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_2PO_4 ratios. The result showed that the compressive strength of the adsorbent increased with the increase of MgO-to-KH_2PO_4 ratio. It was found that the optimization metal ferrocyanide-to-geopolymer and MgO-to-KH_2PO_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 $K_4[Fe(CN)_6]\cdot 3H_2O$ (1M)-to-$ZnSO_4\cdot 7H_2O$ (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_2PO_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_2PO_4 mass ratio of 1:1, 2:1, 3:1, 4:1 and 5:1, respectively.

➢ **Adjustment of KZnFC-to-geopolymer mass ratio**

The KC11, KC21, KC41 and KC61were 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 applies 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_2PO_4 mass ratios. The higher MgO content may brought much more internal stress in sample lead to fast setting. The increase of the MgO-to-KH_2PO_4 mass ratios, the amount of crystallized phase decreased while the amount of amorphous phase increased as shown in Fig. 3. The adsorption capacity was increased with the decrease of MgO-to-KH_2PO_4 mass ratios as shown in Fig. 4. In contrast, the compressive strength was increased with the increase of MgO-to-KH_2PO_4 mass ratios as result of more compact granular inorganic adsorbents formed.

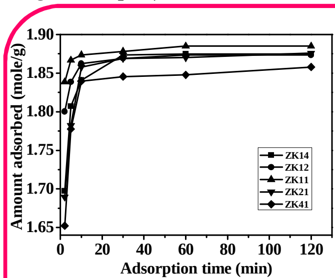

Fig. 1 Time-dependent cesium uptake (mole/g) for powder KZnFC

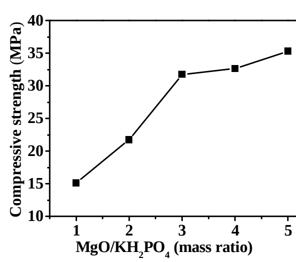

Fig. 2 Compressive strength of the geopolymer with different MgO-to-KH_2PO_4 mass ratios

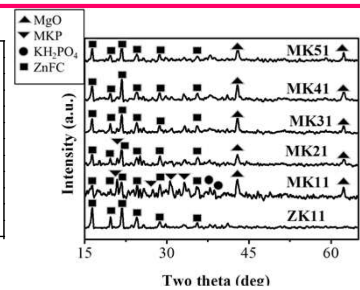

Fig. 3 XRD diffraction patterns of granular KZnFC adsorbents with different MgO-to-KH2PO4 mass ratios

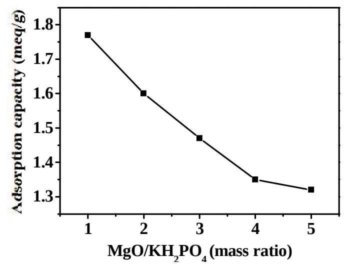

Fig. 4 Adsorption capacity of granular KZnFc adsorbents with different MgO-to-KH2PO4 mass ratios

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.

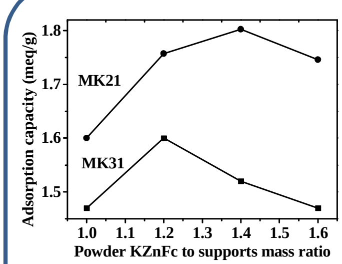

Fig. 5 Adsorption capacity of granular KZnFC adsorbents with different KZnFc-to-geopolymer mass ratios

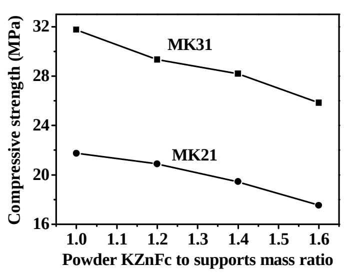

Fig. 6 Compressive strength of the bulk with different KZnFc-to-geopolymer mass ratios

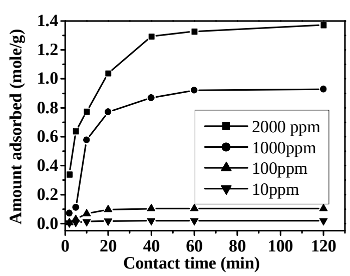

Fig. 7 Time-dependent adsorption of cesium on MK21-KC41 under various Cs concentrations

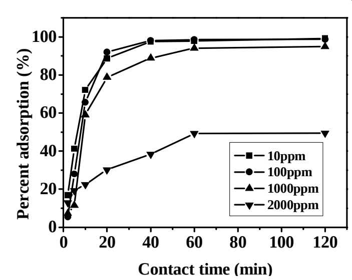

Fig. 8 Time-dependent cesium adsorption efficiency on MK21-KC41 under various Cs concentrations

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_L could be evaluated (0.99). The R_L value ($0<R_L<1$) 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.

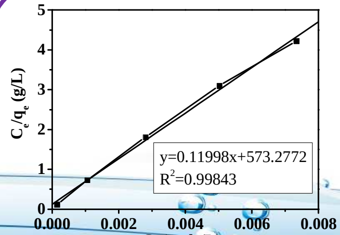

Fig. 9 Langmuir adsorption isothermal or cesium ions adsorption on the MK21-KC41

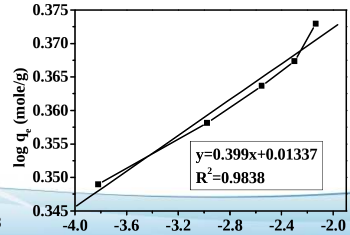

Fig. 10 Freunchlich adsorption isothermal or cesium ions adsorption on the MK21-KC41

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, the optimal KZnFC-to-geopolymer ratio in achieving maximum adsorption capacity was 1.8 for MK21-KC41, and 1.6 for MK31-KC21.