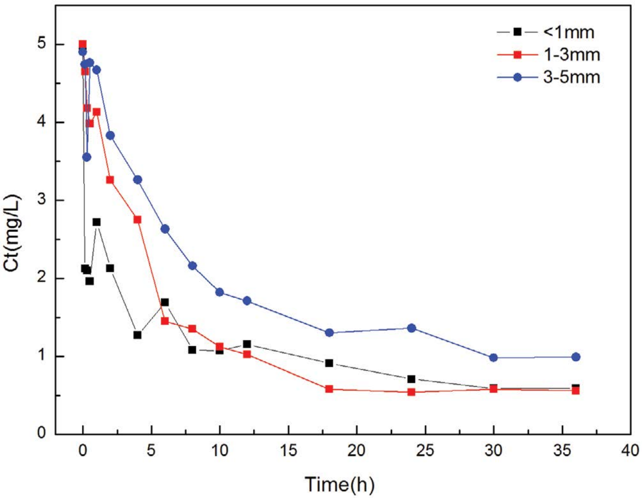

Fig. 2. Phosphate concentration of cement blocks at different contact times (phosphate concentration: 5 mg·L^{-1}, temperature: 5°C, pH: 7).

3.3. Effect of the initial concentration

The effect of the initial concentration of adsorbate on the adsorption capacity was studied by controlling the pH of the solution at 7. The phosphate concentration is generally in the range of 0–5 mg L^{-1} in stormwater [4]. Hence, the initial phosphate concentration was controlled at 1, 2, 3, 4, and 5 mg L^{-1}, respectively. As shown in Fig. 3, the equilibrium adsorption (Q_e) was positively correlated with the increasing initial concentration. It was increased from around 15 to 95 mg kg^{-1}, while the initial concentration ranged 1–5 mg L^{-1}. It was different from other studies in that the Q_e changed little when the initial concentration reached a high stage due to the lower initial concentrations set in the experiments [6]. In addition, Q_e changed little with the different grain sizes due to the low initial concentrations.

3.4. Effect of pH on phosphate removal

The effect of pH (5, 7, and 9) on phosphate adsorption at a phosphate concentration of 5 mg L^{-1}, brick dosage of 50 g L^{-1}, temperature of 5°C, and contact time of 54 h is plotted in Figs. 4 and 5. The range in pH applied in the experiment was narrow, while other studies chose a range from 2 to 11 [11,23].

The results showed that pH had an important effect on the adsorption reaction. Compared with the solution with a

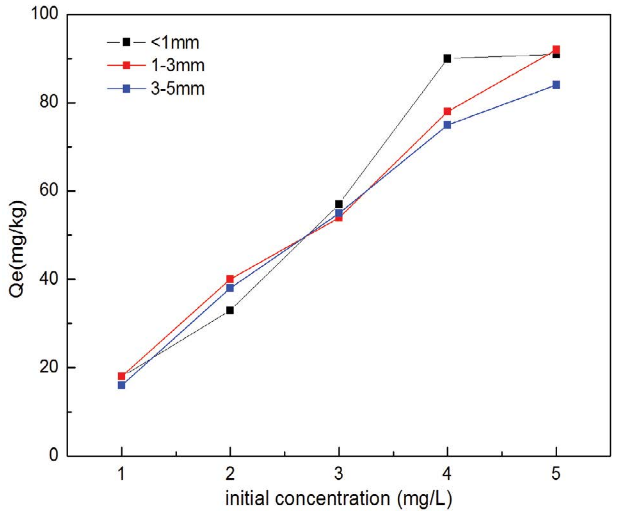

Fig. 3. Effects of initial phosphate concentration on adsorption capacity.

pH of 5 and 9, that with a pH of 7 showed a higher adsorption capacity according to Fig. 5. The final phosphate concentration was around 0.5 mg L^{-1}, while it was around 2 mg L^{-1} at a pH of 9 and 1.5 mg L^{-1} at a pH of 5. Furthermore, the solution with a neutral pH condition had a higher adsorption rate, which may have been related to the chemical composition of the cement blocks. Under acidic conditions, phosphorus is removed mainly by the electrostatic attraction of metal oxides, such as calcium and aluminum, with phosphate (in this case, the main forms of phosphorus were $H_2PO_4^-$ and HPO_4^{2-}), and by ion exchange [24]; Al^{3+} and Ca^{3+} form complex polynuclear hydroxyl ions that can adsorb and complex PO_4^{3-}. Under neutral conditions, Ca^{2+} eluted from cement block powder easily interacts with phosphate (which mainly exists in the form of HPO_4^{2-} and PO_4^{3-}) and precipitation occurs, and in alkaline conditions, these metal ions will preferentially react with OH^- ions, thereby affecting adsorption. According to the pH and different forms of calcium ions and phosphate ions in water, many calcium phosphate compounds, such as hydroxyapatite ($Ca_5H(PO_4)_3OH$) and brushite ($CaHPO_4 \cdot 2H_2O$), can be generated [25]. Additionally, it was found that the adsorption

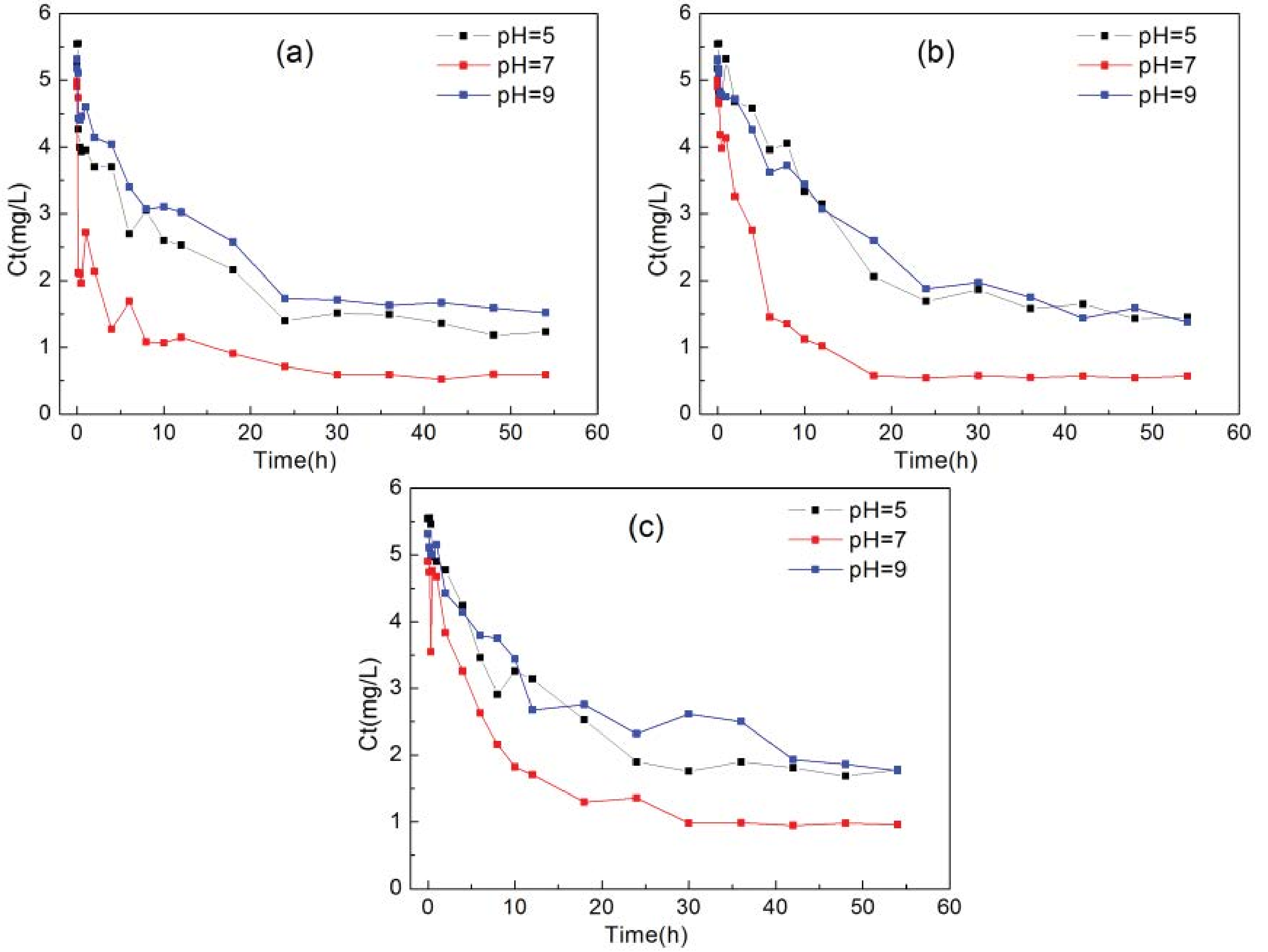

Fig. 4. Phosphate concentration of cement blocks at different contact times at different pH conditions (5, 7, and 9) (a: <1 mm, b: 1–3 mm, and c: 3–5 mm).

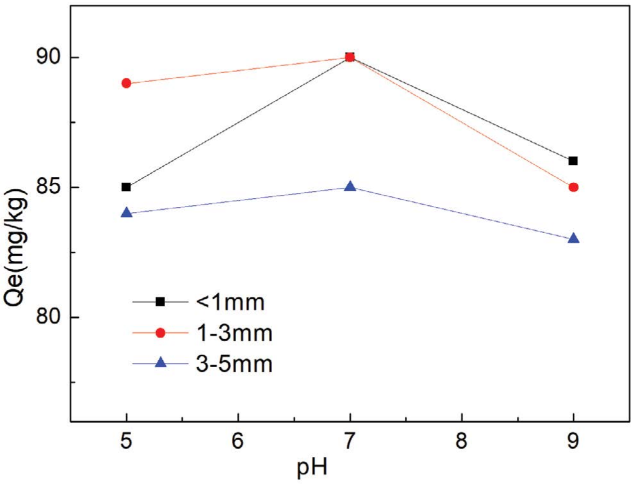

Fig. 5. Equilibrium adsorption capacity at different pH conditions.

capacity of larger brick particles was less influenced by the solution pH, which was probably due to the smaller specific surface area of the cement blocks with large particle sizes in contact with the solution [2].

3.5. Adsorption isotherms and kinetics

The calculated kinetics parameters with regression coefficients (R^2) for the three models are presented in Table 2. Adsorption kinetics can reflect the adsorption and removal mechanisms of matrix materials to a certain extent [26]. The data were fitted by a pseudo-first-order kinetic model, pseudo-second-order kinetic model, and intraparticle diffusion model. Table 2 shows the kinetic parameters of the pseudo-first-order, pseudo-second-order, and intraparticle diffusion model used for different particle sizes of cement blocks in the same adsorption conditions. As can be seen from the table, the correlation coefficients of the pseudo-first-order kinetic model and the pseudo-second-order kinetic model of the three sizes of cement granules were all above 0.9, but the simulated pseudo-second-order kinetic model was more accurate and the Q_e used in the pseudo-first-order model was more similar to the actual experimental results, which proved that the pseudo-second-order kinetic model is more suitable for describing the process of phosphate adsorption by used cement blocks. This was in agreement with the conclusions obtained in other studies on the adsorption of phosphorus by similar materials [27].

In the intraparticle diffusion model, the whole adsorption process can be composed of three parts [28]. The first is the adsorption reaction stage. In this stage, the adsorption rate is the highest, the mass transfer process is mainly from the solution of phosphate ions to the adsorbent surface, and the resistance is small. The second stage is the intragranular diffusion stage of the adsorbent. At this time, the surface adsorption is basically completed, the adsorption rate decreases, and the adsorbent begins to enter the pore for adsorption, which is the rate control step of the reaction. In the third stage, the adsorption no longer changes with time, thereby indicating that the adsorption reaction has reached saturation [29]. It can be concluded that the intraparticle diffusion is the main phase of the adsorption reaction. At this time, the linear relationship between q_t and $t^{0.5}$ is good, but the fitted curve does not pass through the origin, thereby indicating that the adsorption reaction is mainly controlled by intraparticle diffusion. However, it is not the only step that controls the reaction rate. Adsorption may also be affected by extragranular diffusion, such as surface adsorption and liquid film diffusion [30].

4. Conclusions and prospects

Used cement blocks are a construction waste that is locally available in large quantities, especially in developing countries. The results indicated that used cement blocks with a large specific surface area had a favorable performance in removing phosphate from aqueous solutions at low temperatures. The hydraulic conductivity of the three cement block particle sizes in this experiment could meet the requirements of stormwater infiltration systems. The main factors, such as contact time, initial concentration, and pH, could affect phosphate adsorption, and the efficiency in neutral conditions was greater. The pseudo-second-order kinetic model and intraparticle diffusion model were suitable for describing the process of phosphate adsorption by used cement blocks.

Thus, the results of the study suggested that used cement blocks have the potential to effectively remove phosphate from stormwater, and are suitable for use as media in stormwater infiltration systems. The application of cement blocks is an environmentally friendly method that enables both phosphate removal and reuse of building wastes. The phosphate adsorption capacity of used bricks will be improved by using a series of modified methods in the future.

Acknowledgement

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Table 2
Kinetic parameters for phosphate removal

Particle size (mm)	Pseudo-first-order equation			Pseudo-second-order equation			Intraparticle diffusion equation	
	Q_m	k_1	R^2	Q_e	k_2	R^2	K	C
<1	31.73	8.45	0.944	32.82	0.059	0.979	16.380	9.780
1–3	29.79	1.85	0.976	33.15	0.436	0.966	21.276	–1.020
3–5	26.32	1.50	0.927	29.48	0.511	0.969	18.623	–0.913

Symbols

t — Contact time, min
q_e — amounts of phosphate removed at time t, mg g^{-1}
q_t — Amounts of phosphate removed at equilibrium time, mg g^{-1}
k_1 — Equilibrium rate constant of pseudo-first-order kinetics, min^{-1}
k_2 — Equilibrium rate constant of pseudo-second-order kinetics, g mg^{-1} min^{-1}
k — Intraparticle diffusion rate constant, mg g^{-1} min$^{-0.5}$
C — Constant that is proportional to the boundary layer thickness

References

[1] J. Li, A.P. Davis, A unified look at phosphorus treatment using bioretention. Water Res., 90 (2016) 141–155.

[2] S. Mor, K. Chhoden, K. Ravindra, Application of agro-waste rice husk ash for the removal of phosphate from the wastewater. J. Clean. Prod., 129 (2016) 673–680.

[3] Y.H. He, H. Lin, Y.B. Dong, L. Wang, Preferable adsorption of phosphate using lanthanum-incorporated porous zeolite: characteristics and mechanism. Appl. Surf. Sci., 426 (2017) 995–1004.

[4] L. Gan, J. Zuo, B. Xie, P. Li, X. Huang, Zeolite (Na) modified by nano-Fe particles adsorbing phosphatein rainwater runoff. J. Environ. Sci-China., 24 (2012) 1929–1933.

[5] S. Jellali, M.A. Wahab, M. Anane, K. Riahi, L. Bousselmi, Phosphate mine wastes reuse for phosphorus removal from aqueous solutions under dynamic conditions. J. Hazard. Mater., 184 (2010) 226–233.

[6] C.J. Liu, Y.Z. Li, Z.K. Luan, Z.Y. Chen, Z.G. Zhang, Z.P. Jia, Adsorption removal of phosphate from aqueous solution by active red mud. J. Environ. Sci., 19 (2007) 1166–1170.

[7] S.J. Allen, G. Mckay, J.F. Porter, Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems. J. Colloid Interf. Sci., 280 (2004) 322–333.

[8] S. Agarwal, A. Rani, Adsorption of resorcinol from aqueous solution onto CTAB/NaOH/flyash composites: equilibrium, kinetics and thermodynamics. J. Environ. Chem. Eng., 5 (2017) 526–538.

[9] W.Y. Huang, Y.M. Zhang, D. Li, Adsorptive removal of phosphate from water using mesoporous materials: a review. J. Environ. Manage., 193 (2017) 470–482.

[10] L. Zhang, S. Hong, J. He, F.X. Gan, Y.S. Ho, Adsorption characteristic studies of phosphorus onto laterite, Desal. Water Treat., 25 (2011) 98–105.

[11] C.R. Jia, Y.R. Dai, J.J. Chang, C.Y. Wu, Z.B. Wu, W. Liang, Adsorption characteristics of used brick for phosphorus removal from phosphate solution. Desal. Water Treat., 51 (2013) 5886–5891.

[12] A. Domínguez, M.I. Domínguez, S. Ivanova, M.A. Centeno, J.A. Odriozola, Recycling of construction and demolition waste generated by building Infrastructure for the production of glassy materials. Ceram. Int., 42 (2016) 15217–15223.

[13] A. Arulrajah, M.M. Disfani, S. Horpibulsuk, C. Suksiripattanapong, N. Prongmanee, Physical properties and shear strength responses of recycled construction and demolition materials in unbound pavement base/subbase applications. Constr. Build. Mater., 58 (2014) 245–257.

[14] M.C.S. Nepomuceno, A.S. Rui, J.P.G. Catarino, Mechanical performance evaluation of concrete made with recycled ceramic coarse aggregates from industrial brick waste. Constr. Build. Mater., 165 (2018) 284–294.

[15] L. Huang, L.X. Chen, L.B. Yan, B. Kasal, Y.X. Jiang, C.Y. Liu, Behavior of polyester FRP tube encased recycled aggregate concrete with recycled clay brick aggregate: size and slenderness ratio effects. Constr. Build. Mater., 154 (2017) 123–136.

[16] J.E. Grebel, S.K. Mohanty, A.A. Torkelson, A.B. Boehm, C.P. Higgins, R.M. Maxwell, K.L. Nelson, D.L. Sedlak, Engineered infiltration systems for urban stormwater reclamation. Environ. Eng. Sci., 30 (2013) 437–454.

[17] P. Nanta, K. Kasemwong, W. Skolpapa, Isotherm and kinetic modeling on superparamagnetic nanoparticles adsorption of polysaccharide. J. Environ. Chem. Eng., 6 (2018) 794–802.

[18] A.O. Babatunde, Y.Q. Zhao, A.M. Burke, M.A. Morris, J.P. Hanrahan, Characterization of aluminium-based water treatment residual for potential phosphorus removal in engineered wetlands. Environ. Pollut., 157 (2009) 2830–2836.

[19] K.J. Winter, D. Goetz, The impact of sewage composition on the soil clogging phenomena of vertical flow constructed wetlands. Water Sci. Technol., 2003, 48 (2013) 9–14.

[20] A.R.A. Zidan, M.M. El-Gamal, A.A. Rashed, EH. Eid, Wastewater treatment in horizontal subsurface flow constructed wetlands using different media (setup stage). Water Sci., 29 (2015) 26–35.

[21] W.F. Hunt, A.P. Davis, R.G. Traver, Meeting hydrologic and water quality goals through targeted bioretention design. J. Environ. Eng., 138 (2012) 698–707.

[22] J. Vymazal, Horizontal sub-surface flow and hybrid constructed wetlands systems for wastewater treatment. Ecol Eng., 25 (2005) 478–490.

[23] H.S. Altundogan, F. Tumen, Removal of phosphates from aqueous solutions by using bauxite. I: effect of pH on theadsorption of various phosphates. J. Chem.Technol. Biot., 77 (2001) 77–85.

[24] D.G. Grubb, M.S. Guimaraes, R.Valencia, Phosphate immobilization using an acidic type F fly ash. J. Hazard. Mater., 76 (2003) 217–236.

[25] S.G. Lu, S.Q. Bai, L. Zhu H.D. Shan, Removal mechanism of phosphate from aqueous solution by fly ash. J. Hazard. Mater., 161 (2009) 95–101.

[26] X. Liu, S.L. Huang, X.G. Liu, Characteristics of phosphorous adsorption on three substrates used in constructed wetland. Chinese J. Environ. Eng., 6 (2012) 3367–3372.

[27] J. Chen, H. Kong, D. Wu, X. Chen, D. Zhang, Z.H. Sun, Phosphate immobilization from aqueous solution by fly ashes in relation to their composition. J. Hazard. Mater., 139 (2007) 293–300.

[28] F.C. Wu, T. Ruling, J. Rueyshin, Initial behavior of intraparticle diffusion model used in the description of adsorption kinetics. Chem. Eng. J., 153 (2009) 1–8

[29] F.C. Wu, R.L.Tseng, R.S. Juang, Comparisons of porous and adsorption properties of carbons activated by steam and KOH. J. Colloid Interf. Sci., 283 (2005) 49–56

[30] M.H. Jnr, J. Vicente, Kinetic study of liquid-phase adsorptive removal of heavy metal ions by almond tree (Terminalia catappa L.) Leaves waste. B. Chem. Soc. Ethiopia, 21 (2007) 349–362.