A Granular Inorganic Adsorbent Highly Selective to Cesium
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Abstract
The adsorbent was synthesized from the acid-base reaction between metal ferrocyanide and acidic phosphate at room temperature. In this work, the compressive strength of granular inorganic adsorbent was investigated under different liquid-to-solid, metal ferrocyanide-to-geopolymer and MgO-to-KH$_2$PO$_4$ ratios. The result showed that the compressive strength of the adsorbent increased with the increase of MgO-to-KH$_2$PO$_4$ ratio. It was found that the optimization metal ferrocyanide-to-geopolymer and MgO-to-KH$_2$PO$_4$ ratios was important in improving both the compressive strength and the adsorption capacity of the adsorbent. In this study, the synthesized granular inorganic adsorbent has demonstrated a Cs removal efficiency of over 99% and an adsorption capacity of 1.1-1.8 meq/g in simulation wastewater containing 2000 ppm Cs under adsorbent dose of 0.0067 g/ml.

Experimental
- Preparation of Potassium zinc ferrocyanide powder (KZnFC)
The KZ41, KZ21, KZ11, KZ12 and KZ14 were designated for the prepared KZnFC with K$_3$Fe(CN)$_3$·3H$_2$O (1M)-to-ZnSO$_4$·7H$_2$O (1M) volume ratio of 4:1, 2:1, 1:1, 1:2 and 1:4, respectively.
- Preparation of phosphoric acid-based geopolymer for granulation of KZnFC
  - Adjustment of MgO-to-KH$_2$PO$_4$ mass ratio
    The MK11, MK21, MK31, MK41 and MK51 were designated for the prepared KZnFC granules via phosphoric acid-based geopolymer with MgO-to-KH$_2$PO$_4$ mass ratio of 1:1, 1:2, 1:3, 1:4 and 1:5, respectively.
  - Adjustment of KZnFC-to-geopolymer mass ratio
    The KC11, KC21, KC41 and KC61 were designated for the prepared KZnFC granules with KZnFC-to-geopolymer mass ratio of 1:1, 1:2.1, 1:4.1 and 1:6.1, respectively.

Results and Discussion
Fig. 1 shows the result shows that ZK11 has higher uptake of cesium among the adsorbents tested, especially in a short period of adsorption time, meaning it requires less residence time when applied in the column. Therefore, ZK11 was selected for the granulation of KZnFC via phosphoric acid-based geopolymer. Fig. 2 shows the compressive strength of geopolymer increases with the increase of MgO-to-KH$_2$PO$_4$ ratios as shown in Fig. 4. In contrast, the compressive strength was increased with the increase of MgO-to-KH$_2$PO$_4$ mass ratios as result of more compact granular inorganic adsorbents formed.

Fig. 5 shows the amount of adsorbed cesium ions for MK21 increases with the increase of KZnFc-to-geopolymer mass ratios, reaching a maximum at the mass ratio of 1.8. On the other hand, the maximum adsorption for MK31 is at the KZnFc-to-geopolymer ratio of 1.6. Fig. 6 shows the compressive strength of MK31 and MK21 decreased with the increase of KZnFc-to-geopolymer mass ratios. With the increase of the contacting time, the cesium ion uptake increased and remained constant after the equilibration time of 60 min as shown in Fig. 7. Fig. 8 shows the percentage of cesium ion adsorption increased from 49.5 to 99.28 % with the decrease of initial concentration in the range from 2000 to 10 ppm.

Taking experimental data of different weigh adsorbent with fixed initial concentration result in different adsorptive equilibrium concentration into the Langmuir adsorption equation for isothermal were shown in Fig. 9. Taking the energy of adsorption constant b data into equilibrium R$_b$ could be evaluated (0.99). The R$_b$ value (0<R$_b$<1) indicated that the adsorption of cesium ion by MK21-KC41 is favorable. Taking experimental data of different weigh adsorbent with fixed initial concentration result in different adsorptive equilibrium concentration into the Freundlich adsorption equation for isothermal were shown in Fig. 10. The inverse of adsorption intensity was evaluated and the result was greater than one (2.5). The result suggests that surface of the adsorbent was heterogeneous in nature with an exponential distribution of active sites.

Conclusion
To optimize both the adsorption capacity and the mechanical stability, only MK21 (1.47 meq/g) and MK31 (1.35 meq/g) were selected to run column operations. To improve the adsorption efficiency of MK21 and MK31, KZnFc content was increased. However, excess KZnFc content did not benefit granular KZnFC’s adsorption efficiency due to the limited pore sites on the adsorbent. As a result, an optimal KZnFc-to-geopolymer ratio in achieving maximum adsorption capacity was 1.8 for MK21-KC41, and 1.6 for MK31-KC21.