Assessment of the adsorption kinetics, equilibrium and thermodynamic for Pb(II) removal using a hybrid adsorbent, eggshell and sericite, in aqueous solution

Hee-Jeong Choi

ABSTRACT

Hybrid adsorbents (ES) were prepared with mixing of eggshell and sericite as binders, and Pb(II) was removed from aqueous solutions. Sericite has the advantage of not only serving as a binder for hybrid adsorbent but also having a negative charge on the surface to improve the removal efficiency of heavy metals. Various parameters affecting the removal of Pb(II) from aqueous solutions were investigated using the optimal conditions derived. In addition, adsorption kinetics, adsorption isotherms and thermodynamic analyses were performed using the experimental results of each parameter. The ES had a more specific surface area and porosity than sericite or eggshell and contained a large number of OH groups favoring heavy metal adsorption. As a result of the adsorption of Pb(II) using the ES, the adsorption process was physical and suitable for the Freundlich isotherm. In addition, the adsorption process of Pb(II) by the ES was a spontaneous endothermic reaction. The ES can quickly reach the adsorption equilibrium and strong adsorption strength.

In addition, the CaOH contained in the ES can neutralize the pH of wastewater, and it is possible to treat heavy metal ions in industrial wastewater and acid mine wastewater without controlling the pH. ES adsorbents using waste eggshells are very economic because they recycle what would otherwise be waste and have great significance in terms of resource reuse.

Key words | adsorption, eggshell, hybrid adsorbent, lead, sericite

NOMENCLATURE

A Tempkin isotherm equilibrium binding constant (L/g)

bT Temkin constant related to the heat of sorption (kJ/mol)

Co Initial concentration of heavy metal ion (mg/L)

Ce Equilibrium concentration of heavy metal ion (mg/L)

Ct Concentration of heavy metal ion at time t (mg/L)

ΔGo Gibbs free energy (kJ/mol)

ΔH° Enthalpy (kJ/mol)

k1 Adsorption rate constants of the pseudo-first-order model (1/min)

k2 Adsorption rate constants of the pseudo-second-order model (g/mg · min)

kid Intra-particle diffusion rate constant (mg/g · h0.5)

kL Langmuir constant (L/g)

kF Freundlich constants referring to the adsorption capacity (mg/g)/(L/mg)1/n

M Amount of adsorbent (mg)

n Freundlich isotherm constants, intensity of sorption

qe Amount adsorbed per unit weight of adsorbent at equilibrium (mg/g)

qt Amount of heavy metal ions adsorbed at time t (mg/g)

qm Langmuir monolayer maximum adsorption capacity (mg/g)

R Removal (%)

R Ideal gas constant, 8.314 (J/mol · K)

R2 Correlation coefficient

ΔS° Entropy (J/mol · K)

t Time (min)

T Absolute temperature (K)

V Volume of solution (L)

α Elovich constant which gives an idea of the adsorption rate constant (mg/g · min)

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INTRODUCTION

Heavy metals emitted from industrial processes can adversely affect living organisms in the water system. Pb(II) is a heavy metal that is widely used in industry, because it is easily processed and inexpensive (Naushad & Alothman 2013; Lee & Choi 2018). Thus, Pb(II) is one of the most widespread toxic heavy metals in water and soil. Among the various processes for Pb(II) treatment, the adsorption method has many advantages, such as high efficiency, possible regeneration, low operating costs and low sludge production, which is very attractive to remove heavy metals from industrial wastewater (Largitte & Pasquier 2016; Pugazhendhi et al. 2018; Naushad et al. 2019). As a result, researchers are attempting to remove heavy metals from aqueous solutions using various adsorbents. However, despite these numerous studies and the development of various adsorbents, the industry still needs to develop cheap and efficient adsorbents which are economically satisfactory. The excellent combination of abandoned waste eggshell and sericite to be proposed in this study may be an alternative to provide the cheap and efficient new adsorbents required in industry.

Egg production in the world is 66 million tons/year in 2015, and the number of eggs is approximately one trillion (Baláž 2018). In Korea, egg production is increasing yearly, and in 2018, it increased by 9.53% compared to the previous year (Korean Statistical Information Service 2018). Therefore, more than 90,000 tons of waste eggshells were discharged in 2017. Approximately 35% of the enormous amount of waste eggshells used is a mixture of fertilizer and animal feed, but the rest is disposed of as garbage (Baláž et al. 2016). The primary component of eggshell is calcium carbonate, which causes an ion exchange reaction with heavy metals. In addition, according to previous studies, the zeta potential of eggshells up to pH 6 has a strong negative value and is very effective at removing cationic heavy metals (Choi & Lee 2015). However, when the eggshell is used alone to remove the heavy metals from the wastewater, there is a disadvantage that the removal time is long, and after the adsorption process the powder adsorbent is difficult and costly to treat (Choi 2017a). To overcome this problem, this study attempts to remove heavy metals from wastewater by creating spherical media with mixed sericite and eggshell. Sericite has the characteristics of clay minerals and is highly viscous, and it is easy to use as a spherical adsorbent (Yu & Choi 2018a). Treatment with the adsorbent after the adsorption process produces a spherical adsorbent that is easier to use than when the powder form is the adsorbent. In addition, sericite, a type of clay mineral, has a large number of hydroxyl groups on the surface, which can easily adsorb and remove inorganic and organic pollutants from aqueous solutions (Choi & Kim 2016). Therefore, when sericite is used as a binder, it is not only a spherical adsorbent, but it also has a synergistic effect of improving heavy metal adsorption efficiency. Thus, this experiment was performed to increase the removal efficiency of heavy metals and to shorten the removal time using sericite, which is a type of clay mineral with a negative charge, as a binder and to make eggshell powder + sericite (ES). Many studies have been reported to remove heavy metals from aqueous solutions using various adsorbents (Al-Othman et al. 2012; Ghasemi et al. 2014a; Naushad 2014; Naushad et al. 2015a, 2015b; Mittal et al. 2016; Naushad et al. 2016; Alqadami et al. 2017a; Naushad et al. 2017; Naushad et al. 2019). However, this is the first study which reports the preparation of ES composite for the adsorption of Pb(II) in the aqueous solution. In this study, first, the optimal conditions to produce the composite adsorbent with the mixture of the eggshell and the sericite were determined, and various parameters influencing the removal of Pb(II) from the aqueous solution were investigated using the optimum conditions examined. Finally, adsorption kinetics, adsorption isotherms and thermodynamic analyses were performed using the experimental results of each parameter.

MATERIAL AND METHODS

Adsorbate and adsorbent

The waste eggshell was collected at a bakery in G City, Korea. The waste eggshell was washed several times with deionized water to remove various pollutants onto the eggshell surface, and then dried in an oven at 80 °C for 5 h. The dried eggshells were pulverized using a mixer, and particles smaller than 325 mesh (0.035 mm) were used. The clay minerals used as binders for the hybrid adsorbents were 325 mesh particles, such as eggshell powder, washed in the same manner as eggshell powder and dried in an oven at 80 °C for 12 h to remove moisture. Pb(II) was used as GR grade Pb(NO₃)₂ (Duksan Pure Chem., Co. Ltd, Korea, purity ≥ 99%). Pb(II) was prepared at a concentration...
of 1,000 mg/L, diluted with distilled water and used to prepare the required concentration of solution.

The ES adsorbent was prepared as follows: the dried eggshell powder and sericite were mixed at various weight ratios, and a small amount of distilled water was added to make a paste. A various paste of different weight ratios was extruded using syringes in spherical shapes of 3 mm in diameter. The hybrid ES adsorbent was calcinated at various temperatures of 300–800 °C for 3 h in an oven. The prepared adsorbent was stored in a desiccator for future use in experiments.

Experimental design and analytical methods

The experiment was carried out using a batch test. The ES was added to the 1 L containing Pb(II) based on the experimental plan. To investigate the effect of various pH values on the removal of Pb(II), the pH was controlled from 3 to 10 using NaOH/HCl. Various initial concentrations of Pb(II) were examined from 1 to 50 mg/L. To examine the effect of contact time and temperature on the Pb(II) removal, contact time and temperature were controlled from 0 to 2 h and from 10 to 50 °C, respectively. The mixture was stirred at 120 rpm with a magnetic bar and sampled at a predetermined time. The collected samples were centrifuged at 2,500 rpm for 20 min, filtered using 0.45 μm (membrane filter), and the amount of heavy metals was measured using an AAS (atom absorption spectrometer, Perkin Elmer, AAS 3300). The other parameters were fixed to test one parameter in all experiments. The FT-IR of the adsorbent was measured using infrared spectroscopy (Vertex 80v, Bruker) in the range of 400–4,000 cm⁻¹. The size and zeta potential of the adsorbent were measured using a Zeta-Sizer nano ZS (Malvern Panalytical), and the specific surface area and pore size of the adsorbent were measured using a BET (Brunauer, Emmett and Teller) surface analyzer (Micromeritics, ASAP-2010). The amount of eggshell and sericite was measured using an electronic balance (XP26, Mettler Toledo, Switzerland), and the pH was measured using a pH meter (SevenGO pro, Mettler Toledo). The adsorption amount at the time t and removal efficiency of Pb(II) onto ES were calculated using Equations (1) and (2) (Lee & Choi 2018).

\[
q_t = \frac{(c_0 - c_t)V}{M} \quad (1)
\]

\[
R = \left(\frac{c_0 - c_t}{c_0}\right) \times 100 \quad (2)
\]

RESULTS AND DISCUSSION

Characteristics of the adsorbent

Physical property

The specific surface area, pore size, and pore volume of the eggshell, sericite, and ES adsorbent were analyzed, and the results are shown in Table 1. The BET specific surface area is an important factor, because it is related to the active site of the adsorbent when adsorbing heavy metals using an adsorbent in aqueous solution (Largitte & Pasquier 2016). The BET surface area was the smallest at 3.51 m²/g of sericite, and the sericite with a dense surface structure had a smaller specific surface area than the eggshell with a large porosity. The ES adsorbents had a surface area that was 13-fold larger than that of the sericite and seven-fold more than the eggshell. It is hypothesized that the specific surface area is increased due to the calcination of the ES adsorbent.

Zeta potential

The zeta potential is a physical property that represents all the particles in an aqueous solution (Largitte & Pasquier 2016). The behavior of the particles in aqueous solution can be seen through the zeta potential. When the particles in the aqueous solution have a high zeta potential of negative or positive charge, the repulsive force of the particles is strong, and they do not try to bond with each other (Choi 2017a). However, when the zeta potential is low, the repulsive force of the particles decreases, and the bonding force between the particles increase (Choi 2017b). The zeta potential of the eggshell, sericite and ES are shown in Figure 1(a). The zeta potential of the ES was determined ±10 in the 3–10 pH range. The ES has a relatively low zeta potential compared to sericite and eggshell. In particular, the lowest zeta potential of the ES was observed at pH 5 and 7. This suggests that the ES can be useful for adsorbing Pb(II) ions in a neutral aqueous solution.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Specific surface area (m²/g)</th>
<th>Pore size (nm)</th>
<th>Pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sericite</td>
<td>2.32 ± 0.31</td>
<td>2.13</td>
<td>0.11</td>
</tr>
<tr>
<td>Eggshell</td>
<td>1.91 ± 0.12</td>
<td>3.27</td>
<td>0.19</td>
</tr>
<tr>
<td>ES</td>
<td>61.68</td>
<td>5.28</td>
<td>0.33</td>
</tr>
</tbody>
</table>
According to the FT-IR analysis of the ES, N-containing bioligands of 480–650 cm\(^{-1}\) and PO\(_4\) stretching of 950–1,200 cm\(^{-1}\) were significantly reduced compared to the sericite. In addition, the C-O stretch of 1,300–1,450 cm\(^{-1}\) was decreased compared to the eggshell but increased more than the sericite. Interestingly, in the FT-IR analysis, the ES adsorbent increased the carboxyl groups of 1,500–1,650 cm\(^{-1}\), the C-O carbonyl groups of 1,680–1,740 cm\(^{-1}\) and the CH stretching of 2,800–2,900 cm\(^{-1}\). In particular, bonded -OH groups of 3,000–3,500 cm\(^{-1}\) were significantly increased compared to the sericite and eggshell (Figure 1(b)). The carboxyl group dissociates into -COO- and H\(^+\) in aqueous solution, and most of the carboxyl group becomes the -COO- form above a certain pK value, and cationic heavy metals are efficiently adsorbed (Choi 2018). When heavy metal ions are adsorbed on the adsorbent surface, they are adsorbed by the substitution reaction between the H and heavy metal ions in the surface.
OH group (Yu & Choi 2018b). As shown in the FT-IR analysis, carboxyl group, carbonyl groups and -OH groups, which are favorable for heavy metal adsorption, were increased in the ES adsorbents compared to the sericite and eggshell. These functional groups of ES adsorbents are thought to have a great effect on the adsorption of Pb(II) in aqueous solution.

The EDX spectra of the eggshell and ES are shown in Figure 1(c) and 1(d). The elements of C and O were significantly increased in the ES adsorbent compared that of eggshell. In addition, K, Al and Si were newly appeared in ES adsorbent. This suggests that when the ES was produced, the components of the sericite and egg shells were mixed with each other, and C, O, K, Al and Si were increased or newly appeared. The K⁺ existing between the sericite layers has a cation exchange ability. When Al³⁺ is substituted for Si⁴⁺ at the octahedral site, the cation is bonded to the electronegative site because it is electrically negative.

Optimization of the ES adsorbent preparation

Calcinated temperature of the ES on Pb(II) removal

The experimental results show that the mass of the ES decreased 0.4 g at 200 °C and 1.67 g at 400 °C, and as the pyrolysis temperature increased, the mass of the ES decreased (Table 2). In addition, the mass of the ES decreased significantly until 800 °C and determined a decrease of 18.84 g. At 1,000 °C, the mass of ES decreased by 20.45 g, but at temperatures above 800 °C, the change of the mass loss was not significant.

The removal efficiency of Pb(II) was found to be 43.5% with natural ES and less than 60% when the pyrolysis temperature was below 600 °C. However, the Pb(II) removal efficiency was higher than 80% above 800 °C and was not significantly different at calcinate temperatures between 800 °C and 1,000 °C. The eggshell contains more than 93% CaCO₃. CaCO₃ is converted to CaO and CO₂ (g) when calcinated (Angelis et al. 2017). CaCO₃ contained in the eggshell is present as CaCO₃ at a calcination temperature of less than 500 °C; CaCO₃ and CaO coexist at 700 °C, and CaCO₃ completely changed to CaO at calcination temperatures above 800 °C (Ahmad et al. 2012; Pettinato et al. 2015). CaO plays an important role in the adsorption of heavy metals in aqueous solutions (Pettinato et al. 2015). CaO is shared with the oxygen of the triangular structure, and an octahedral structure is formed. Thus, the space of the CaO is wider than that of the other compounds (Al-Ghouti & Salih 2018). In this structure, heavy metals are substituted for Ca-ions or adsorbed on a wide space in the structure (Guru & Dash 2014). Thus, the pyrolysis temperature of the ES was set to 800 °C based on the results of the mass reduction and Pb(II) removal rate determined from the firing temperature. Therefore, the calcination temperature of ES was selected at 800 °C by combining the results of the mass reduction and Pb(II) removal efficiency.

Effect of eggshell and sericite ratio on Pb(II) removal

To investigate the effect of the mixing ratio of the eggshell and sericite on the removal of Pb(II), the experimental conditions were 20 ppm of Pb(II), pH 7, 25 °C, a reaction time of 30 min, 1 g/L of ES adsorbent, and various ratios of eggshell to sericite. As a result, the eggshell and sericite ratio of 8:2 and 6:4 resulted in Pb(II) adsorption of 19.18 mg/g and 19.25 mg/g, respectively (Figure 1(e)). The ratio of 6:4 was slightly higher than that of 8:2, but the adsorption amount of Pb(II) was almost similar. However, as the amount of sericite increased in the ratio of eggshell and sericite, the adsorption amount of the Pb(II) decreased, and the lowest adsorption amount was 12.42 mg/g at the ratio of 2:8. When the content of sericite was low in the preparation of ES adsorbent, it was difficult to make the spherical adsorbent because of its low viscosity. In particular, when the mixture ratio of the eggshell and sericite was 8:2, the spherical adsorbent did not form well. Because of this, it was difficult to separate the aqueous solution and the adsorbent after the experiment, and secondary treatment was required to remove the ES adsorbent. Therefore, to maintain the removal efficiency of Pb(II) and the shape of the spherical adsorbent, the weight ratio of 6:4 of the eggshell to sericite was recommended for the optimal ratio for Pb(II) removal using the ES in the aqueous solution.

Parametric study for Pb(II) removal using ES

Effect of initial concentration

As the concentration of Pb(II) increased, the adsorption amount increased, but the removal efficiency decreased.

Table 2 | Mass reduction and Pb(II) removal by the ES with various calcinated temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Natural</th>
<th>200</th>
<th>400</th>
<th>600</th>
<th>800</th>
<th>1,000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass reduction (g)</td>
<td>0</td>
<td>0.4</td>
<td>1.67</td>
<td>3.78</td>
<td>18.84</td>
<td>20.45</td>
</tr>
<tr>
<td>Mass reduction rate (%)</td>
<td>100</td>
<td>99.6</td>
<td>98.33</td>
<td>96.22</td>
<td>81.16</td>
<td>79.55</td>
</tr>
<tr>
<td>Removal of Pb(II) (%)</td>
<td>43.5</td>
<td>51.5</td>
<td>55.3</td>
<td>59.8</td>
<td>81.4</td>
<td>82.5</td>
</tr>
</tbody>
</table>
At the concentration of 10 mg/L Pb(II), the removal efficiency was 99.79%; however, the removal efficiency of Pb(II) reached 56.77% at the concentration of 200 mg/L Pb(II) (Figure 2(a)). This is a common phenomenon in the adsorption process. Generally, the adsorbent in contact with the adsorbate in an aqueous solution is adsorbed onto the adsorbent through four steps (Pettinato et al. 2015; Yu & Choi 2018a). The first step is the step of moving to the interface of the adsorbent by bulk transport. The second step is the process of the adsorption material reaching the surface of the adsorbent through the interface of the adsorbent by film diffusion. The third step is the process of intraparticle diffusion and, finally, step 4 is a state in which the adsorbent is adsorbed onto the adsorbent. The adsorption rate and efficiency are determined in steps 2 and 3. The reason for lowering the removal efficiency with an increase in the initial concentration of Pb(II) is that it can be adsorbed into pores inside the adsorbent that gradually decrease. In this study, the removal efficiency was determined to be 91.15% for 20 mg/L Pb(II). Considering that the concentration of Pb(II) contained in wastewater is less than 10 ppm, it is possible to remove Pb(II) from industrial wastewater using ES.

Effect of pH

Among the various adsorption parameters, the pH is one of the important parameters of the adsorption process, because the ionic form of the adsorbate in the aqueous solution varies depending on the pH.

As a result, the adsorption efficiency was found to be lower than 47.2% at less than pH 5, but higher than 98.7% over pH 7 (Figure 2(b)). In this study, the adsorption efficiency of Pb(II) increases as the pH increases. This is probably due to the decrease in the number of H⁺ and the increase in the number of ligands containing anions as the pH is increased in the aqueous solution. In addition, as the pH value increases, Pb(II) is exchanged with Pb(OH)₂ or Pb(OH)₃⁻, and adsorption increases rapidly on the adsorbent surface (Heraldy et al. 2018; Lee & Choi 2018).

Alternatively, this study showed high Pb(II) removal efficiency even at pH 6 compared with the previous
studies, suggesting that the pH was increased by dissolving the calcium oxide contained in the eggshell. \( \text{CaCO}_3 \) is produced by pyrolyzing calcium carbonate \( \text{CaCO}_3 \) contained in the eggshell. When the \( \text{CaO} \) is dissolved in an aqueous solution, calcium hydroxide \( \text{Ca(OH)}_2 \) is produced and ionized to render the aqueous solution alkaline \citep{Ahmad2012, Choi2015}. In addition, the relatively high Pb(II) removal rate at pH 6 is also related to the zeta potential of the ES. According to zeta potential analysis of the ES, the lowest value between pH 5–7 was measured. Thus, the amount of \( \text{Ca(OH)}_2 \) and the value of the zeta potential in the aqueous solution seemed to have an overall effect on the removal efficiency of Pb(II) by the ES. According to previous studies, there are different pH ranges that favor adsorption in the aqueous solution depending on the heavy metals. Examples include pH 4 for Fe(II), pH 5 for Al(III), pH 6 for Cr(III), pH 7 for Pb(II) and pH 8 for Ni(II), Cd(II) and Co(II) \citep{Pettinato2015, Yu2018}. Considering that the industrial wastewater containing heavy metals has a pH of 5–6, it is possible to neutralize the industrial wastewater by the influence of CaOH contained in the ES. In addition, it can be applied to the heavy metal treatment of acid mine drainage using the ES adsorbent.

**Effect of adsorbent amount and contact time**

The adsorption efficiency based on the amount of adsorbent is a parameter to evaluate the adsorbability and economic efficiency of the adsorbent \citep{Ahmad2012, Lee2018}. The Pb(II) adsorption efficiency was as low as 27.65% by 0.3 g/L ES, while it was 95.4% and 100% for 1 g/L and 1.5 g/L ES adsorbent, respectively, indicating a high adsorption efficiency with a small amount of adsorbent (Figure 2(c)). \( q_e \) (mg/g) was found to be similar at 27.65–28.62 mg/g from 0.3 to 1 g/L ES. However, as the amount of adsorbent increased from 1.5 g/L, indicating 100% adsorption efficiency, \( q_e \) decreased with the increasing amount of ES. This is because the amount of adsorbent varied from 0.5 to 20 g/L, but the concentration of Pb(II) was fixed at 30 mg/L.

The adsorption efficiency of Pb(II) according to the mixing time is a parameter to evaluate the quality of the adsorbent, as well as the adsorption efficiency depending on the amount and initial concentration of the adsorbent. As a result, the adsorbed amount of Pb(II) onto the ES increased with increasing reaction time, in which 52.57% Pb(II) was adsorbed in 3 min and 99.92% in 30 min of reaction time on the ES (Figure 2(d)). After 30 min of reaction time, the adsorption amount of Pb(II) was almost unchanged, and it can be seen that the adsorption process of Pb(II) onto the ES reached its adsorption equilibrium. Considering these results, the adsorption process of removing Pb(II) using the ES was optimal for the amount of adsorbent of 1–1.5 g/L and the mixing time of 30 min.

**Kinetics of adsorption**

To design an efficient model for the adsorption process, it is necessary to understand the kinetic analysis. To obtain quantitative data on the adsorption kinetics of Pb(II) onto the ES, four models, including pseudo-first-order, pseudo-second-order, intra-particle diffusion and Elovich models, were used. The parameters of pseudo-first-order, pseudo-second-order, intra-particle diffusion and Elovich are calculated and shown in Table 3.

The adsorption rate constant \( (k_f) \) and adsorption amount \( (q_e) \) obtained from the pseudo-first-order linear slope and intercept increased with the increase in the initial concentration of Pb(II). It is hypothesized that the higher the concentration of the Pb(II), the greater the possibility that the Pb(II) comes into contact with the ES adsorbent, and the difference in the concentration of the Pb(II) between the ES adsorbent surface and the solution becomes larger. The \( k_2 \) decreased as the initial concentration of Pb(II) increased, and the adsorption behavior decreased as the concentration of Pb(II) increased. In addition, if a straight line passing through the zero point is shown when \( q(t) \) and \( t^{1/2} \) are expressed in a straight line (Figure 3), it can be said that the adsorption reaction is dominated by the internal diffusion \citep{Yu2018}, and the \( K_{id} \) value can be obtained from the slope of this straight line. \( K_{id} \), the diffusion rate constant in the adsorbent pore, increased as the initial concentration of Pb(II) increased. It can be seen that the diffusion rate of the intra-particles increases with the increasing difference between the adsorbed Pb(II) concentration onto the ES adsorbent and the Pb(II) concentration in the aqueous solution.

The number of sites available for adsorption \( (1/\beta) \) analyzed by the Elovich model increased with the increase in the Pb(II) concentration. Thus, it can be seen that as the concentration increases, the number of adsorption available sites that can be adsorbed on the ES adsorbent increase \citep{Renu2017}. As the Pb(II) concentration in the aqueous solution increases, the adsorption efficiency decreases, but the adsorption amount increases. In addition, as the Elovich rate constant, \( \alpha \), which can determine the initial adsorption rate, increased with increasing concentrations of Pb(II).
can be seen that the adsorption rate also increased with increasing initial concentration. This is consistent with an increase in the \(k_1\) of the pseudo-first-order. According to the correlation coefficient (R\(^2\)) analysis, the adsorption removal process of Pb(II) using ES was most the suitable for the pseudo-second-order (Table 3). In addition, the correlation in intra-particle diffusion was lower than that of the pseudo-second-order, indicating that intraparticle diffusion is not a rate limiting step in the adsorption process. The adsorption equilibrium was reached 30 min after the reaction, indicating that the adsorption process proceeds rapidly. The most basic condition of a good adsorbent is to adsorb large quantities of contaminants in a short period of time. The ES is an eco-friendly adsorbent capable of adsorbing large amounts of heavy metals in a short time.

### Isothermal adsorption

The parameters of Langmuir, Freundlich and Tempkin were analyzed using the results of this experiment are

<table>
<thead>
<tr>
<th>Kinetic models</th>
<th>Parameters</th>
<th>(C_e) (mg/L)</th>
<th>10</th>
<th>20</th>
<th>50</th>
<th>100</th>
<th>1000</th>
<th>10000</th>
<th>100000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first-order</td>
<td>(k_1) (1/min)</td>
<td></td>
<td>0.0037</td>
<td>0.0081</td>
<td>0.0168</td>
<td>0.0353</td>
<td>0.0560</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>R(^2)</td>
<td></td>
<td>0.9213</td>
<td>0.9783</td>
<td>0.9422</td>
<td>0.9985</td>
<td>0.9738</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pseudo-second-order</td>
<td>(k_2) (g/mg·min)</td>
<td></td>
<td>0.21*10(^{-1})</td>
<td>0.16*10(^{-1})</td>
<td>0.72*10(^{-3})</td>
<td>0.14*10(^{-3})</td>
<td>0.62*10(^{-4})</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>R(^2)</td>
<td></td>
<td>1.0000</td>
<td>1.0000</td>
<td>0.9913</td>
<td>1.0000</td>
<td>1.0000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intra-particle diffusion</td>
<td>(k_{id}) (mg·g(^{-0.5}))</td>
<td></td>
<td>0.6492</td>
<td>1.3944</td>
<td>2.5358</td>
<td>4.9475</td>
<td>6.3783</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>R(^2)</td>
<td></td>
<td>0.9731</td>
<td>0.9979</td>
<td>0.9777</td>
<td>0.9843</td>
<td>0.9716</td>
<td></td>
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</tr>
<tr>
<td>Elovich</td>
<td>(\frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t)</td>
<td>(\alpha) (mg/g·min)</td>
<td>1.44</td>
<td>2.25</td>
<td>5.81</td>
<td>8.04</td>
<td>20.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\beta) (g/mg)</td>
<td></td>
<td>1.18</td>
<td>0.61</td>
<td>0.35</td>
<td>0.20</td>
<td>0.18</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>R(^2)</td>
<td></td>
<td>0.9652</td>
<td>0.9702</td>
<td>0.9645</td>
<td>0.9480</td>
<td>0.9725</td>
<td></td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Models</th>
<th>Parameters</th>
<th>Pb(II)</th>
<th>33.90</th>
<th>0.015</th>
<th>0.8696</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir isotherm</td>
<td>(q_o) (mg/g)</td>
<td>(K_L) (L/g)</td>
<td>(R^2)</td>
<td>(10.001)</td>
<td>(247.73)</td>
</tr>
<tr>
<td></td>
<td>(\frac{C_e}{q_o} = \frac{1}{q_mK_L})</td>
<td>(K_F) (mg/g)/(L/mg(^{1/n}))</td>
<td>(n)</td>
<td>(1.1989)</td>
<td>(0.9974)</td>
</tr>
<tr>
<td>Freundlich isotherm</td>
<td>(\log q_e = \log K_F + \frac{1}{n}\log C_e)</td>
<td>(K_F) (mg/g)/(L/mg(^{1/n}))</td>
<td>(n)</td>
<td>(1.1989)</td>
<td>(0.9974)</td>
</tr>
<tr>
<td>Tempkin isotherm</td>
<td>(q_e = B \ln A + B \ln C_e)</td>
<td>(b_T) (kJ/mol)</td>
<td>(10.001)</td>
<td>(247.73)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\frac{RT}{b_T})</td>
<td>(A) (L/g)</td>
<td>(0.71)</td>
<td>(0.9752)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th></th>
<th>298 K</th>
<th>308 K</th>
<th>318 K</th>
<th>328 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K_C)</td>
<td></td>
<td>14.32</td>
<td>22.62</td>
<td>34.25</td>
<td>49.50</td>
</tr>
<tr>
<td>(\Delta G^0) (kJ/mol)</td>
<td></td>
<td>6.59</td>
<td>10.64</td>
<td>14.75</td>
<td>18.86</td>
</tr>
<tr>
<td>(\Delta H^0) (kJ/mol)</td>
<td></td>
<td>10.00</td>
<td>16.74</td>
<td>23.49</td>
<td>30.24</td>
</tr>
<tr>
<td>(\Delta S^0) (J/mol·K)</td>
<td></td>
<td>151.88</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

shown in Table 3. According to the Langmuir adsorption isotherm, the maximum adsorption capacity of Pb(II) was 33.90 mg/g. The separation factor $R_L$ ($1/(1 + K_L C_0)$) is unfavorable if it is greater than 1, favorable if it is between 0 and 1, linear if it is 1 and irreversible if it is 0 (Ali et al. 2016; Lee & Choi 2018). In this experiment, the $R_L$ obtained was 0.8696, and the $R_L$ was greater than 0 and smaller than 1. The adsorption of Pb(II) using the ES was favorable. The $K_F$ value of the Freundlich adsorption isotherm is a function related to the adsorption capacity, and $1/n$ is a function which indicates the adsorption strength between the adsorbent and the adsorbent (Yu & Choi 2018a). As a result, the value of $1/n$ of Pb(II) was 0.8341, indicating that the adsorption strength between the ES and Pb(II) was strong and exhibited the isothermal adsorption characteristics of the L type. In addition, the $K_F$ was 1.49 (L/g), indicating that the adsorbability of Pb(II) onto the ES is excellent and rapidly adsorbed. The interaction between the Pb(II) and ES adsorbent can be determined using the Temkin isothermal adsorption equation. The Tempkin isotherm constants $B$ and $A$ determined by the slopes of $q_e$ and $\ln C_e$ were found to be 10.00 J/mol and 0.71 L/g, respectively, corresponding to the physical adsorption region $B < 20$ J/mol (Ahmad et al. 2012; Lee & Choi 2018). Therefore, the adsorption of Pb(II) by the ES is closer to the physical adsorption, which is due to the action of van der Waals forces, which is composed of dispersion force and electrostatic force, rather than chemical adsorption, which changes the chemical form of the adsorbent material due to the reaction between adsorbate and adsorbent. According to the analysis of the correlation coefficient ($R^2$), the Freundlich adsorption isotherm was the most suitable for the Pb(II) adsorption process by the ES, while Langmuir isotherm was 0.8696, Freundlich isotherm was 0.9974 and Temkin isotherm was 0.9752.

Table 4 summarized the results of suitable adsorption isotherm, kinetic and adsorption capacity using various adsorbents for removal of Pb(II). The adsorption capacity of ES was higher than that of the heavy metal adsorbed
Table 4 | Comparison of heavy metal ions removal by different adsorbent

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Metal ion</th>
<th>Isotherm</th>
<th>Kinetic</th>
<th>q_max (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂ iodovanadate</td>
<td>Pb(II)</td>
<td>L</td>
<td>PS2</td>
<td>18.80</td>
<td>Naushad et al. (2015a)</td>
</tr>
<tr>
<td></td>
<td>Hg(II)</td>
<td></td>
<td></td>
<td>17.20</td>
<td></td>
</tr>
<tr>
<td>Sodium dodecyl sulfate acrylamide Zr(IV) selenite</td>
<td>Pb(II)</td>
<td>F</td>
<td>PS1</td>
<td>21.01</td>
<td>Naushad (2014)</td>
</tr>
<tr>
<td>Fig sawdust</td>
<td>Pb(II)</td>
<td>L</td>
<td>PS2</td>
<td>80.65</td>
<td>Ghasemi et al. (2014a)</td>
</tr>
<tr>
<td>nFe-A</td>
<td>Pb(II)</td>
<td>L</td>
<td>PS2</td>
<td>833.33</td>
<td>Ghasemi et al. (2014b)</td>
</tr>
<tr>
<td>Peanut shell</td>
<td>Cr(VI)</td>
<td>L</td>
<td>PS2</td>
<td>14.31</td>
<td>Al-othman et al. (2012)</td>
</tr>
<tr>
<td>NiFe₂O₄-NH</td>
<td>Hg(II)</td>
<td>L</td>
<td>PS2</td>
<td>476.2</td>
<td>Naushad et al. (2017)</td>
</tr>
<tr>
<td>Starch/SiO₂</td>
<td>Hg(II)</td>
<td>F</td>
<td>PS2</td>
<td>192.0</td>
<td>Naushad et al. (2016)</td>
</tr>
<tr>
<td>Fe₃O₄@AMCA-MIL53(Al)</td>
<td>U(VI)</td>
<td>L</td>
<td>PS2</td>
<td>227.3</td>
<td>Alqadami et al. (2017a)</td>
</tr>
<tr>
<td></td>
<td>Th(IV)</td>
<td></td>
<td></td>
<td>285.7</td>
<td></td>
</tr>
<tr>
<td>Fe₃O₄@TAS</td>
<td>Cd(II)</td>
<td>L</td>
<td>PS2</td>
<td>285.7</td>
<td>Alqadami et al. (2017b)</td>
</tr>
<tr>
<td></td>
<td>Cr(III)</td>
<td></td>
<td></td>
<td>370.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Co(II)</td>
<td></td>
<td></td>
<td>270.3</td>
<td></td>
</tr>
<tr>
<td>Sericite</td>
<td>Pb(II)</td>
<td>L</td>
<td>PS2</td>
<td>4.70</td>
<td>Tiwari et al. (2007)</td>
</tr>
<tr>
<td>Eggshells</td>
<td>Pb(II)</td>
<td>L</td>
<td>PS2</td>
<td>22.88</td>
<td>Ahmad et al. (2012)</td>
</tr>
<tr>
<td>Sericite + Coffee</td>
<td>Pb(II)</td>
<td>L</td>
<td>PS2</td>
<td>44.42</td>
<td>Choi (2018)</td>
</tr>
<tr>
<td>ES adsorbent</td>
<td>Pb(II)</td>
<td>L</td>
<td>PS2</td>
<td>33.90</td>
<td>This study</td>
</tr>
</tbody>
</table>

L, Langmuir; F, Freundlich; PS1, Pseudo-first-order; PS2, Pseudo-second-order.

with coffee grounds, eggshells and sericite. The ES adsorbent can compete with the conventional adsorbent, despite their lower adsorption capacity. These waste-based adsorbents are accessible for environmental conservation and sustainable environmental circulation.

**Thermodynamic interpretation**

The adsorption process is affected by the temperature, because it shows the thermodynamic equilibrium between the adsorbed heavy metal on the surface of the ES and the heavy metals in the aqueous solution. The change in the free energy of $\Delta G^\circ$ is a measure of the usefulness of the chemical reaction. It is a state function that determines the direction of the spontaneous change process for a chemical reaction (Meneguin et al. 2017). When a given chemical reaction system moves from a single equilibrium state to a new equilibrium state, $\Delta G^\circ$ has a negative value so that the change occurs spontaneously (Mittal et al. 2016; Yu & Choi 2018a). The experimental results show that $\Delta G^\circ$ is $-6.59$ (kJ/mol) at 298 K and $-10.64$ (kJ/mol) at 328 K. The $\Delta G^\circ$ value decreases with increasing temperature and is negative (Table 3). It can be seen that the adsorption process of Pb(II) by the ES was more favorable at a higher temperature than a low temperature, and the adsorption process was a spontaneous process. Generally, if the value of $\Delta G^\circ$ is between 0 and $-20$ (kJ/mol), it indicates a physical adsorption, and between $-80$ and $-400$ (kJ/mol), it indicates a chemical adsorption in the adsorption process (Barsbay et al. 2018). The Pb(II) adsorption using the ES was determined to be $-6.59$ to $-10.64$ (kJ/mol), indicating that it was a physical adsorption process rather than a chemical adsorption process. In addition, the $\Delta H^\circ$ and $\Delta S^\circ$ values were $38.35$ (kJ/mol) and $151.88$ (J/mol·K), respectively, the Pb(II) adsorption process using ES was an endothermic process and Pb(II) on the ES adsorbent was randomly adsorbed.

**CONCLUSIONS**

The hybrid adsorbent was prepared by mixing the clay minerals, sericite and eggshell, which were used to remove Pb(II) from the aqueous solution. The FT-IR analysis showed that the ES contained a large amount of OH groups, which facilitated the adsorption of heavy metals. For the preparation of the ES adsorbent, the calcination temperature was $800$ ℃, and the ratio of 6:4 of the eggshell to the sericite was the optimal ratio to maintain the adsorbent morphology. In the adsorption kinetic analysis,
pseudo-second-order was the most suitable because of its high correlation coefficient. The concentration of $k_{ad}$ (mg/g·h$^{0.5}$) increased with increasing concentrations, and the diffusion rate of the internal particles increased with an increase in the initial concentration. In addition, $\beta$ (g/min) of Elovich decreased with increasing concentration and the number of active sites of the adsorbent that can be decreased with increasing initial concentration. Analysis of the adsorption isotherm showed that the Freundlich adsorption isotherm was the most suitable for the Pb(II) adsorption process for ES. The value of $1/n$ was determined to be 0.8341, indicating that the adsorption strength between the ES and Pb(II) was strong. According to the analysis of B (J/mol) from the Tempkin isotherm and $\Delta G^o$ (kJ/mol), the adsorption process of Pb(II) using the ES was physical adsorption. In addition, the $\Delta G^o$ value was negative and decreased with increasing temperature. However, $\Delta H^o$ and $\Delta S^o$ were found to be positive values. Thus, the adsorption process of Pb(II) by ES was a spontaneous endothermic reaction.

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