Kinetic studies of phosphate adsorption onto construction solid waste (CSW)
C. Liu, Y. Yang and N. Wan

ABSTRACT
Adsorption of phosphate onto construction solid waste (CSW) was investigated in a batch system. CSW as an inescapable by-product of the construction and demolition process, was used as a composite adsorbent for the removal of phosphate in this study. The adsorption kinetics was investigated under various parameters such as contact time, pH, CSW dosage, initial phosphate concentration and particle size. Greater percentage of phosphate was removed with decrease in the initial concentration and increase in the amount of CSW used. Adsorption of phosphate was pH dependent, and maximum phosphate immobilisation capacity was obtained in alkaline condition. Lagergren first-order, second-order, intra-particle diffusion and external diffusion model were used to test the experimental data. Kinetic analysis showed that the adsorption was best fitted with the pseudo-second-order kinetic model. Adsorption mechanism studies revealed that both external mass transfer and intra-particle diffusion had rate limiting effects on the removal process. These results demonstrated that the CSW could be used as a low-cost adsorbent media for phosphate removal, and the data were relevant for optimal design of wastewater treatment plants.

Key words | adsorption, construction solid waste, diffusion, kinetics, phosphate

INTRODUCTION
Phosphorus is essential to the growth of aquatic organisms for most ecosystems; however, its oversupply can result in eutrophication which will disturb the balance of organisms present in the water and affect water quality (Correll 1998). Therefore, the amount of phosphorus compounds in wastewater must meet the discharge limits. Phosphorus is often present in wastewater as phosphates, including organic phosphate and inorganic phosphate (orthophosphate) (Ensar 2004; Zeng et al. 2004). Orthophosphate forms are principal phosphorus compounds in wastewater together with smaller amounts of organic phosphate (Jenkins et al. 1971).

In wastewater treatment technology, various biological and chemical techniques have been applied for phosphate removal. However, only 10–30% phosphorus of wastewater can be removed during the conventional biological treatment processes (Can & Yildiz 2006). Biological nutrient removal has proved to be more efficient; however, it is relatively expensive and requires complex aerobic effluent cycling (Monclús et al. 2010). More important removal processes are chemical removals including adsorption, chemical precipitation, ion exchange and electrodialysis. Among these methods, adsorption has been extensively used for phosphate removal. In recent years, considerable research has been focused on the removal of phosphate using waste materials or by-products as novel adsorbents. For example, activated red mud (Pradhan et al. 1998), alunite (Özacar 2005), iron oxide tailings (Zeng et al. 2004), blast furnace slag (Ensar 2004) and fly ash (Ugurlu & Salman 1998) have been used for the adsorption of phosphate in recent years.

Construction solid waste (CSW) is another low-cost adsorbent generated in the construction process. Due to its enormous quantities, the management of CSW has drawn more and more public attention. In China,
approximately 40 million tonnes of CSW are generated daily, furthermore, a two-fold increase has been forecast by the end of the next decade (Yang et al. 2011). Fly ash bricks were the major components of CSW used in this work, comprising a mixture of materials consisting of fly ash, lime, plaster and also impurities in trace amounts. The chemical components were also determined. Due to the relative high percentages of metal ions, it can be a promising alternative material for phosphorus removal in wastewater. Therefore the use of CSW will provide both environmental and economic benefits. Several case studies have been processed for the treatment of municipal wastewater, in which the CSW was taken as constructed wetland substrate for phosphate removal (Liu et al. 2012; Yang et al. 2012).

A main objective of this work is to carry out studies on the kinetics and mechanism of phosphate adsorption onto CSW, and another aim is to investigate the influence of initial phosphate concentration, pH, adsorbent dosage and particle size from the kinetic point of view. Important information could be provided for optimising the adsorption process. The rate limiting step and mechanisms were also investigated from adsorption kinetic results.

MATERIALS AND METHODS

Adsorbents and their characterisation

CSW used in the experiments was a waste product obtained from a demolition site of Xi’an University of Architecture and Technology. It was collected and sieved by a sieve set. The grain size of CSW used was in the range of 0.355–0.6, 0.15–0.355, 0.05–0.15 and <0.05 mm, respectively. Before batch experiments, the CSW was dried at 110 °C for dewatering.

The chemical composition of CSW was analysed after the sample was digested by inductively coupled plasma mass spectrometry (ICP-MS, XSeries II). Very fine powdered CSW was dried at 103 °C. A 100 mg of sample were accurately weighed into a 100 mL Teflon beaker, and then digested with aqua regia. The beaker was heated until the solution was evaporated to near dryness. After most of the CSW sample was digested into solution, the solution was filtered through 0.45 μm membrane filter and then diluted to volume with deionised water in a 100 mL volumetric flask. The element concentrations in the solutions were determined by ICP-MS.

The surface area of CSW was measured by Brunauer, Emmett and Teller (BET) method using a surface area analyser (V-Sorp 2008). The BET analysis is the standard method for determining the surface area’s porous materials. A 0.2 g sample was placed into a sample tube and connected to the analyser. The sample was weighed before and after analysis to ensure that no material was lost. The nitrogen BET surface areas were calculated automatically by the system software.

The morphological structure of adsorbent was characterised by a scanning electron microscopy (SEM). First, the sample was platinum coated in an argon atmosphere. Then the coated sample was transferred to the SEM specimen chamber and observed.

Batch adsorption experiments

The standard phosphate solutions used in experiments were prepared from a stock solution of 2 g/L of anhydrous KH₂PO₄. The adsorption studies were carried out at initial phosphate concentrations of 20, 40, 60, 80 and 100 mg/L. CSW samples were placed in 250 mL sealed plastic bottles and mixed with phosphate solution of known concentration. The mixtures after adsorption were taken at predetermined time intervals and the supernatant was filtered by 0.45 μm filter paper. Then the phosphate concentration was analysed in a UV-visible spectrophotometer (UNICOUV-2100) at a wavelength of 700 nm. All measurements were performed in duplicate or more. The experiment was carried out for 96 h to ensure the adsorption equilibrium had been reached (over a 72 h predetermined equilibrium time).

Batch studies were conducted in a temperature-controlled orbital shaker at room temperature (22 ± 3 °C). The agitation speed of the shaker was fixed at a speed of 200 rpm for all experiments. Effect of pH was studied by adjusting the pH of solutions using dilute HCl and NaOH solutions, and the pH-meter was calibrated with standard buffer solutions before measurement. Deviations
of pH up to 0.3 units from the desired value were acceptable.

Due to fly ash being a main composition of the CSW used, previous studies of phosphate adsorbed onto fly ash provided a reference for the batch experiments. The experiments were conducted with various amounts of the adsorbent (0.5, 0.75, 1.0, 1.25 and 1.5 g/L), initial phosphate concentrations (20, 40, 60, 80 and 100 mg/L), particle size (0.55–0.6, 0.15–0.355, 0.05–0.15 and <0.05 mm) and initial pHs (3, 5, 7, 9 and 11). Furthermore, kinetic character was analysed at different initial phosphate concentrations (20, 40, 60 and 80 mg/L, respectively).

The amount of phosphate adsorbed at equilibrium was calculated using the following equation:

\[ q_e = \frac{(C_0 - C_e)}{W} \]  

(1)

where \( q_e \) (mg/g) is the equilibrium adsorption capacity, \( C_0 \) and \( C_e \) are the phosphate concentration (mg/L) at initial and equilibrium time, \( V \) is the volume of solution (L) and \( W \) is the mass of the adsorbent (g).

RESULTS AND DISCUSSION

Characterisation of the adsorbent material

By using ICP-MS, the chemical composition of CSW was \( \text{Al}_2\text{O}_3, 5.03\%; \text{Fe}_2\text{O}_3, 3.37\%; \text{CaO}, 4.28\%; \) and \( \text{MgO}, 0.69\% \). The specific surface area determined by BET method was 33.67 m\(^2\)/g. CSW samples were weighed before and after being dried at 110°C, and the moisture content could be measured as \( \frac{(m_0 - m)}{m_0} \), where \( m_0 \) and \( m \) are the weight of CSW samples before and after dewatering, respectively. Then the moisture content was obtained as 3.4%. The bulk density of the adsorbents was 0.95 g/cm\(^3\), determined from the weight and volume of the CSW samples.

SEM was used to identify the morphological structure of the CSW. The SEM observation is shown in Figure 1. The SEM image clearly indicates that CSW particles are irregular and porous, and these pores provide high specific surface areas, which are favourable for phosphate to be trapped and adsorbed. This would have a positive effect on adsorption.

![SEM micrograph of CSW.](image)
Adsorption experiment studies

Effect of initial phosphate concentration on phosphate removal

The effects of initial phosphate concentrations on the rate of adsorption are shown in Figure 2. Table 1 shows the phosphate removal percentages in different initial solution concentrations. With the initial concentration of phosphate increased from 20 to 100 mg/L, the phosphate removal efficiency decreased from 74.5 to 37.9% and the amount of phosphate removed at equilibrium increased from 15.0 to 38.1 mg/g.

Clearly, the rate of adsorption was fast at the beginning of adsorption, and then decreased with time until it achieved an equilibrium. The high adsorption rate was due to the adsorption on the exterior surface where a large number of vacant surface sites were available during the initial period (Hameed et al. 2008; Hameed & El-Khaiary 2008). When the exterior surface reached saturation, it was difficult for the remaining vacant sites of the surface exterior to be occupied (Srivastava et al. 2006) and the phosphate was adsorbed by the interior surface of the CSW. However, after a certain time point, the amount of phosphate adsorbed on the CSW was in a state of dynamic equilibrium with the amount desorbed.

Effect of pH on phosphate removal

The effect of pH on adsorption behaviour is presented in Figure 3. It was evident that the adsorption capacity was found to be strongly pH dependent, and the greater amounts of phosphate were captured in an alkaline environment. The optimum pH was found to be 9, and high phosphate removal was achieved at pHs 9 and 11, with the removal percentage as high as 95.2 and 94.7%.

The pH of the solution affected the adsorption process through dissociation of functional groups on the adsorbent surface active sites, as well as the speciation of different pollutants (Srivastava et al. 2006). Both calcium phosphate precipitation and P adsorption on the surface were key mechanisms in phosphate removal, which were influenced by the pH. Calcium phosphate precipitation was the predominant mechanism in P immobilisation at alkaline pH (Pengthamkeerati et al. 2008). At initial stages, the precipitate was in amorphous form, then it evolved towards the thermodynamically more stable crystalline form of possible hydroxyapatite (\( \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \)) (Ugurlu & Salman 1998). In alkaline condition, the supersaturation needed to precipitate hydroxyapatite was lower, which was favourable for calcium phosphate precipitation (Johansson & Gustafsson 2000). Solid phase phosphate compounds may remain in the water and cause turbidity, thus it could be separated.

![Figure 2](image1.png)

**Figure 2** | Effect of initial concentration on adsorption of phosphate: adsorbent dose \(= 1 \text{ g/L} \) and initial pH \(= 7.0 \).

<table>
<thead>
<tr>
<th>Initial phosphate concentration (mg/L)</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Removal efficiency (%)</td>
<td>74.5</td>
<td>68.1</td>
<td>54.8</td>
<td>45.0</td>
<td>37.9</td>
</tr>
</tbody>
</table>

**Table 1** | Removal efficiency of phosphate for different initial concentrations

![Figure 3](image2.png)

**Figure 3** | Phosphate removal percentage at different pHs of suspensions: adsorbent dose \(= 1 \text{ g/L} \) and initial phosphate concentration \(= 40 \text{ mg/L} \).
from solution by sedimentation or classical filtration (Ahmaruzzaman 2010).

However, at neutral and acidic pH, precipitation would be less favourable, while the surfaces of Fe and Al oxides are protonated, and then phosphate adsorption through ligand exchange became predominate (Chen et al. 2006; Lu et al. 2009). It was regulated by the electrostatic attractions of the phosphate ions and adsorbent surface (Grubb et al. 2000). It was observed that chemical precipitation was dominant when pH was above 9 and adsorption was dominant when pH was below 7.

**Effect of adsorbent dosage on phosphate removal**

The effect of adsorbent quantity on phosphate removal is shown in Figure 4. The figure revealed that the removal of phosphate increases with an increase in adsorbent dosage.

The adsorbent dosage was 0.050, 0.075, 0.100, 0.125 and 0.150 g/L, respectively. It could be concluded that the amount of phosphate adsorbed per unit mass of CSW decreased. At adsorbent dosage <1.00 g/L, the residual phosphate concentration in the solution is large. The removal percentage was 35.2 and 49.8% for adsorbent dosages of 0.50 and 0.75 g/L. At adsorbent dosage >1 g/L, phosphate removal percentage was 68.1, 71.8 and 85.6% for adsorbent dosage of 1.00, 1.25 and 1.50 g/L. When adsorbent dosage was >1 g/L there was very little difference in phosphate removal percentage. Thus, considering the adsorption capacity and phosphate removal percentage, adsorbent dosage of 1.00 g/L was the optimum dose of adsorbent.

The increase of phosphate uptake rate could be attributed to greater surface area and the availability of more adsorption sites (Srivastava et al. 2006). The decrease of the amount of phosphate adsorbed with increasing dose of adsorbent is due to adsorption sites remaining unsaturated during the adsorption process (Bulut & Aydınoğlu 2006).

**Effect of adsorbent particle size on phosphate removal**

The effect of CSW particle size on adsorption behaviour is shown in Figure 5. With CSW particle size increased, the time required to reach equilibrium significantly increased, and also removal efficiency decreased. This was attributed to the fact that the smaller particles could provide large surface areas. However, this increase was not proportionate to the increase of surface area. A similar trend using fly ash, Portland cement has already been noted by different authors (e.g., Agyei et al. 2002), which suggests that chemisorption is more significant than physical adsorption for the removal of phosphate.

**Kinetic studies**

The kinetic parameters provided important information for the design adsorption process, which was helpful for selecting optimum adsorption conditions. Furthermore, the diffusional mechanisms can be investigated from kinetic models. Pseudo-first-order, pseudo-second-order,
intra-particle and external diffusion models were analysed and the best-fit model was selected based on the linear regression correlation coefficient, $r^2$. Equilibrium time was found to be 72 h, and the adsorption was rapid in the first 12 h and thereafter it proceeded at a slower rate and finally attained saturation. The observation showed that external diffusion and pore diffusion affected the adsorption process, which is discussed in more detail below.

The adsorption dynamics can be described as follows (Guibal et al. 1998; Ahmaruzzaman 2010): diffusion from the solution to the film surrounding the particle; molecular transport through liquid film to adsorbent surface (external diffusion); solute diffusion into pore of adsorbent except for a small quantity of sorption on external surface (pore diffusion); uptake. Bulk diffusion is non-limiting when agitation is sufficient to avoid concentration gradients in solution (Guibal et al. 1998), and the last step is rapid and negligible to these steps. Thus the adsorbate transfer is usually characterised by either external mass transfer (boundary layer diffusion) or pore diffusion or both (Kalavathy et al. 2005).

The pseudo-first-order model

The pseudo-first-order kinetic model has been widely used to predict adsorption kinetics. The experimental data were treated with the model given by Lagergren (1898) as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

where $q_e$ and $q_t$ (mg/g) are the amounts of adsorbate adsorbed at equilibrium and at any time, $t$ (h), respectively. $k_1$ is the adsorption rate constant.

Integrating the above equation for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$ gives:

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

The rate constant $k_1$ could be obtained from the slope of the plot of $\log(q_e - q_t)$ vs time, as shown in Figure 6. The calculated $q_e$, $k_1$, and $r^2$ are given in Table 2. It can be seen that the sorption data fit the first-order reaction well only in the first 12 h and then deviate. However, correlation coefficients $r^2$ were relatively lower for the entire adsorption process. Thus, the reaction was not likely to be a first-order reaction.

Besides, $q_e$ could also be obtained from the intercept of the curve. The calculated values did not agree with the experimental values obtained from the intercept of the straight line. It also showed no applicability of the pseudo-first-order model in predicting the adsorption kinetics (Ho & McKay 1998b).

![Figure 6](image-url) Pseudo-first-order kinetics for phosphate adsorption onto CSW: adsorbent dose = 1 g/L, and initial pH = 7.0.

### Table 2 | Pseudo-first-order and pseudo-second-order adsorption rate constants for different initial concentrations

<table>
<thead>
<tr>
<th>$C_0$ (mg/L)</th>
<th>$q_e$ (cal) (mg/g)</th>
<th>$k_1$ (min⁻¹)</th>
<th>$r^2$</th>
<th>$q_e$ (cal) (mg/g)</th>
<th>$k_2$ (min⁻¹)</th>
<th>$r^2$</th>
<th>$q_e$ (exp) (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>3.49</td>
<td>0.067</td>
<td>0.8908</td>
<td>16.16</td>
<td>0.0075</td>
<td>0.9950</td>
<td>14.98</td>
</tr>
<tr>
<td>40</td>
<td>4.15</td>
<td>0.059</td>
<td>0.8765</td>
<td>26.74</td>
<td>0.0044</td>
<td>0.9934</td>
<td>24.82</td>
</tr>
<tr>
<td>60</td>
<td>4.55</td>
<td>0.060</td>
<td>0.9239</td>
<td>35.46</td>
<td>0.0034</td>
<td>0.9958</td>
<td>33.14</td>
</tr>
<tr>
<td>80</td>
<td>5.09</td>
<td>0.047</td>
<td>0.9393</td>
<td>39.53</td>
<td>0.0026</td>
<td>0.9972</td>
<td>36.23</td>
</tr>
</tbody>
</table>
It is often incorrect to apply a simple kinetic model to the sorption with solid surfaces which are rarely homogeneous (Ho & McKay 1998a). The initial fast stage was the binding of phosphate molecules with the active spots of CSW surface. The microporous structure of CSW provided a higher surface area, which enhanced the reaction. There was an initial fast adsorption and was then followed by a slow stage. Similar trends have been previously reported by Singh et al. (1996) and Ho & McKay (1998a).

\( k_1 \) was found to be 0.067, 0.059, 0.052 and 0.060 min\(^{-1}\) for different initial phosphate concentrations. \( k_1 \) was irregular, which proved that pore diffusion limited the adsorption rate. For strict surface adsorption, the relationship between initial adsorbent concentration and rate of adsorption should be linear (Kalavathy et al. 2005).

**The pseudo-second-order model**

The second-order kinetic model is expressed as:

\[
\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{4}
\]

integrating this equation for the boundary conditions \( t = 0 \) to \( t = t \) and \( q_t = 0 \) to \( q_t = q_e \) gives:

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e} t \tag{5}
\]

where \( k_2 \) is the equilibrium rate constant of pseudo-second-order sorption, determined from the plot of \( t/q_t \) vs \( t \). The linear plot is shown in Figure 7. The calculated \( q_e \), \( k_2 \) and the corresponding linear regression correlation coefficient \( r^2 \) are all summarised in Table 2.

As shown in Table 2, the value of \( q_e \) increased with the increasing initial phosphate concentration, and the correlation coefficients were all greater than 0.99. The good straight line fit observed indicates that the kinetics of adsorption could be successfully described. As well, the normalised standard deviation \( \Delta q_e(\%) \) was obtained to compare the validity of kinetic models.

\[
\Delta q_e(\%) = 100\% \sqrt{\frac{\sum (q_{e,exp} - q_{e,cal})^2}{N(N-1)}} \tag{6}
\]

where \( N \) is the number of data points, \( q_{e,exp} \) and \( q_{e,cal} \) are the experimental and calculated equilibrium adsorption capacity values, respectively. For the pseudo-second-order kinetic model \( \Delta q_e \) was 1.19\%, which was relatively lower compared to the 12.51\% for the pseudo-first-order kinetic model. This suggested that the pseudo-second-order model was more suitable to describe the adsorption kinetics of phosphate on CSW. This also suggested that the rate limiting step was chemical sorption involving valency forces through sharing or exchange of electrons (Ho & McKay 1999).

From the second-order kinetics model, the initial sorption rate could also be calculated. The initial adsorption rate, \( h \) (mg/g min) can be defined as (Ho & McKay 1998b):

\[
h = k_2q_e^2 \tag{7}
\]

The calculated \( h \) values for different initial concentrations were 1.959, 3.146, 4.275 and 4.063 mg/g h, respectively. The \( h \) value increased when the initial phosphate concentration increased; however, \( h \) value’s increasing rate gradually decreased and began decreasing when the initial concentration was higher than 60 mg/L. The possible reason might be that the CSW amount was not enough for a high concentration of phosphate to adsorb rapidly when the initial concentration was too high. Similar phenomena have been observed in which the initial sorption rate decreased when the initial phosphate concentration was too high (Kavitha & Namasivayam 2007; Hameed et al. 2008).
Intra-particle diffusion model

Since the above two models cannot identify a diffusion, an intra-particle diffusion model was introduced as the most commonly used technique. It is an empirically functional relationship, where adsorption varies almost proportionally with $t^{1/2}$ rather than with the contact time $t$ (Tan et al. 2009). The adsorbate was most probably transported into adsorbent through an intra-particle diffusion process, which is often the rate limiting step of adsorption processes (Bulut & Aydin 2006).

The empirical equation is expressed as:

$$q_t = k_{id} t^{1/2} + C$$

where $C$ is the intercept and $k_{id}$ is the intra-particle diffusion rate constant (mg/g h$^{1/2}$). A plot of $q_t$ vs $t^{1/2}$ should be a straight line when adsorption mechanism follows the intra-particle diffusion process.

The adsorption data for $q_t$ vs $t^{1/2}$ is shown in three stages in Figure 8. The different stages indicate that three steps took place in the adsorption process. The initial part of the plots is sharper, which indicates a boundary layer effect. Phosphate ions diffuse to the surface of sorbent and into the pores very quickly. The external resistance to mass transfer surrounding the particles exists in this stage. The second region is gradual adsorption stage, which represents micropore diffusion. In this stage, intra-particle diffusion is the rate limiting step. As shown in Figure 8, there was also a third region where intra-particle diffusion starts to slow down. The probable reason is that CSW has been saturated and the solute concentrations were low (Wu et al. 2005).

It also can be seen from Figure 8 that the line of the second part did not pass through the origin. This deviation from the origin was due to the difference of mass transfer rate in various adsorption stages (Stivastava et al. 2006). Furthermore, the intercept provided the measure of the boundary layer thickness. The deviation showed that intra-particle diffusion was not the only rate controlling step (Horsfall & Vicente 2007), and the film diffusion also affected the adsorption process. The larger the intercept was, the greater contribution of surface sorption in the rate controlling step (Kannan & Sundaram 2001; Kalavathy et al. 2005).

External diffusion model

Adsorption was a complex transient process involving Fickian diffusion in both the fluid and adsorbed phases (Dizge et al. 2008). However, at early times the adsorption process can be simplified by external diffusion model, assuming that the concentration at the sorbent surface tends towards zero and the intra-particle was negligible (Guibal et al. 1998). The external diffusion could be expressed as:

$$\ln \frac{C_t}{C_0} = -k_i \frac{A}{V} t$$

where $C_0$, $C_t$ are the initial phosphate concentration and the concentration at time $t$. $k_i$ is the external mass transfer coefficient, which could be determined by plotting $\ln (C_t/C_0)$ vs $t$. $A/V$, the external adsorption area of adsorbent to the total solution volume, could be estimated as (Dizge et al. 2008):

$$\frac{A}{V} = \frac{3m}{\rho d}$$

where $m$ (g/cm$^3$) is the adsorbent dosage, $d$ (μm) is the particle diameter and $\rho$ (g/cm$^3$) is the apparent density of the adsorbent.

External and internal diffusion occurred simultaneously in the adsorption process, only one mechanism predominated. However, both mechanisms were thought to be significant in some adsorption systems (Khraisheh et al. 2008).
To simplify the complex diffusion equations, adaptations of Fick’s law were proposed. Assuming the adsorption rate was independent of the stirring speed and the external mass transfer was not the rate limiting step, the following equation could be derived (Urano & Tachikawa 1991; Dizge et al. 2008):

\[- \log \left[ 1 - \left( \frac{q_t}{q_e} \right)^2 \right] = \left( \frac{4 \pi^2 D}{2.3 d^2} \right) t\]  

(11)

where \(D\) (cm²/s) is the sum of pore and surface diffusion and \(d\) (cm) is the diameter of the adsorbent. The values of \(D\) were obtained from the slopes of the linear relationships of

\[- \log \left[ 1 - \left( \frac{q_t}{q_e} \right)^2 \right] \quad \text{and} \quad \frac{4 \pi^2}{2.3 d^2} t\]

The values of \(D\) are 3.717 × 10⁻⁶, 1.108 × 10⁻⁷, 1.201 × 10⁻⁷ and 1.330 × 10⁻⁷ cm²/s for different initial phosphate concentrations, respectively. All the values fell well within the chemisorption systems (10⁻⁵–10⁻¹³ cm²/s) magnitudes (Dizge et al. 2008).

Thus, the Biot number, which represents the ratio of internal to external resistance in the system, could also be obtained from the following equation:

\[B_N = k_f \frac{d}{D}\]  

(12)

Obviously, the Biot number was greater than 100, which indicates that the intra-particle diffusion was the rate determining step (Khraisheh et al. 2002).

**Bangham’s equation**

Furthermore, Bangham’s equation was studied to further verify whether pore diffusion is the only rate controlling step, which was suggested as (Aharoni et al. 1979):

\[\log \log \left( \frac{C_0}{C_0 - q_m} \right) = \log \left( \frac{k_0 m}{2.503 V} \right) + \alpha \log t\]  

(13)

where \(C_0\) (mg/L) is the initial concentration of adsorbate in solution, \(V\) (mL) is the volume of solution, \(m\) (g/L) is the weight of adsorbent per litre of solution, \(q_t\) (mg/g) is the amount of adsorbate adsorbed at time \(t\), \(k_0\) and \(\alpha\) (<1) are constants.

As shown from Figure 9, the plot of \(\log \log (C_0/C_0 - q_m)\) to \(\log t\) yielded linear curves, and the \(r^2\) values varied from 0.9764 to 0.9944. Perfectly linear curves revealed the pore diffusion was the rate limiting step, which controlled the adsorption process (Tutem et al. 1998). While, in consideration of the intra-particle diffusion model discussed above, it led to the conclusion that pore diffusion was not the only rate controlling step, especially in the early stages of adsorption; however, external mass transfer also affected the entire adsorption process.

**Boyd model**

Adsorption kinetic data were further analysed as given by Boyd et al. (1947) and Reichenberg (1953) to determine the rate limiting step. Assuming the adsorbent particle to be all uniform spheres and the diffusion follows Fick’s law, the kinetic data could be analysed using the Boyd model given by:

\[F = \frac{q_t}{q_e} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp (- \frac{n^2 B t}{d^2})\]  

(14)

where \(q_e\) (mg/g) is the amount of phosphate adsorbed at infinite time and \(q_t\) (mg/g) is the amount of phosphate adsorbed at any time \(t\) (h). \(F\) is the fractional attainment of
equilibrium at time $t$, $Bt$ is a mathematical function of $F$, and $B$ (cm$^2$/h) could be defined as:

$$B = \left(\frac{\pi D_{ij}}{r^2}\right)$$  \hspace{1cm} (15)

where $D$ is the effective diffusion coefficient, and $r$ is the radius of the adsorbent particle assuming spherical shape.

By applying the Fourier transform and then integration, Reichenberg (1953) obtained the following approximations:

for $F$ values $> 0.85$,

$$Bt = 0.85, \quad Bt = 0.4977 - \ln (1 - F)$$  \hspace{1cm} (16)

and for $F$ values $< 0.85$,

$$Bt = 2\pi - \frac{\pi^2 F^2}{3} - 2\pi \left(1 - \frac{\pi F}{3}\right)^{1/2}$$  \hspace{1cm} (17)

The calculated $Bt$ values were plotted vs time $t$ (h), as shown in Figure 10. All linear lines did not pass through the origin, which showed that the film diffusion affected adsorption rate (Hameed & El-Khaiary 2008). With the increase of concentrations, the $Bt$ vs $t$ plot moved towards the origin (from $-0.4649$ to $-0.2326$). This was an indication that the particle diffusion was the rate controlling parameter.

On the other hand, the data should be discussed separately according to the $F$ value (El-Khaiary & Malash 2011). Because $Bt$ values became sensitive to changes in $q_t$ when $q_e$ is approached, it is not recommended to extend the Boyd plot to times close to equilibrium (Malash & El-Khaiary 2010). In this study, $Bt$ values less than 1.3 (<36 h) were considered individually. The plots show a linear segment for the first 36 h ($F$ values $<0.85$), with the $r^2$ values varying from 0.9881 to 0.9993; the intercepts were different from zero, which suggested that film diffusion was the rate controlling mechanism in this stage.

**CONCLUSIONS**

The removal of phosphate ions from water using a construction waste material was studied. The experimental studies indicated that CSW has the potential to be an adsorbent for the removal of phosphate. Adsorption of phosphate was found to increase with the increase of adsorption time and initial concentration. Phosphate adsorption was also found to be pH dependent and the maximum removal
percentages were 95.2 and 94.7% at pHs 9 and 11, respectively. Equilibrium adsorption was achieved within about 72 h.

Kinetic data were tested using the pseudo-first-order, pseudo-second-order kinetic, intra-particle diffusion and external diffusion models. The kinetics of the adsorption process was found to follow the pseudo-second-order kinetic model.

The adsorption process was found to be controlled by external diffusion at the initial part of the adsorption process, and later pore diffusion became the rate controlling parameter. Adsorption mechanism study indicated that the process was complex and controlled by both surface adsorption and pore diffusion.

Overall, CSW used in this study showed excellent adsorptive characteristics for removal of phosphate from solution.

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