Novel self-assembled 3D flower-like magnesium hydroxide coated granular polyurethane: Implication of its potential application for the removal of heavy metals

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A B S T R A C T

Novel nanostructured three-dimensional flowerlike Mg(OH)2-incorporated granular polyurethane (designated as gPU-FMH) was prepared using a simple hydrothermal method, for which commercial MgO, water, and granular polyurethane (gPU) were applied. Interestingly, it is found that gPU and the hydrothermal process are the key factors for the assembly of the flowerlike structures of the Mg(OH)2, as its hexagonal nanosheet petals provide a high surface area. Temperature significantly controlled the morphologies of the flowerlike Mg(OH)2, and the granular gPU-FMH showed the superb adsorption capacities of 472, 1050, and 1293 mg g⁻¹ (maximum adsorption capacities, qm, from Langmuir model) for Cu(II), Cd(II), and Pb(II), respectively. The proposed hypothesis for the synthesis of gPU-FMH and the removal mechanism of the heavy metals has been proved through various spectroscopic analyses. In the result of the continuous-flow column study, gPU-FMH showed a long breakthrough and a high removal capacity (184 mg g⁻¹) of Cu(II).

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1. Introduction

The discharging of heavy metals into the environment results in hazardous impacts on the health of human beings, animals, and plants. The remediation of heavy metals from industrial effluents and discharges is of great importance. Among the numerous reported mechanisms for the removal of heavy metals, adsorption has attracted much attention due to its simplicity and cost-effectiveness (Park et al., 2016). Since conventional adsorbents such as low-cost adsorbents (Salam et al., 2011), waste materials (Bhatnagar and Sillanpää, 2010), and especially nanosized metal oxides (Cao et al., 2012) have been reported with low adsorption capacities, a practical adsorbent with a high removal capacity is in huge demand.

In association with a water-treatment demand, much attention has been paid to the evolution of metal oxides with three-dimensional (3D) flowerlike nanostructured materials that use nanosized building blocks to remove heavy metals (Zhang et al., 2012). It is believed that compared with the traditional adsorbents, the specific surface areas of the 3D flowerlike nanomaterials are much larger, which could improve its heavy-metal adsorption capacities (Ma et al., 2018; Nasiri et al., 2018). Among all of the metal oxides, magnesium oxide (MgO) and magnesium hydroxide [Mg(OH)₂] have been considered since they are not only cheap, innocuous, and environmentally friendly, but their adsorption properties for heavy-metal removal are also excellent (Cao et al., 2012). However, the synthesis of the 3D flowerlike metal oxide
using a simple and economic route is still a significantly required research field. An ethylene—glycol-mediated process, for example, was developed for the synthesis of 3D flowerlike nanostructured materials in an earlier research study (Zhong et al., 2006), but this process is costly and complicated because various expensive chemicals such as polyvinylpyrrolidone (PVP), polyethylene glycol (PEG), urea, and numerous preparation methods are needed (Ma et al., 2014). Chang and Jin (Cao et al., 2012) developed a microwave-assisted solvothermal process to obtain flowerlike MgO (FMO) nanostructures with a superb adsorption capacity for the removal of heavy metals. The FMO was prepared using magnesium nitrate [Mg(NO3)]2, urea, and ethanol, and the synthesized product was irradiated using a microwave (at 150 °C), followed by a calcination at 400 °C. Flowerlike Mg(OH)2 (FMH) have been also synthesized using various chemicals such as ammonia (NH3), urea, and Mg(NO3)2 via a continuous procedure that includes heating, centrifuging, and calcination (Liu et al., 2015). As fine-sized powders, however, synthesized FMO and FMH seem to be impractical not only because it is complicated to separate them from the liquid phase once they are saturated, but also they cannot be applied in a column system since they significantly reduce the hydraulic conductivity. Self-assembled 3D-FMH-incorporated granular polyurethane (gPU) has been synthesized and designated as “gPU-FMH” for the removal of heavy metals such as copper (Cu(II)), lead (Pb(II)), and cadmium (Cd(II)) from the aqueous phase. The gPU-FMH can be prepared via a simple, rapid, and economic one-step route using gPU, commercial MgO, and water (H2O). A similar study on the synthesis of gPU-FMH without the use of solvents and a subsequent calcination has not been presented in the literature. We also made the hypothesis on the mechanisms for the synthesis of gPU-FMH and its heavy metals adsorption that were being verified through various spectroscopic analyses and batch tests. The gPU-FMH showed a high rigidity and superb adsorption capacities for the removal of the heavy metals, implying that its potential is great in the remediation of water that has been contaminated by heavy metals.

2. Method and materials

2.1. Preparation of self-assembled 3D-FMH-incorporated granular polyurethane

Polyol and methylene diphenyl diisocyanate (MDI) were purchased from Portal Trading (Penang, Malaysia). The commercial MgO powder with a purity of more than 99% was purchased from RM & Marketing (Essex, U.K.). The PU material was synthesized using the exothermic reactions between the polyol with a reactive hydroxyl (−OH) groups and the MDI containing the isocyanate group (−NCO). The gPU was simply synthesized by the transferal of 17 g of the polyol into a paper cup, followed by the addition of 34 g of the MDI. The mixture was immediately stirred for a few seconds at room temperature (RT) using a mixer (1000 rpm). The prepared gPU was ground and sieved to the size range of 70–20 U.S. Mesh (210–841 μm). Moreover, the water-absorption degree of the gPU was measured as 3 mL g⁻¹. Then 18 g of the MgO were dissolved in 60 g of distilled H2O. Once 20 g of the gPU was placed into a plastic bottle, the MgO suspension was gradually added and homogeneously mixed with the gPU. The description of all prepared samples was listed in Table S1. The gPU–MgO mixture was divided into three separated samples, and the different hydrothermal temperatures of 50 °C, 80 °C, and 120 °C, corresponding to the gPU-FMH80, gPU-FMH120, and gPU-FMH180, respectively, were applied for 24 h. To investigate the roles of the gPU and the hydrothermal treatment for the synthesis of gPU-FMH80, two control samples were prepared as follows: a control sample 1 (CS-1) was prepared using the same procedure as that of the gPU-FMH80, but it was directly dried at 80 °C for 24 h without an autoclave heating. For the control sample 2 (CS-2), the same gPU-FMH80-synthesis procedure was applied to the MgO without incorporation of the gPU to investigate the effect of the gPU in the growth and formation of the 3D flowerlike structure.

2.2. Characterization

The PANalytical Empyrean X-ray diffractometer (XRD) device (PANalytical Empyrean, The Netherlands) was used to obtain copper (Cu)–Kz-radiation (λ = 1.54443 Å at 40 kV and 40 mA) patterns for an assessment of the retention capacity of the gPU-FMH80 regarding the Cu(II), Cd(II), and Pb(II) that correspond to the Cu(II)/gPU-FMH80, Cd(II)/gPU-FMH80, and Pb(II)/gPU-FMH80, respectively. A morphological study of the commercial MgO, gPU-FMH80, Cu(II)/gPU-FMH80, Cd(II)/gPU-FMH80, and Pb(II)/gPU-FMH80 was also conducted, for which the SU 8000 field-emission scanning electron microscope (FE-SEM) device (Hitachi, Japan) was used with the XFlash 6/30 energy-dispersive X-ray spectroscopy (EDS) device (Bruker, Germany) and the Octane Super EDS device (EDA, U.S.A.). The surface area was measured using the Brunauer–Emmett–Teller (BET) theory, while the pore-size distributions (PSDs) of the gPU, commercial MgO, and gPU-FMH80 (before and after the metal sorption) were calculated using the TriStar II 3020 surface-area and porosity analyzer (Micromeritics, U.S.A.) according to the desorption branch of the nitrogen (N2) isotherms and the Barrett–Joyner–Halenda (BJH) method. An infrared (IR) spectrum of gPU and gPU-FMH80 was identified using the Tensor 27 Fourier transform infrared spectrophotometer (FTIR) device (Bruker, Germany) over the frequency range of 4000–400 cm⁻¹ at a resolution of 4 cm⁻¹. The heavy metals in the samples were analyzed using the Optima 8300 inductively coupled plasma atomic emission spectrometry (ICP-OES) device (Perkin Elmer, U.S.A.).

2.3. Isotherms and kinetics

The effect of the gPU-FMH80 on the removal of the heavy metals, sorption isotherms, and kinetic tests were studied. For the isotherm studies, Cu(II), Cd(II), or Pb(II) containing H2O were prepared with various concentrations ranging from 50 to 1400 mg L⁻¹ under a 0.1 M ionic strength (0.1 M NaCl). The pH value of the prepared solution was adjusted to 4 ± 0.1 to avoid the possibility of the heavy-metal hydrolysis. For the isotherm study, 0.1 g of the gPU-FMH80 was added to 100 mL of a heavy-metal solution, and it was then shaken for 24 h at room temperature (25 ± 1 °C) at 150 rpm. A mass of the heavy-metal ions that were absorbed at equilibrium, qeq (mg g⁻¹), was calculated using the following equation:

\[
q_{\text{eq}} = \frac{(C_0 - C_{\text{eq}}) V}{W}
\]

where \(C_0\) and \(C_{\text{eq}}\) are the initial and equilibrium concentrations of the metal ions (mg L⁻¹), respectively, and \(V\) and \(W\) are the solution volume and the adsorbent mass (g), respectively.

The adsorption data were fitted with the Langmuir model, as follows:

\[
q_{\text{eq}} = \frac{q_m K_C C_{\text{eq}}}{1 + K_C C_{\text{eq}}}
\]

where \(q_m\) is the maximum adsorption capacity and \(K_C\) is the equilibrium constant that is related to the adsorption energy.

For the kinetic studies, a 500-mL solution containing 500 mg L⁻¹ of the initial concentration of the Cu(II), Cd(II), or Pb(II) (0.1 M ionic strength) was poured into a conical flask, and 0.5 g of the gPU-
FMH\textsubscript{80} was added to each solution. The pH of the solution was adjusted at the pH of 4 \pm 0.1, and the conical flask was shaken at 150 rpm for 24 h at room temperature (25 \pm 1\,^\circ\text{C}). At specific time intervals, 50-ml samples were collected and filtered using a 0.45- \mu\text{m}-pore filter. The filtrates were analyzed using ICP-OES. The experiment data were fitted using the pseudo second-order model, as follows:

\[
\frac{1}{q_t} = \frac{1}{k_2q_e^2} + \left(\frac{1}{q_e}\right)t
\]

where \(k_2\) is the rate constant of the pseudo second-order equation (g mg\(^{-1}\) min\(^{-1}\)), \(q_t\) is the amount of adsorption at a specific time (mg g\(^{-1}\)), and \(q_e\) is the amount of adsorption at equilibrium (mg g\(^{-1}\)). The parameters \(k_2\) and \(q_e\) can be determined from the intercept and the gradient of the linear graph that are obtained from the plotting \((1/q_t)\) versus \(t\).

### 2.4. Small-scale column tests

Small-scale column tests were carried out in a column with a dimension of 16-mm internal diameter (ID) and 50-mm length (L). Glass wool was used at the bottom and top of each column. Three columns were filled with 2.0 g of the gPU (column 1), 0.44 g of the commercial MgO (column 2), and 1.80 g of the gPU-FMH\textsubscript{80} (column 3). All the materials were washed by passing 100 mL of distilled H\textsubscript{2}O through the columns before the treatment process. Then, the Cu(II) solution (65 mg L\(^{-1}\)) was added to each solution, and the samples at the outlet were obtained at various bed volumes (BVs). The initial pH of the Cu(II) solution was adjusted to 4.0 \pm 0.1 to avoid the hydrolysis and precipitation of the heavy metals. The breakthrough point (BTP) according to the Environmental Protection Agency (EPA) guideline (0.2 mg L\(^{-1}\)) is the maximum acceptable discharge Cu(II) concentration. The ionic strength was also adjusted to 0.1 M using sodium chloride (NaCl).

### 3. Results and discussion

#### 3.1. Characterization of self-assembled 3D-FMH-incorporated granular polyurethane

Because of the loss of the CO\textsubscript{2} during the synthesis process, the ground-gPU structure with the particle sizes between 210 and 841 \mu m is concave/hollow, as can be seen in Fig. 1 (a), and it shows a smooth surface with no pore structures, as can be seen in Fig. 1 (b). The morphology of the commercial MgO that is shown in Fig. 1 (c) is irregular and heterogeneous with a thickness of \(-100\,\text{nm}\) and a diameter from 80 to 500 nm; therefore, it is much smaller than that of gPU particles. Fig. 1 (d) shows the post-treated gPU that had been aggregated into larger particles (30–16 U.S. Mesh, 600–1180 \mu m) and contains the white material in the hollow-gPU area, as shown in Fig. 1 (e). Fig. 1 (f)–(n) display the plentiful well-defined flower-like single or garden structures that formed on the gPU surface; however, different nanostructural morphologies were observed at the various hydrothermal temperatures (50–120\,\text{C}). When a temperature higher than 120 \,\text{C} was applied, the PU foam could be burned. So the maximum temperature applied for the hydrothermal process was 120 \,\text{C}. The micrographs of gPU-FMH that can be seen in Fig. 1 (f)–(n) were prepared at various temperatures, and they show a 3D flower-like structure with irregular and curved-petal morphologies of a \(-10-\text{nm}\) thickness.

Interestingly, the garden structures from 50 to 120 \,\text{C} show different patterns of the 3D flower-like structure with dissimilar petal morphologies; for example, at 50 \,\text{C}, coherent flowers were synthesized using curved and incomplete hexagonal petals. The petal morphology, however, was developed as a complete hexagonal shape at 80 \,\text{C}. Eventually, at the maximum temperature, 120 \,\text{C}, more-compact flowerlike structures with smaller hexagonal petals were prepared.

The gPU/MgO morphology (CS-1) in Fig. 1 (o) did not reveal an FMH formation in the absence of the hydrothermal treatment. Fig. 1 (p) shows that Mg(OH)\textsubscript{2} (CS-2) nanoplates were formed with a thickness from 20 to 50 nm and a diameter of \(-500\,\text{nm}\). Therefore, without forming 3D flowerlike structures, CS-2 had much larger and thicker nanoplates than gPU-FMH. The production of these MgO nanoplates might be due to the epitaxial growth of the Mg(OH)\textsubscript{2} nanoplates in the H\textsubscript{2}O vapor under the hydrothermal treatment (Fruhwirth et al., 1985).

Since the complete 3D flowerlike morphology was produced and an appropriate range of temperatures was considered, the gPU-FMH\textsubscript{80} was selected for the heavy-metal adsorption, and it was further characterized by XRD (Fig. 51), elemental mapping, EDS (Fig. S2), FTIR (Fig. S3), and N\textsubscript{2}-gas isotherms (Fig. S4 and Table S2).

The XRD results show that all of the diffraction peaks can be labeled as Mg(OH)\textsubscript{2} crystallites, and this is consistent with the values of the JCPDS 7-239 standard of the International Centre for Diffraction Data (ICDD). MgO peaks were not observed, so the MgO became fully hydrated to the Mg(OH)\textsubscript{2}. The elemental-mapping and EDS data of the single-flower displays that are presented in Fig. S2 (a) show that the Mg and oxygen (O) are significantly dispersed on the FMH spots, while carbon (C) is not shown on the FMH. In Fig. S3, the FTIR peak for the stretching vibration of the O–H of Mg(OH)\textsubscript{2} was observed at 3700 cm\(^{-1}\) (Cao et al., 2010). The symmetric- and asymmetric-stretching vibrations of the N–H correspond to the broad absorption bands in gPU near 3340 cm\(^{-1}\) and 3360 cm\(^{-1}\), as shown in Fig. 53 (a), and gPU-FMH\textsubscript{80}, as shown in Fig. 53 (b). After the FMH was incorporated, however, the sharp-peak intensity at 1512 cm\(^{-1}\) was reduced to support the claim that the N species of gPU might be extracted during the hydrothermal-treatment process (Jiao et al., 2013).

The N\textsubscript{2}-gas-isotherm (Fig. S4) results indicate that the surface area of gPU-FMH\textsubscript{80} (20.2 m\(^{2}\) g\(^{-1}\)) is two or 117 times higher than that of MgO (9.6 m\(^{2}\) g\(^{-1}\)) or gPU (0.18 m\(^{2}\) g\(^{-1}\)), and this is because of 3D flowerlike nanostructured Mg(OH)\textsubscript{2}. Based on the previously described results, the following hypothesis is proposed: MgO nanoparticles can grow as hexagonal Mg(OH)\textsubscript{2} nanosheets, and the self-assemble of flowerlike-structure 3D building blocks can occur in the presence of gPU under a hydrothermal treatment.

The hydrothermal temperature might play a key role in the controlling of the FMH morphology.

**Proposed mechanism for the self-assembled flowerlike Mg(OH)\textsubscript{2}–incorporated granular polyurethane**

Based on the FESEM results, the proposed mechanism for the formation of gPU-FMH consists of the following three stages: nucleation, growth, and self-assembly. Prior to the hydrothermal treatment, the nucleation was started by the hydrolysis of the commercial MgO, which is of an irregular round shape, as can be seen in Fig. 1 (c). Then, the hydrolyzed product, Mg(OH)\textsubscript{2}, will be further dissolved into Mg\textsuperscript{2+} and OH\textsuperscript{-}, as follows:

\[
\text{MgO} + \text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 \tag{R1}
\]

\[
\text{Mg(OH)}_2 \rightarrow \text{Mg}^{2+} + 2\text{OH}^- \tag{R2}
\]

At the pH of 9.5, however, the OH\textsuperscript{-} species will rebind to the Mg\textsuperscript{2+}, thereby forming the Mg(OH)\textsubscript{2} nuclei that is the primary Mg(OH)\textsubscript{2}. In the hydrothermal condition, the nanosheet growth will start via the dissolution of the initial Mg(OH)\textsubscript{2}, as shown in
Fig. 1 (p). As a new structure, which is shown in Fig. 1 (f)–(n), Mg(OH)$_2$ nanoplate crystallites might be formed by alternating layers of the Mg$^{2+}$ and OH$^-$ ions, in which the Mg$^{2+}$ ion has a coordination of sixfold oxygen ions (Wu et al., 2008). This reaction develops into the Ostwald ripening process, a thermodynamically driven spontaneous process, during the hydrothermal treatment so that the larger primary Mg(OH)$_2$ particles can grow as the small particles are deposited onto the larger particles due to their different solubilities (Voorhees, 1985). Besides, the gPU is hydrolyzed (with the presence of H$_2$O), and reusable diamines, glycols, and CO$_2$ are subsequently released during the hydrothermal treatment (Siskin and Katritzky, 1991).

Regarding an important role in the control and growth of the self-assembled Mg(OH)$_2$, diamine, benzene, and glycol might act as special bases in the syntheses of the 3D flowerlike Mg(OH)$_2$ due to the lone pair of electrons on the N atom in the diamine compound (Li et al., 2007). The self-assembly process of the Mg(OH)$_2$ nanosheets that occurs through electrostatic repulsion might lead to the formation of 3D flowerlike structures. Since the pH at the isoelectric point (pH$_{IEP}$) of the Mg(OH)$_2$ nanosheet in H$_2$O is 12 and the
measured pH of the MgO suspension is 10.2, the net residual electric charge of the Mg(OH)₂ surface will be positive, which might be a result of the weak bonding interactions with the negatively charged O molecule of the gPU-particle surface (Larson and Buswell, 1940). Especially, the two-dimensional (2D) hexagonal Mg(OH)₂ nanosheets (approximate thickness of 10 nm and width of 300–400 nm) were stacked on the PU surface due to the following fact: all self-assembling systems are driven by energy minimization (Jiao et al., 2006). The electrostatic repulsion between the 2D nanosheets is favorable for self-assembling structures as they align one another perpendicularly to the surface (Cao et al., 2010).

3.2. Heavy-metal adsorption mechanism

The results of the batch experiments revealed that the maximum sorption capacities of gPU-FMH₈₀ regarding Cu(II), Cd(II), and Pb(II) are 472, 1041, and 1321 mg g⁻¹, respectively, which are shown in Fig. 2 (a). The experiment data fitted well with the nonlinear Langmuir model (Table S3). The molar amounts of the removed metal ions and the released Mg(II) per gPU-FMH₈₀ mass in the solution are shown in Tables S4–6. In Fig. 2 (b), the results show that the quantity of the released Mg(II) is fitted with the line (slope = 1) until ~1.8 mmol g⁻¹ of the Cu(II), ~2.0 mmol g⁻¹ of the Cd(II), and ~0.3 mmol g⁻¹ of the Pb(II) were removed from the solution, as displayed in Fig. 2 (b). According to the equal molar amount of the adsorbed metal and the released Mg(II) ions, the ion exchange was expected as the dominant removal mechanism (Cao et al., 2012) (R3) occurred, as follows:

\[
\text{Mg(OH)}_2(s) + \text{Me(II)} \rightarrow \text{Mg(II)} + \text{Me(OH)}_2(s) \quad \text{(R3)}
\]

where Me(II) denotes the metal species. The possibility of ion-exchange metal sorption was found in the order of Cu(II) > Cd(II) > Pb(II) due to a smaller hydrated ionic radius and an electronic metal-ion structure (Amarasinghe and Williams, 2007). Alternatively, when higher amounts of the metal ions [Cu(II) > 1.8 mmol g⁻¹, Cd(II) > 2.0 mmol g⁻¹, and Pb(II) > 0.3 mmol g⁻¹] were removed, the Mg(II) concentrations in the solution were deviated to lower ranges compared with that of the slope with different patterns. Since the Mg(II) can be released in lesser amounts compared to the removed metal ions, another reaction and/or mechanism is speculated here. According to R4, an Mg(OH)₂ dissociation in the metal solution produces two OH⁻ ions that subsequently react with the metal ions. Based on the stoichiometry, this reaction can render the production of insoluble precipitates through coupling with the anionic species that exist in the solution (Brauer, 2012). Further, the precipitates will become trapped in the gaps of the FMH particles, and the precipitation might be the dominant removal mechanism at the higher metal-ion concentrations.

\[
\text{Mg(OH)}_2(s) \rightarrow \text{Mg(II)} + 2\text{OH}^- \quad \text{(R4)}
\]

Fig. 2 (c) shows the kinetics of the heavy-metal removal by gPU-FMH₈₀. The removal speeds of the heavy metals by the gPU-FMH₈₀ are fast, and more than 90% of the metal ions (initial concentration of 500 mg L⁻¹) was removed in the first 60 min (Table S7). According to the pseudo-second-order kinetic model, the K₂ values
Table 1
Magnesium hydroxide [Mg(OH)₂]-incorporated polyurethane (gPU-FMH₈₀)-adsorption results for the Copper(II) Oxide [Cu(II), Cd(II), and Pb(II)], and the comparison with the other flowerlike adsorbents.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Q_max (mg·g⁻¹)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>gPU-FMH₈₀ (this study)</td>
<td>472</td>
<td>1293 4</td>
</tr>
<tr>
<td>Flowerlike MgO (Cao et al., 2012)</td>
<td>inus</td>
<td>1050 1980 7</td>
</tr>
<tr>
<td>Flowerlike γ-AlOOH (Zhang et al., 2012)</td>
<td>inus</td>
<td>124 7</td>
</tr>
<tr>
<td>Flowerlike TiO₂–GO (Lee and Yang, 2012)</td>
<td>inus</td>
<td>66 5</td>
</tr>
<tr>
<td>Flowerlike zinc silicate (Qu et al., 2012)</td>
<td>inus</td>
<td>210 5</td>
</tr>
</tbody>
</table>

are 23.5 × 10⁻⁴, 2.99 × 10⁻⁴, and 2.4 × 10⁻⁴ g·mg⁻¹·min⁻¹ for Pb(II), Cu(II), and Cd(II), respectively (Table S8). The sequence of Pb(II) > Cu(II) > Cd(II) might be strongly related to the hydrolysis condition of the metal ions. Considering the logarithmic values of the hydrolysis constant for the heavy-metal order (log K_Pb = 7.71 > log K_Cu = 8.0 > log K_Cd = 10.8), the adsorption of Pb(II) by the gPU-FMH₈₀ is much faster than those of the Cu(II) and the Cd(II).

The obtained metal-ion sorption capacity of the gPU-FMH₈₀ is much higher than those of the reported materials in the literature that are listed in Table 1, with the exception of the flowerlike MgO (Cao et al., 2012). However, it should be noted that 1 g of the gPU-FMH₈₀ contains 0.44 g of the flowerlike Mg(OH)₂, which was determined using the aqua-regia extraction. Therefore, the heavy-metal sorption densities (mg per g of FMH) for the Cu(II), Cd(II), and Pb(II) can be calculated as 1072, 2383, and 2936 mg·g⁻¹, respectively, which are much higher than the reported flowerlike-MgO values. Especially, the maximum-sorption capacities of the gPU-FMH₈₀ were obtained at the pH of 4, while those of the flowerlike MgO were obtained at the pH of 7.

3.3. Heavy-metal removal characterization

The morphologies of the gPU-FMH₈₀ were studied after the adsorption of the Cu(II), Cd(II), and Pb(II) on the gPU-FMH₈₀ surface. The micrograph of the Cu(II)/PU-FMH₈₀ displays that the Cu precipitants were found on the space gaps of the 3D FMH, as can be seen in Fig. 3 (a). Similar morphologies and SEM-EDS images were observed for the Cd(II)/gPU-FMH₈₀ and the Pb(II)/gPU-FMH₈₀ (Figs. S5, S6, and S7). Overall, as described in the removal-mechanism section, the Mg(OH)₂ could be partly dissolved, and the metal precipitants are trapped in the FMH spaces. An elemental-mapping analysis of the Cu(II)/gPU-FMH₈₀ was also performed; as a result, the Cu(II)-precipitation and Cl⁻ complexation formed at the position indicated by the green and pink color in

Fig. 3. (a) High magnification FE-SEM images of Cu(II)/PU-FMH₈₀, (b) low magnification FE-SEM image of Cu(II)/PU-FMH₈₀, (c–f) elemental mapping of Cu(II)/PU-FMH₈₀, and (g) EDS analysis of Cu(II)/PU-FMH₈₀.
Fig. 4. (a) The concentration of Cu(II) at the outlet of column 1 (gPU), column 2 (commercial MgO), and column 3 (gPU-FMH$_{80}$), (b) breakthrough point (BTP) of PU (column 1) and commercial MgO (column 2), (c) pH changes at the outlet of column 1 (gPU), column 2 (commercial MgO), and column 3 (gPU-FMH$_{80}$) (d) column 3 (gPU- 
FMH$_{80}$) in the column, which is apparent in Fig. 4(d), was changed until 700 BVs had passed. Moreover, the yellowish color of the gPU-
FMH$_{80}$-surface precipitants of Cd(II) and the Pb(II), respectively. These results are closely linked to the conclusion that the metal precipitation can effectively occur on the space of the nanostructured Mg(OH)$_2$.

3.4. Column tests

The Cu(II)-removal performances of the gPU, commercial MgO, and gPU-FMH$_{80}$ were examined in small-scale columns, as shown in Fig. 4 (a). Fig. 4 (b) shows that the BTP of the Cu(II) limitation in drinking water (0.2 mg L$^{-1}$) occurred at the column 1 (gPU) after 1 BV of the Cu(II) solution had passed. In the column 2 (MgO), the Cu(II) was detected after 5 BVs, and the BTP occurred at 25 BVs. As a result, the pH was raised to 10 for the 12 BVs, and it was instantly dropped by 30 BVs to a pH of 4.0 (Fig. 4 (c)). The early BTP might occur since MgO has a low reactive surface area and armoring effect (Stumm and Morgan, 2012), even though its sizes are fine. Along with a low capacity, the commercial MgO is not practical due to its clogging effect.

The longest BTP was found in the column 3 (gPU-FMH$_{80}$) after ~570 BVs. The gPU-FMH$_{80}$ (184 mg g$^{-1}$) showed the highest Cu(II)-sorption capacity, which is much higher than those of all referenced materials (Flowerlike MgO (Cao et al., 2012), flowerlike γ-AlOOH (Zhang et al., 2012), flowerlike TiO$_2$–GO (Lee and Yang, 2012), and flowerlike zinc silicate (Qu et al., 2012)), which are listed in Table 2. The pH in the column 3 increased from a pH of 4.0 to a pH of approximately 11.0 for 600 BVs, and it dropped slowly to a pH of 8.0 until 700 BVs had passed. Moreover, the yellowish color of the gPU-
FMH$_{80}$ in the column, which is apparent in Fig. 4 (d), was changed to the green-bluish color of Fig. 4 (e) after the Cu(II) was saturated.

As a special feature, the gPU-FMH$_{80}$ has a high potential for the sensing or removal of heavy metals because metals can be saturated at the outermost side of media. In the replacement of the saturated media, the color change of the column can be easily understood via the flow direction and the metal contents.

Fig. 5 shows the proposed mechanisms for the synthesis of gPU-FMH and removal of heavy metals. To prove the previously described hypothesis, column tests were conducted in addition to the physicochemical analyses such as XRD, that of the N$_2$-gas isotherm, and SEM-EDS. The XRD peak of Cu(II) retained gPU-
FMH$_{80}$, as shown in Fig. 5, shows that the Cu(II) was removed from the solution as dicopper-trihydroxide-chloride [Cu$_2$(OH)$_3$Cl], as per the JCPDS 19-0389 standard of the ICDD. Likewise, the gPU-FMH$_{80}$ was changed to a green-bluish color after the Cu(II) adsorption, which agreed with the color of Cu$_2$(OH)$_3$Cl (Fig. 5 (a)). Furthermore, the XRD analysis of the Cd(II)/gPU-FMH$_{80}$ and the Pb(II)/gPU-FMH$_{80}$ revealed that the cadmium-hydroxide-chloride [Cd(OH)Cl] (JCPDS 98-009-1087) and the laurionite [Pb(OH)Cl] (JCPDS 98-002-8035) are the gPU-
FMH$_{80}$-surface precipitants of Cd(II) and the Pb(II), respectively (Fig. 5). Since the colors of the particles matched well with the colors of Cd(OH)Cl and Pb(OH)Cl, as can be seen in Fig. 5 (b) and

Table 2: Comparison of the Polyurethane (Column 1), Commercial Magnesium Oxide (Column 2), and gPU-FMH$_{80}$ (Column 3) for the Removal of Cu(II) by Various Adsorbents in the Column Mode.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Inlet pH</th>
<th>EBCT min</th>
<th>Inlet Cu(II) conc. mg L$^{-1}$</th>
<th>Maximum Cu(II) capacity mg g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO-activated carbon (Fan and Anderson, 2005)</td>
<td>6.0</td>
<td>4.0</td>
<td>2</td>
<td>80</td>
</tr>
<tr>
<td>Dihoron trioxide/titanium dioxide (Al-Rashdi et al., 2012)</td>
<td>5.0</td>
<td>30.0</td>
<td>1000</td>
<td>82</td>
</tr>
<tr>
<td>Sargassum sinicola (Patrón-Prado et al., 2013)</td>
<td>5.5</td>
<td>5.0</td>
<td>200</td>
<td>64</td>
</tr>
<tr>
<td>Marine-green alga ulva reticulata (Vijayaraghavan et al., 2005)</td>
<td>5.5</td>
<td>16.0</td>
<td>100</td>
<td>57</td>
</tr>
<tr>
<td>Calcined colloidal pyrite (Chen et al., 2013)</td>
<td>5.0</td>
<td>90.0</td>
<td>99</td>
<td>84</td>
</tr>
<tr>
<td>PU-CaO (Valanenard et al., 2016)</td>
<td>4.0</td>
<td>7.5</td>
<td>65</td>
<td>35</td>
</tr>
<tr>
<td>gPU (this study)</td>
<td>4.0</td>
<td>7.5</td>
<td>65</td>
<td>0</td>
</tr>
<tr>
<td>Commercial MgO (this study)</td>
<td>4.0</td>
<td>7.5</td>
<td>65</td>
<td>17</td>
</tr>
<tr>
<td>gPU-FMH$_{80}$ (this study)</td>
<td>4.0</td>
<td>7.5</td>
<td>65</td>
<td>184</td>
</tr>
</tbody>
</table>
of temperature (80-nanometer nanosheet petals), which were synthesized under the low range of manual power consumption. The estimated cost for producing gPU-FMH is 18.84 US$ per kg, which is a reasonable cost according to the capacity of heavy-metal ions removal capacity, practical and the simple preparation method for gPU-FMH. The estimated cost for transportation and manpower was added in gPU (6.56 US$ kg⁻¹) costs, which might be changed the total cost of gPU-FMH in another regions. Due to the low temperature required for the preparation of gPU-FMH (Only 80°C), the power cost is not affecting much on the final cost even though it could be further reduced in industrial scale.

### 3.5. Cost analysis

Table 3 shows the cost of gPU, MgO, distilled water, and power consumption. The estimated cost for producing gPU-FMH is 18.84 US$ per 1 kg, which is a reasonable cost according to the capacity of metal ions removal capacity, practical and the simple preparation method for gPU-FMH. The estimated cost for transportation and manpower was added in gPU (6.56 US$ Kg⁻¹) and MgO (11.83 US$ Kg⁻¹) costs, which might be changed the total cost of gPU-FMH.

<table>
<thead>
<tr>
<th>Cost descriptions</th>
<th>Price (US$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>gPU-FMH80 (1 kg)</td>
<td></td>
</tr>
<tr>
<td>gPU (including transportation)</td>
<td>6.56</td>
</tr>
<tr>
<td>MgO (including transportation)</td>
<td>11.83</td>
</tr>
<tr>
<td>Distilled water</td>
<td>0.11</td>
</tr>
<tr>
<td>Power generation</td>
<td>0.33</td>
</tr>
<tr>
<td>Total</td>
<td>18.83 US$</td>
</tr>
</tbody>
</table>

(c), this finding can serve as the premise for the existence of Cd(II) and Pb(II) precipiants on the gPU-FMH80 surface.

### 4. Conclusion

Flowerlike-Mg(OH)₂ incorporated gPU was synthesized using a simple method and without the inclusion of toxic and expensive chemicals. The gPU and the hydrothermal treatment played an important role in the morphology of the Mg(OH)₂ and the formation of the regular flowerlike structures (with uniform hexagonal nanosheet petals), which were synthesized under the low range of temperature (80–120°C). Thus, it was speculated that the released organic component (i.e., diamine) of the gPU during the hydrothermal process might be the main key for the synthesis of the gPU-FMH. The Cu(II)–, Cd(II)–, and Pb(II)–removal batch-test results of the gPU-FMH80 showed superb adsorption capacities at 472, 1050, and 1293 mg g⁻¹, respectively. Furthermore, in the column tests, a high Cu(II)-adsorption capacity (184 mg g⁻¹) might occur due to the flowerlike morphology of the Mg(OH)₂ assembled on the surface of the gPU. Due to its facile preparation and high efficiencies in terms of heavy-metal removal, gPU-FMH could be applied as a practical sorbent in water-treatment systems (filtration) for various industrial effluents or acid mine drainages with a simple design and an easy operation.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2018.12.135.

### References


