Phosphorus removal from aqueous solutions by adsorptive concrete aggregates

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Phosphorus removal from aqueous solutions by adsorptive concrete aggregates

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A B S T R A C T

The purpose of this study is to investigate the adsorption characteristics of granular aggregates under identical experimental conditions for potential applications in highly adsorptive concrete. In this study, industrial by-products (steel slag), lightweight aggregates (expanded silica) and bio-materials (peach shell and miscanthus) are used for phosphorus (P) removal from aqueous solutions. The effects of several parameters such as the initial concentrations of P, reaction time and pH value on adsorption capacity and efficiency of P are investigated using an IC analyzer. Results show that the phosphorus adsorption of all absorbents follows the adsorption isotherms with a varying phosphorus concentration from 5 mg/L to 700 mg/L, and the adsorption isotherms data are fitted well by Langmuir equation. The steel slag exhibits a higher P-adsorption capacity and adsorption efficiency compared to lightweight aggregates and bio-materials, with an estimated maximum adsorption capacity by steel slag of 20.4 mg/g. Moreover, the P-desorption results show that steel slag has a very low P-desorption. Heat treatment is used to increase the adsorption capacity of the miscanthus owing to the change in pore structure characteristics determined by BET. The adsorption kinetic data of the steel slag follows a pseudo-second-order model. The ICP-AES, XRD and SEM-EDS analyses show that the P-adsorption of the miscanthus and peach shell follows physical adsorption, whereas the adsorption mechanism of the steel slag can be attributed to the Ca\(^{2+}\) released from the steel slag, which can react with P and form a stable Ca–P precipitate. It is suggested that steel slags can function as effective adsorptive aggregate for the manufacture of highly adsorptive concrete.

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1. Introduction

The development of urbanization leads to an increasing impact of human activities on aqueous environments (Gizińska-Górna et al., 2017). Stormwater runoff from urban catchment areas is one of the biggest sources of water pollution (Bannerman et al., 1993). During the rainy season, the pollutants on road surfaces such as heavy metals, pesticides and organic contaminants etc. are entrained into the stormwater and flow into the nearest water body (Wang et al., 2018), which pose a huge threat to ecological safety and public health (Rizzo and Rizzo, 2015). Among these pollutants, phosphorus (P) is one of the main pollutants from stormwater runoff (Park et al., 2017; Zhu et al., 2018). In extreme conditions, the excess supply of P causes the eutrophication and excessive algal blooms, which leads to the degradation of water quality, and the mortality of fish and aquatic plants (Guo et al., 2018). Therefore, it is vital to remove the P from stormwater before they are discharged into the water body.

In recent years, ordinary pervious concrete has been used for pollutants removal from stormwater runoff. Shabalala et al. (2017) reported that pervious concrete can remove more than 75% of the heavy metals from acid mine drainage. Jo et al. (2015) investigated...
the use of fly ash geopolymer paste in pervious concrete for the removal of faecal coliforms and P and the average removal of faecal coliforms and P are 43.1% and 21.9%, respectively. Rivera et al. (2015) studied that the addition of fly ash and iron oxide nanoparticles in pervious concrete improves P removal. The adsorption capacity of different pervious concrete for pollutants removal is summarized in Table 1. The adsorption capacity of ordinary pervious concrete is very limited because gravel or sand without adsorption capacity is used as aggregates in ordinary pervious concrete. Moreover, a very long contact time is often required, even at a low initial pollutant concentration (Haselbach et al., 2014). Therefore, in order to improve the adsorption capacity of ordinary pervious concrete, a potentially effective method is to replace non-adsorptive aggregates with high adsorptive aggregates.

Currently, various methods such as ion exchange, chemical precipitation, biological processes and physical adsorption, etc. have been used for P removal from the aqueous environment (Naghipour et al., 2015). With the requirements of sustainable development, different low-cost and high-adsorption materials are gradually employed for wastewater treatment, such as fly ash (Agyei et al., 2002), pumice (Taylor et al., 2014), steel slag (Barca et al., 2014; Bowden et al., 2009), lightweight expanded materials (Forbes et al., 2004; Nkansah et al., 2012), peach shell (PS) (Dastgheib and Rockstraw, 2001), miscanthus (M) (Osman et al., 2018), plantago ovata (Yaghoobi et al., 2017), etc. Although most of these materials show good adsorption characteristics, they are not suitable as adsorptive concrete aggregates considering size and strength requirements. Besides, most of the current studies mainly focus on the adsorption capacity of powdery materials. The adsorption capacity of the low-cost, available and high adsorptive aggregates for the manufacture of highly adsorptive concrete should be evaluated by granular aggregate rather than powder.

Steel slag (SS) is a by-product from the steel industry, which has been widely used as an aggregate and a cement component for construction and building materials. The main dominant components of the SS are calcium oxide (CaO) and iron oxide (Fe$_2$O$_3$), which are the result of the addition of the fluxing agent during the steelmaking process (Barca et al., 2012). The high content of metal oxide makes it a potential adsorbent, and it has attracted more attention to remove P from wastewater (Park et al., 2017; Shilton et al., 2006). The release of calcium ions (Ca$^{2+}$) from the SS can be combined with phosphorus ions (PO$_4^{3-}$) by Ca–P precipitation-coagulation mechanism (Bowden et al., 2009). More than 50% of the SS is composed of calcium-containing minerals (Shi, 2004), indicating sufficient calcium ions can be supplied for the precipitation-coagulation process. Porous lightweight aggregates also can be used to remove the heavy metals and organic pollutants from wastewater due to the well-developed pore structure (Lee et al., 2011; Sayari et al., 2005). Adsorptive aggregates should be low-cost, eco-friendly and available, thus bio-based aggregates (PS, M, etc.) may be feasible for recyclable adsorptive materials for pollutant removal. Although these materials are potential adsorptive aggregates that can be used for the manufacture of high adsorptive concrete, different experimental conditions affect the physico-chemical properties of materials, even the same material exhibits different adsorption capacities with varying conditions such as initial concentration, reaction time, pH, temperature and agitation mode, etc (Barca et al., 2012). Therefore, a direct comparison of the adsorption capacity of these materials is not feasible (Park et al., 2017). The adsorption properties of different adsorptive aggregates under identical experimental condition should be investigated and the optimized aggregates for potential application in highly adsorptive concrete should be obtained.

The purpose of this study was to investigate the adsorption characteristics of granular aggregates under identical experimental conditions for potential applications in highly adsorptive concrete. The industrial by-products (SS), lightweight aggregates (expanded silica (ES)) and bio-materials (PS and M) were used for P removal from aqueous solutions. The effects of the initial concentration of P, reaction time and pH on the adsorption capacity and efficiency of P were investigated using an ion chromatography (IC) analyzer. The adsorption isotherms and adsorption kinetics models of P-

### Table 1
AdSORPTION Capacity of Different Pervious Concrete for Pollutants Removal

<table>
<thead>
<tr>
<th>Types of Concrete</th>
<th>Pollutants</th>
<th>Initial concentration</th>
<th>Removal capacity</th>
<th>Contact time</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pervious concrete</td>
<td>Cu, Co, Ni</td>
<td>0.1–1.3 mg/L</td>
<td>&gt;75%</td>
<td>6 months</td>
<td>Shbabala et al. (2017)</td>
</tr>
<tr>
<td>Pervious concrete containing fly ash</td>
<td>P</td>
<td>2.58–3.4 mg/L</td>
<td>25–85%</td>
<td>0.5–8 h</td>
<td>Jo et al. (2015)</td>
</tr>
<tr>
<td>Pervious concrete containing iron oxide</td>
<td>P</td>
<td>10 mg/L</td>
<td>&gt;90%</td>
<td>72 h</td>
<td>Vázquez-Rivera et al. (2015)</td>
</tr>
<tr>
<td>Ordinary pervious concrete</td>
<td>Cu &amp; Zn</td>
<td>20 μm/L &amp; 100 μm/L</td>
<td>87% &amp; 90%</td>
<td>10 cycles</td>
<td>Haselbach et al. (2014)</td>
</tr>
<tr>
<td>Ordinary Portland cement</td>
<td>P</td>
<td>400 mg/L</td>
<td>20.75%</td>
<td>–</td>
<td>Agyei et al. (2002)</td>
</tr>
<tr>
<td>Aluminium hydroxide-coated sand</td>
<td>P</td>
<td>25 mg/L</td>
<td>0.239 mg/g</td>
<td>24 h</td>
<td>Han et al. (2009)</td>
</tr>
</tbody>
</table>
absorption were derived. The pore structural properties of the materials were analyzed using Brunauer Emmett Teller (BET) method. The adsorption mechanism of phosphorus was discussed based on the results analyzed from inductively coupled plasma atomic emission spectroscopy (ICP-AES), X-ray diffraction (XRD) and scanning electron microscope combined with energy dispersive spectrometer (SEM-EDS).

2. Materials and methods

2.1. Materials

The steel slag (SS) (TATA Steel, The Netherlands), commercial expanded silica (ES), miscanthus (M) (NNRGY, The Netherlands) and commercial PS biochar are used as absorptive materials in this study. The heat-treated miscanthus (M-3 hour) under nitrogen condition at 250 °C for 3 h is also used as an absorbent for comparison (Luo et al., 2013). All raw materials with a particle size of 1–2 mm are selected to investigate the adsorption performance of the granular aggregates. They are washed twice with distilled water to remove any contaminations, and then oven-dried at 105 °C for 24 h and stored in air-tight containers until the test.

The high content of metal oxides contributes to a strong affinity for P-adsorption (Kaasik et al., 2008). The chemical compositions of steel slag and expanded silica are determined by X-ray fluorescence spectroscopy (XRF), as presented in Table 2. The main chemical components of the SS are CaO (40.0%), Fe2O3 (31.5%) and SiO2 (10.4%). The ES is mainly composed of SiO2 (51.3%), Al2O3 (19.6%) and Na2O (14.8%). The PS and M are organic matter, and their chemical compositions are mainly composed of C, H, O and N (Wu et al., 2018). The SEM images of the adsorbents are shown in Fig. 1. Many micropores are observed on the surface of the PS, ES and M-3 hour (Fig. 1a, c and 1e). The SS displays a denser surface with larger cracks compared to the ES and M-3 hour (Fig. 1b, d and 1f).

2.2. P-adsorption experiments

In this study, artificial P solution is prepared for the adsorption test. A stock P solution of 1000 mg/L is prepared by dissolving the chemically pure potassium dihydrogen phosphorus (KH2PO4) in distilled water. All standard P solutions with the desired concentration in the solution at equilibrium (mg/L), M is the mass of sample (g), and V is the volume of solution (L).

2.2.1. Effect of different adsorbents on adsorption

A preliminary experiment is conducted to evaluate the adsorption capacity of different raw materials. 1 g of the adsorbent material is added to a 25 ml P solution with a concentration of 50 mg/L. The mixture is stirred at 225 rpm in the thermostatic water bath shaker for 24 h and then is filtered and determined for residual concentration.

The P-adsorption capacity (q, mg/g) and P-removal rate (PR, %) are calculated as follows:

\[ q = \frac{C_0 - C_e}{m} \times V \]  

\[ P_R = \frac{C_0 - C_e}{C_0} \times 100\% \]

Where \(C_0\) is the initial P concentration (mg/L), \(C_e\) is the P concentration in the solution at equilibrium (mg/L), \(M\) is the mass of sample (g), and \(V\) is the volume of solution (L).

2.2.2. Adsorption isotherms

The adsorption isotherms of P are evaluated by batch experiments. For the sorption isotherms, 1g of the adsorbent is loaded in 50 ml polyethylene centrifuge tube and mixed with 25 ml of various P solution (5–700 mg/L). The flask is covered and stirred at 225 rpm for 24 h to ensure approximate equilibrium. After P adsorption, the solution is filtered through a 0.45 μm membrane filter and then analyzed for P concentration.

The Langmuir and Freundlich equations are used for analyzing the adsorption isotherms of adsorbents, as described below:

\[ \text{Langmuir equation: } A_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \]

\[ \text{Freundlich equation: } A_e = K_F C_e^n \]

Where \(A_e\) is the adsorption removal capacity (mg/g), \(C_e\) is the P concentration in the solution at equilibrium (mg/L), \(Q_m\) is maximum adsorption capacity in Langmuir isotherm, \(K_L\) is adsorption constant in Langmuir isotherm, \(K_F\) is the constant of Freundlich isotherm, and \(n\) is heterogeneity factor of Freundlich isotherm.

2.2.3. Adsorption kinetics

The adsorption kinetics experiments are performed using a procedure similar to the one used for the adsorption isotherm test. A series of bottles with 1g of adsorbent and 100 ml of solution with a set P concentration of 100 mg/L, then mixed and shaken for different contact time (0.25, 0.5, 1, 2, 4, 6, 8, 12, 16 and 24 h). The solution is filtered and determined for residual concentration.

The Lagergren pseudo-first-order equation, pseudo-second-order equation and simple Elovich equation are used for describing the adsorption kinetics of adsorbents in this study:

\[ \frac{dA_t}{dt} = k_1 (A_e - A_t) \]

\[ \frac{dA_t}{dt} = k_2 (A_e - A_t)^2 \]

\[ q = \alpha + \beta \ln t \]

Where \(A_t\) is the amount of P adsorbed by the adsorbent at any time (mg/L), \(A_e\) is the adsorption removal capacity (mg/g), \(K_1\) and \(K_2\) is the rate constant of Lagergren pseudo-first-order and pseudo-second-order kinetic models.

2.2.4. Effects of pH on adsorption capacity

The effects of pH on P-adsorption are determined by a series of experiments with constant initial P concentration (100 mg/L) and adsorbent dosage (1g) and various pH values (3, 5, 7, 9 and 11). 1M NaOH and 0.5 M HCl are used to adjust the pH value of the tested P solution.
2.3. P-desorption experiments

P-saturated adsorbent (1g) with 50 mg/L P-solution is placed in a 50 ml tube with 25 ml distilled water. After that, the tube is continuously shaken in a shaker at 225 rpm for 24 h. The mixture is centrifuged and filtered, and the P is determined by the same method described above. P-desorption capacity \( q_d \) (mg/g) is calculated:

\[
q_d = \frac{CV}{M} \tag{8}
\]

The P-desorption rate \( P_d \) is calculated:

\[
P_d = \frac{CV}{T_P} \times 100\% \tag{9}
\]

where \( C \) is the P concentration in the solution (mg/L), \( M \) is the mass of sample (g), \( V \) is the volume of the solution (L), and \( T_P \) is the P content in the P-saturated sample.

2.4. Analytical methods

The microstructural properties of all samples including BET-surface area, pore volume and pore size are determined by nitrogen adsorption/desorption test. The mineralogical composition of all samples before and after absorption of P is determined by XRD. The microstructure of all samples before and after the test is observed by SEM-EDS, all samples are coated with Au. Metal ions such as calcium (Ca\(^{2+}\)), iron (Fe\(^{2+}\)), magnesium (Mg\(^{2+}\)), etc. are measured through ICP-AES. The concentration of P is analyzed by IC.

3. Results and discussion

3.1. Pore structure of materials

The P-adsorption capacity depends on the differences in chemical composition, microstructure, and pore characteristics (Jiang et al., 2014). Most of powders or aggregates such as clay, pigment, cement exhibited Type II isotherms, and the narrow hysteresis loop is generated by inter-particle capillary condensation (Rouquerol et al., 2013). As shown in Fig. 2, the adsorption-desorption isotherm curves of all materials belonged to the Type II isotherms based on the International Union of Pure and Applied Chemistry (IUPAC) classification (Rouquerol et al., 2013). Moreover, a narrow hysteresis loop is observed in the adsorption-desorption isotherm curves, which indicates that the micropores and mesopores are well developed (Jung et al., 2015; Lin et al., 2016). The results also show that the PS adsorbed more nitrogen than other materials under the same relative pressure conditions, which indicates that the PS has more developed pore structures.

The pore size of adsorbents can be divided into micropores (<2 nm), mesopores (2–50 nm) and macropores (>50 nm) (Zhang and Li, 2011). The pore size distribution of the material is estimated by the Barrett-Joyner-Halenda (BJH) method from the desorption data of BET test, as shown in Fig. 3. The pore structure properties of the material are shown in Table 3. As shown in Fig. 3, most of the pores of the PS and SS are less than 10 nm, which indicates that they may have better adsorption capacity compared to the ES and the M. Generally, the mesopores mainly play the role of the channel for the solution to enter the interior of the PS. The most of pore volume of the ES and M is less than 50 nm, and they are in the range of mesopores. The cumulative pore volume of the M and M-3hour are 0.0088 cm\(^3\)/g and 0.0073 cm\(^3\)/g, respectively, which indicates that the heat treatment reduces the pore volume and pore size of the M.
Fig. 2. The nitrogen adsorption-desorption isotherms of the material.

Fig. 3. The Barrett-Joyner-Halenda (BJH) pore size distribution of the material.

Table 3
Physical properties of materials.

<table>
<thead>
<tr>
<th>Materials</th>
<th>BET surface area (m²/g)</th>
<th>Micropore area (m²/g)</th>
<th>Pore size (nm)</th>
<th>Pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peach shell (PS)</td>
<td>297.4</td>
<td>237.3</td>
<td>2.01</td>
<td>0.1494</td>
</tr>
<tr>
<td>Steel slag (SS)</td>
<td>5.14</td>
<td>0.58</td>
<td>13.18</td>
<td>0.0017</td>
</tr>
<tr>
<td>Expanded silica (ES)</td>
<td>1.03</td>
<td>0.07</td>
<td>14.49</td>
<td>0.0037</td>
</tr>
<tr>
<td>Miscanthus (M)</td>
<td>0.12</td>
<td>0.54</td>
<td>30.66</td>
<td>0.0066</td>
</tr>
<tr>
<td>Heat-treated miscanthus (M-3hour)</td>
<td>1.98</td>
<td>1.40</td>
<td>12.75</td>
<td>0.0063</td>
</tr>
</tbody>
</table>

Fig. 4. The P removal capacity and rate of the material in the P solution of 50 mg/L (Adsorbent: 1g, P solution volume: 25 ml, Revolution per minute: 225, Time: 24 h).

Fig. 5. The ions released from steel slag.
consequently increasing the specific surface area, as shown in Table 3. Therefore, the M-3hour may have better uptake of P because of the well-developed mesoporous structure and high specific surface area compared to the untreated M (Luo et al., 2013).

3.2. P-adsorption

3.2.1. Effect of different materials on adsorption

The P removal capacity and removal rate of the material after 24 h in P solution of 50 mg/L are shown in Fig. 4. The results show that the SS and ES have a higher capacity for P removal compared with other bio-materials. The P-removal rate of the SS is 100%, while the adsorption capacity of other materials for P removal is very limited, with a range of 8%–19%. The high P adsorption capacity of the SS is attributed to the calcium ions leached from the SS surface, which can be bound with P ions in the solution to form a stable precipitate (Jiang et al., 2014; Yin et al., 2011).

The ions released from the SS surface are presented in Fig. 5. Some metals ions such as K, Na and Mg ions do not significantly affect the P-adsorption capacity (Helyar et al., 1976a, 1976b), whereas metal ions (i.e. Ca, Fe, Al) released from the materials have a strong affinity with P. Previous studies have reported that the relative effects of the different cations on P-adsorption capacity (Helyar et al., 1976a), with the order of Ca > Mg > K > Na (Lehr and Van Wesemael, 1952). Hence, among the metal ions, the Ca$^{2+}$ concentration is one of the key parameters for the Ca–P precipitation (Barca et al., 2012), the adsorption process is shown in Fig. 6a. Although sodium ions are also leached from the solution of the SS, the sodium ions have no significant effect on the adsorption of P, as reported by Bowden et al. (2009) and Yin et al. (2011). For the SS, the P-removal capacity is dominated by a chemical process, a large amount of calcium ions leach from the SS surface supply enough dissolved calcium ions to the solution and react with P and precipitate in the form of hydroxyapatite following the chemical reactions (Barca et al., 2012; Park et al., 2017):

\[ \text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{OH}^- \]  \hspace{1cm} (10)
\[ 5\text{Ca}^{2+} + 3\text{PO}_4^{3-} + \text{OH}^- \rightarrow \text{Ca}_5(\text{PO}_4)_3(\text{OH})_3 \]  \hspace{1cm} (11)

However, the PS and M are organic matter, which are mainly composed of C, N and O elements, indicating that the P-removal is achieved by pore-filling and electrostatic attraction (Tan et al., 2015), as shown in Fig. 6b. The high specific surface area and more mesoporous structure are crucial for improving the uptake capacity of P (Jung et al., 2015). The results confirm that the M-3hour increases the adsorption capacity compared to the M. Previous researches show that the bio-materials made from bamboo, maize residue and soybean stover have a low P-removal rate with a range of 2–9% (Jung et al., 2015). The results also indicate that the SS has better P-adsorption capacity and adsorption efficiency compared to lightweight aggregates and bio-materials.

3.2.2. Adsorption isotherms

The adsorption isotherms of the materials are presented in Fig. 7. The results show that the P-adsorption capacity increases as the initial P concentration increases. However, the P-removal rate decreases with the increase in P concentration. At the initial P concentration of 700 mg/L, the maximum adsorption capacity of the SS is 9.76 mg/g, while the adsorption capacity of other materials varies from 1.45 mg/g to 1.80 mg/g. When the initial P concentration is less than 200 mg/L, the P-removal rate of the SS reaches 100%. When the initial P concentration further increases, the P-removal rate of the SS decreases. For instance, the removal rate of the SS lows down to about 55% at the initial P concentration of 700 mg/L. This is because a stepwise adsorption reaction occurs at low P concentrations due to Ca$^{2+}$ released from SS is sufficient to...
ensure precipitation of P (Barca et al., 2012), while the precipitation of CaP occurs at higher P concentrations with the adsorbed P acting as a core for crystal growth (Koiv et al., 2010; Yin et al., 2011). Nevertheless, the P-removal rate of other adsorbents is about 10%, which is significantly lower than that of the SS.

The P-adsorption isotherms are analyzed by Langmuir and Freundlich equation, respectively, as shown in Fig. 8. The Langmuir and Freundlich isotherm parameters for P-adsorption are presented in Table 4. The results show that both Langmuir and Freundlich models fitted the experimental data well with very high correlation coefficient ($R^2$). The estimated maximum adsorption capacity of the SS is 20.40 mg/g according to the Langmuir model. The maximum adsorption capacity of the M-3hour is very close to that of the PS. However, the extraction of P from the M and the M-3hour may more easily occur than other materials because of the low holding capacity (Jung et al., 2015). The desorption results of P will be analyzed in the later section.

### 3.2.3. Adsorption kinetics

Kinetic studies are usually used to evaluate the relationship between reaction time and the maximum adsorption capacity (Jung et al., 2015). The adsorption rate of the adsorbent usually increases rapidly during the initial reaction time and then slowly.

![Fig. 8. The Langmuir and Freundlich isotherms of the materials.](image)

![Fig. 9. The adsorption kinetics of the materials.](image)

<table>
<thead>
<tr>
<th>Materials</th>
<th>Langmuir model</th>
<th>Freundlich model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q_m$</td>
<td>$K_L$</td>
</tr>
<tr>
<td>PS</td>
<td>3.676</td>
<td>0.00131</td>
</tr>
<tr>
<td>SS</td>
<td>20.40</td>
<td>0.00137</td>
</tr>
<tr>
<td>ES</td>
<td>4.067</td>
<td>0.00125</td>
</tr>
<tr>
<td>M</td>
<td>3.390</td>
<td>0.00101</td>
</tr>
<tr>
<td>M-3hour</td>
<td>3.677</td>
<td>0.00105</td>
</tr>
</tbody>
</table>

![Table 4](image)
reaches equilibrium (Ghaedi et al., 2011). As shown in Fig. 9, the adsorption capacity of all materials increases as the reaction time increases. At the end of 2 h, the adsorption capacity of the SS only reaches 52% of the adsorption equilibrium capacity. The results also show that the adsorption rate of the SS gradually reduces with contact time increases until reaching the equilibrium after 16 h. The equilibrium time of the SS and ES are significantly longer than that of bio-materials. The varying equilibrium time may be attributed to the distinguishing characteristics of the materials, which leads to different adsorption processes and adsorption mechanisms (Yin et al., 2011).

However, the adsorption capacity of the M rapidly increases at the first 2 h, which reaches 92% of the adsorption equilibrium capacity. Previous researches reported that the adsorption capacity of the peanut shell biochar exceeds 80% of its maximum adsorption capacity within the first 4 h (Jung et al., 2015). This is attributed to a large amount of mesopores available for adsorption at the first contact time (Ghaedi et al., 2011). Moreover, the high water adsorption of the M results in the mesopores being rapidly filled by the P solution in the first 2 h, then the adsorption rate rapidly decreases until reaching the equilibrium. However, the use of the SS to remove P is a slow and continuous process, indicating sufficient calcium ions gradually leach from the SS surface and then react with P for the precipitation-coagulation process. Besides, the precipitation also needs time to finish the reaction (Park et al., 2017). Therefore, as long as calcium ions are continuously released for the SS surface, the P-removal process will keep proceeding.

The experimental data are matched by the pseudo-first-order, pseudo-second-order and simple Elovich kinetic models. As shown in Fig. 9, the experimental data of P-adsorption in this study can be described well by the pseudo-second-order kinetic model. The evaluated kinetic parameters are presented in Table 5. The values of the calculated adsorption capacity are close to the experimental data according to the pseudo-second-order model. Although the Elovich model also can fit the adsorption kinetic data of the SS and the ES, the fitting quality for the M and PS are poor.

### 3.2.4. Effect of pH on adsorption capacity

The high pH causes the adsorbent surface to carry a more negative charge, which significantly repulses negatively charged solutes, consequently, a high pH generally reduces the adsorption capacity of P due to the presence of repulsive forces (Park et al., 2017; Yang et al., 2006). As shown in Fig. 10, the adsorption capacity of all materials decreases by 11%–19% when the pH value increases from 3 to 11. This result is consistent with previous studies reported by Yin et al. (2011) and Bolan et al. (1986), with the maximum P-adsorption capacity appears at a pH value of around 3–4. When the pH value of the solution less than 2, the species of the P predominantly exist in H3PO4, which is difficult to attach to exchange sites for anion exchange. When the pH value varies from 3 to 5, the H2PO4/CO32–HPO4/CO32– and PO4/CO32– are major species for the P solution, which are available for ion exchange, especially H2PO4–. When the pH value is more than 8, more OH– ions are available in solution, which may compete with the species of the P for ion exchange, resulting in the reduction in the P-adsorption (Ruixia et al., 2002).

The results also show that the adsorption capacity of the SS reduces sharply when the pH values of the P solution change from acidic to alkaline. Previous studies indicate that the amount of Ca2+ ions leaching from the adsorbent decreases with an increase in pH value of the initial solution (Gan et al., 2009; Yin et al., 2011). Moreover, when the pH value of the solution is decreased, the

<table>
<thead>
<tr>
<th>Materials</th>
<th>Pseudo-first-order</th>
<th>Pseudo-second-order</th>
<th>Elovich</th>
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<tr>
<td></td>
<td>Q</td>
<td>R²</td>
<td>K₁</td>
</tr>
<tr>
<td>PS</td>
<td>0.443</td>
<td>0.947</td>
<td>2.667</td>
</tr>
<tr>
<td>SS</td>
<td>2.345</td>
<td>0.394</td>
<td>0.919</td>
</tr>
<tr>
<td>ES</td>
<td>0.414</td>
<td>0.741</td>
<td>1.065</td>
</tr>
<tr>
<td>M</td>
<td>0.353</td>
<td>0.844</td>
<td>2.849</td>
</tr>
<tr>
<td>M-3-hour</td>
<td>0.369</td>
<td>0.937</td>
<td>2.990</td>
</tr>
</tbody>
</table>

Fig. 10. Effects of pH values on the adsorption capacity (Adsortent: 1g, P solution: 25 ml, Initial P concentration: 100 mg/L).

Fig. 11. The P desorption capacity and desorption rate of the material (Adsorbent: 1g, Distilled water: 25 ml, Revolution per minute: 225, Time: 24 h).
positively charged surface sites formed on the adsorbent promotes the P-adsorption because of the electrostatic attraction (Gan et al., 2009). An approximate 20% reduction in P adsorption capacity is observed in the calcium-rich sepiolite adsorbent (Yin et al., 2011). This is because the positively charges surface of the adsorbents is more easily combine with P in an acidic solution due to electrostatic attraction (Gan et al., 2009). Besides, the types of the P ions in solution are affected by the pH value of the solution. When the pH value varies between 3 and 7, the predominant species of P are a negatively charged H$_2$PO$_4^-$, which could react with the dissolved Ca$^{2+}$ to form the precipitation by the chemical reactions as follows (Johansson and Gustafsson, 2000; Yin et al., 2011):

\[
\text{Ca}^{2+} + 2\text{H}_2\text{PO}_4^- \rightarrow \text{Ca}({\text{H}_2\text{PO}_4})_2 \quad (12)
\]

\[
\text{Ca}({\text{H}_2\text{PO}_4})_2 + \text{Ca}^{2+} \rightarrow 2\text{CaHPO}_4 + 2\text{H}^+ \quad (13)
\]

\[
6\text{CaHPO}_4 + 2\text{Ca}^{2+} \rightarrow \text{Ca}_8({\text{H}_2\text{PO}_4})_6 + 4\text{H}^+ \quad (14)
\]

\[
\text{Ca}_8({\text{H}_2\text{PO}_4})_6 + 2\text{Ca}^{2+} + \text{H}_2\text{O} \rightarrow \text{Ca}_{10}({\text{PO}_4})_6(\text{OH}_2) + 4\text{H}^+ \quad (15)
\]

Fig. 12. The XRD patterns of the material before and after the test (a) SS, (b) ES, (c) PS, (d) M and (e) M-3 hour.
3.3. P-desorption

The P desorption capacity and desorption rate of the material are shown in Fig. 11. The results show that the P-desorption rate of the M and the M-3hour is significantly higher than that of other materials, which are more than 60%. This phenomenon indicates that the M is an unstable physical absorption, and the adsorbed P could easily be desorbed from the M, resulting in secondary pollution in the aquatic environment. It should be noted that no desorbed P is detected in the SS solution, which confirms that the combination of Ca–P is a stable precipitation process and barely desorption occurs once bonding is formed (Drizo et al., 2006; Yin et al., 2011). Therefore, the SS can be safely used as adsorptive aggregates in concrete for P-removal from water and no secondary pollution occurs.

3.4. Characterization of the adsorbents after the test

3.4.1. Mineralogical phase analysis

The XRD patterns of the material before and after the test are presented in Fig. 12. The main mineral components of the SS are 3CaO SiO$_2$ (C$_3$S), 2CaO SiO$_2$ (C$_2$S) and RO (Fe$_2$O$_3$, MgO and MnO) (Wang and Yan, 2010), as shown in Fig. 12a. After the P-adsorption, the diffraction peaks corresponding to C$_3$C and C$_2$S mineral phases of the SS are decreased, especially at about 35° diffraction angle compared to the pattern before adsorption, which can be explained by the hydrolysis of calcium-containing oxides (Han et al., 2015). This phenomenon indicates that the calcium-containing oxides are involved in the adsorption of P, which leads to the better adsorption capacity of the SS than other materials. The crystallized structure of the ES is characterized as silicon oxide, sodium aluminium silicate and iron oxide. Metal elements such as iron and aluminium also contributed to the P-adsorption (Zhao et al., 2007).

Similar to other bio-materials such as wood, soybean, bamboo, etc., the structure of the PS is crystalline cellulose and a distinct peak appears near the diffraction between 25° and 30°. The shape of the diffraction curve of the PS is somewhat lower than that of the M-3-hour, which is similar to that of the PS. The M-3-hour shows a wide diffraction peak compared to the M due to the heat treatment effect (Asadi Zeidabadi et al., 2018; Wu et al., 2018). PS and M are mainly composed of C and O, which account for about 90% of the total dry weight (De Jong et al., 2003; Kaynak et al., 2005). They cannot react with P to form a new crystal.

![Fig. 13. The SEM images and EDS analysis of the material after adsorption test (a) PS, (b) SS, (c) ES, (d) M and (e) M-3-hour.](image-url)

Table 6

<table>
<thead>
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<tbody>
<tr>
<td>Au</td>
<td>42.89</td>
<td>91.71</td>
<td>39.68</td>
<td>51.08</td>
<td>62.95</td>
</tr>
<tr>
<td>C</td>
<td>40.77</td>
<td>5.51</td>
<td>–</td>
<td>–</td>
<td>12.07</td>
</tr>
<tr>
<td>N</td>
<td>11.19</td>
<td>1.86</td>
<td>–</td>
<td>–</td>
<td>11.55</td>
</tr>
<tr>
<td>O</td>
<td>2.85</td>
<td>0.50</td>
<td>15.52</td>
<td>13.39</td>
<td>4.31</td>
</tr>
<tr>
<td>Si</td>
<td>–</td>
<td>2.81</td>
<td>0.80</td>
<td>3.77</td>
<td>4.89</td>
</tr>
<tr>
<td>Ca</td>
<td>–</td>
<td>31.93</td>
<td>12.98</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>P</td>
<td>2.3</td>
<td>0.42</td>
<td>3.88</td>
<td>0.94</td>
<td>1.21</td>
</tr>
</tbody>
</table>

The elemental content obtained by SEM-EDS analysis.
structure. Therefore, the changes in the peaks of the M and the M-3 hour after P-adsorption near the diffraction angle of 18° and 40° are caused by the amorphous P on the surface or micropores of the material (Han et al., 2015).

3.4.2. SEM-EDS analyses

The SEM images and the EDS analyses of the material after P adsorption are shown in Fig. 13. The results show that several small spots are selected and analyzed on the surface of other materials (Fig. 13) and the distributed crystalline substance is observed on the M-3-hour surface, as shown in Fig. 13e. The finely distributed P crystals are observed on the surface of furnace slag by EDS analysis, which is the precipitate of Ca/P/O. The same phenomenon is also observed in other materials, such as furnace slag (Park et al., 2017), oil-shale ash (Kaasik et al., 2008), sepiolite (Yin et al., 2011), namely suspended Ca–P precipitation formed on the surface of the adsorbent after P-adsorption. In this study, the strong peak of P is observed in all EDS spectra and the P is detected on the surface of all materials. A higher Ca and P content is detected on the surface of the SS, as shown in Table 6. The results indicate that the surface structure of the SS has no significant effect on the P-adsorption, the chemical adsorption is predominant to the SS for P adsorption due to the dissolution of calcium and precipitation of hydroxyapatite (Barca et al., 2012).

3.5. Low-cost materials used for P-adsorption

The low-cost materials used for P-adsorption including industrial by-products, synthetic materials, natural and bio-based materials are presented in Table 7. The results indicate that the SS generally has better P adsorption capacity than most of the biomaterials and unmodified natural materials, but lower than synthetic materials and modified natural materials. However, although the synthetic materials have higher adsorption capacity, they are powdery and are not suitable for application as aggregates in concrete. Similar to the modified natural aggregates coated with chemical solvents, the use of synthetic materials in concrete may lead to secondary pollution of the water environment (Sabhi and Kiwi, 2001).

Bio-based activated carbon such as bamboo, juniper fibre and date palm fibre has been widely used as adsorbents in water treatment, but the adsorption capacity of bio-materials is relatively limited compared to the SS. Besides, they are generally elongated and flaky particle, and their application as aggregates results in a weak interfacial transition zone and low mechanical properties of concrete (Wu et al., 2018). However, the granular SS has a much higher strength than other biological materials, which is feasible to be directly used as aggregates in concrete. Therefore, SS can be considered as an effective adsorptive aggregate to replace the non-adsorptive aggregate for increasing the P-removal of adsorptive concrete because of the excellent mechanical and adsorption properties.

4. Conclusions

In this study, the adsorption characteristics of the industrial by-product (SS), lightweight aggregates (ES) and bio-materials (PS and M) under identical experimental conditions are evaluated for potential applications in highly adsorptive concrete. The effects of parameters such as the initial concentrations of P, reaction time and pH value on adsorption capacity and efficiency of P are investigated using an IC analyzer. The adsorption mechanism of P is discussed based on BET, ICP-AES, XRD and SEM-EDS analyses. The following conclusions can be drawn:

1. The SS exhibits high P adsorption capacity and adsorption efficiency compared to lightweight aggregates and biomaterials. The maximum adsorption capacity of the SS is 20.40 mg/g according to the Langmuir model. The adsorption kinetics are fitted well by the pseudo-second-order kinetic model. Moreover, the SS has very low P-desorption, which indicates that the SS can be safely used as adsorptive aggregates in concrete for P removal and no P-desorption occurs.

2. The adsorption mechanism of the SS is attributed to the Ca2+ leached from the SS surface, which can react with P to form Ca–P precipitate. Moreover, the chemisorption process is continuous and stable, indicating sufficient calcium ions gradually leach from the SS surface and then react with P for the precipitation-coagulation process. It is suggested that the

<table>
<thead>
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<tr>
<td>Low-cost materials used for P-adsorption.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Materials</th>
<th>Particle size (mm)</th>
<th>Adsorption capacity (mg/g)</th>
<th>Initial concentration (mg/L)</th>
<th>Agitation mode (rpm)</th>
<th>Contact time (h)</th>
<th>P removal (%)</th>
</tr>
</thead>
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<td><strong>Industrial materials</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Steel slag (SS) in this study</td>
<td>1–2</td>
<td>9.76</td>
<td>700</td>
<td>225</td>
<td>24</td>
<td>55</td>
</tr>
<tr>
<td>Basic oxygen furnace slag (Park et al., 2017)</td>
<td>0.8–2.3</td>
<td>2.81</td>
<td>100</td>
<td>4000</td>
<td>24</td>
<td>–</td>
</tr>
<tr>
<td>Steel slag (Barca et al., 2012)</td>
<td>5–10</td>
<td>2.49</td>
<td>100</td>
<td>125</td>
<td>24</td>
<td>&gt;90</td>
</tr>
<tr>
<td>Furnace slag (Xu et al., 2006)</td>
<td>&lt;5</td>
<td>8.89</td>
<td>400–600</td>
<td>200</td>
<td>24</td>
<td>–</td>
</tr>
<tr>
<td>Fly ash (Agyei et al., 2002)</td>
<td>&lt;0.3</td>
<td>32</td>
<td>400</td>
<td>120</td>
<td>16</td>
<td>–</td>
</tr>
<tr>
<td>Coal ash (Drizo et al., 1999)</td>
<td>&lt;2.8</td>
<td>0.86</td>
<td>35–45</td>
<td>–</td>
<td>12</td>
<td>–</td>
</tr>
<tr>
<td><strong>Synthetic materials</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe–Cu binary oxide (Li et al., 2014)</td>
<td>Powder</td>
<td>35.2</td>
<td>30</td>
<td>160</td>
<td>24</td>
<td>–</td>
</tr>
<tr>
<td>Aluminium oxide hydrous (Tanada et al., 2003)</td>
<td>Powder</td>
<td>35</td>
<td>8</td>
<td>600</td>
<td>4</td>
<td>–</td>
</tr>
<tr>
<td>Modified iron hydrous oxide (Seida and Nakano, 2002)</td>
<td>Powder</td>
<td>28.8</td>
<td>–</td>
<td>–</td>
<td>24</td>
<td>–</td>
</tr>
<tr>
<td><strong>Natural materials</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Modified polyglyosate (Gan et al., 2009)</td>
<td>&lt;0.15</td>
<td>42</td>
<td>1000</td>
<td>200</td>
<td>24</td>
<td>–</td>
</tr>
<tr>
<td>Modified sepiolite (Yin et al., 2011)</td>
<td>&lt;0.15</td>
<td>32</td>
<td>100</td>
<td>160</td>
<td>24</td>
<td>86</td>
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<tr>
<td>Quartz sand (Han et al., 2009)</td>
<td>0.5–2</td>
<td>0.30</td>
<td>25</td>
<td>140</td>
<td>24</td>
<td>87.7</td>
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<tr>
<td><strong>Bio-based materials</strong></td>
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<tr>
<td>Peanut shell (Jung et al., 2015)</td>
<td>Powder</td>
<td>3.8</td>
<td>5</td>
<td>200</td>
<td>48</td>
<td>61.3</td>
</tr>
<tr>
<td>Bamboo (Ranola et al., 2014)</td>
<td>Powder</td>
<td>&lt;2.5</td>
<td>6.5</td>
<td>200</td>
<td>24</td>
<td>42.15</td>
</tr>
<tr>
<td>Juniper fiber (Han et al., 2005)</td>
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<td>&lt;0.5</td>
<td>10</td>
<td>150</td>
<td>24</td>
<td>–</td>
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<tr>
<td>Date palm fiber (Riahi et al., 2009)</td>
<td>Powder</td>
<td>1.75</td>
<td>50</td>
<td>200</td>
<td>2</td>
<td>–</td>
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steel slag can function as effective adsorptive aggregates for the manufacture of high adsorptive concrete. (3) Heat treatment can be used to increase the adsorption capacity of the M. The adsorption capacity of the M after 3-h heat treatment increases from 3.39 mg/g to 3.68 mg/g due to the change in pore structure characteristics. The adsorption of the M and PS follows a physical adsorption mechanism due to the well-developed mesoporous structure and high specific surface area. However, the high water adsorption of the M results in the rapid P-adsorption in the initial reaction time and also leads to the high P-desorption.

CRediT authorship contribution statement

Fan Wu: Methodology, Investigation, Data curation, Formal analysis, Validation, Writing - original draft. Qiangliang Yu: Conceptualization, Supervision, Project administration, Writing - review & editing. F. Gauvin: Writing - review & editing. H.J.H. Brouwers: Supervision, Project administration, Writing - review & editing. Changwu Liu: Supervision.

Declaration of competing interest

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

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