Supplementary materials

Synthesis of semicoke-based geopolymer as a delivery vehicle for slow release of herbicide

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1. Test of water absorption

1.00 g of MCPA@MSC-GP/SA were immersed entirely in 250 mL of distilled water at room temperature and allowed to reach the swelling equilibrium. Then, swollen samples were filtered through a 100-mesh nylon cloth and suspended for 10 min until there was no free water on the surface. The water absorption rate (WH%) of the samples were calculated according to Eq. 1:

$$WH\ (\%) = (W_1 - W_o)/W_o \times 100\% \quad (1)$$

Where WH% (g/g) is the water absorbency per gram of dried sample and Wo (g) and W_1 (g) are the weights of the dry and the swollen samples, respectively.

2. Test of water retention performance

0.5 g of samples and 35 g of dry soil were fully mixed and placed in PVC pipe (height 15 cm * diameter 4.5 cm) and weighed (W_0). Then, the mixtures were drenched with distilled water until water no longer seeped out the bottom, and the PVC pipe was weighed (W1). PVC pipe was incubated at room temperature and weighed every 3 days (W_i) for 30 days (Relative humidity at room temperature was 30%-50%). The sample water retention rate (WR%) was calculated according to Eq 2. Then, 40 mL of distilled water was slowly dripped into the beaker and weighed (W1). When no more water seeped out the bottom, the tube was weighed and marked as W2.

$$WR\ (\%) = (W_i - W_o)/(W_1 - W_o) \times 100\% \quad (2)$$

3. Measurement for regulation of soil acidity

In order to study the effect of pH on water absorption of samples, simulated soil solutions with different pH value were prepared. 200 g of dry soi was soaked in 1.0 L of water left to settle for 24 h, pouring out the supernatant and filtering, then simulated soil solutions with different pH values (4, 5, 6, 7, 8, 9, 10) were adjusted with 0.1 mol/L HCl and NaOH. An amount of samples were added in 50 mL simulated soil solutions with different pH values. Being soaked for 90 min, the swollen water-absorbing agent was filtered. The pH value of the filtrate was measured as reported method [1].

4. Swelling capacity and kinetics

The measurement of the swelling kinetics was carried out as following steps: 1.0 g of MCPA@MSC-GP/SA was put in nylon bags, and immersed in water. At planned intervals (1, 3, 5, 10, 15, 20, 30, 45, 60, 90, 120, 180 and 240 min), the bag was quickly taken out of water and weighed, and the water absorbency (Qt, g/g) of the sample at time t were calculated as Eq. 3. Schott's second-order swelling kinetics model was used to study the swelling kinetics [2].

$$\frac{t}{Q_t} = \frac{1}{K_{is}} + \frac{1}{Q_m}t \tag{3}$$

In the formula, Qt (g/g) and Qm (g/g) respectively represent the swelling capacity and theoretical equilibrium water absorption at particula time t(s), and Kis (g/gs) is the initial expansion rate constant.

5. Degradation efficiency

The degradation performance of slow-release herbicide in the soil is determined by measuring the quality difference at different times as reported method [3]. 0.5 g of samples (M_0) was placed in the soil at room temperature and 40% relative humidity. Being kept a certain period of time, the samples residues were taken out, dried and weighed (denoted as M_i). The degree of degradation (Dd%) was calculated as Eq. 4:

$$Dd\ (\%) = (M_0\text{-}M_i) \times 100 / M_0 \tag{4}$$

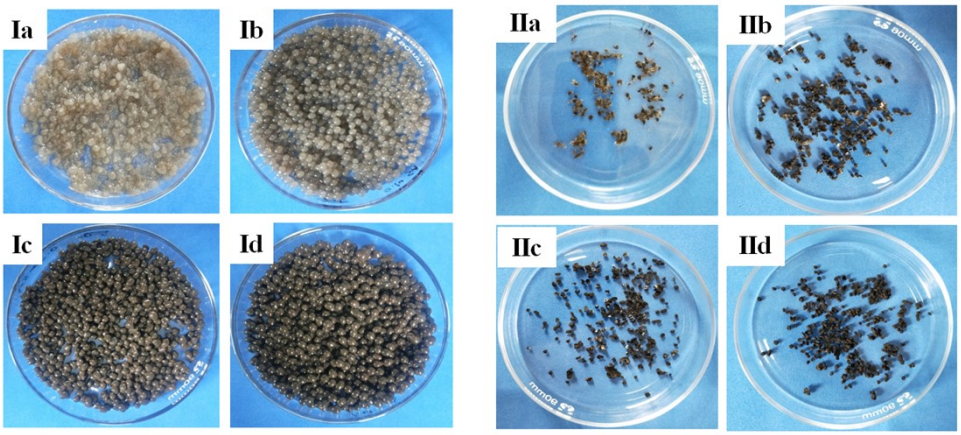

Fig. S1 Magnetic MCPA@MSC-GP/SA gel beads of different mass of SC-GP before (I) and after drying (II) :0.05 g MSC-GP (a); 0.10 g MSC-GP (b); 0.50 g MSC-GP (c); 1.0 g MSC-GP (d)

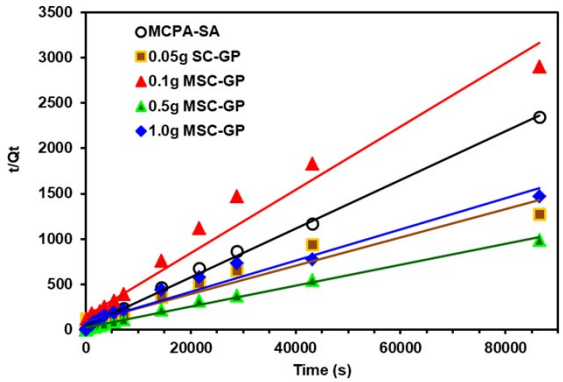

Fig. S2 Swelling kinetics of MCPA@MSC-GP/SA with different contents of MSCGP in NaCl solution

Table S1 Parameters of swelling kinetics

No	Swelling media	K_{is}	Q_m	R^2
1	MCPA-SA	0.0269	38.811	0.9979
2	0.05 MSC-GP	0.0156	82.367	0.9509
3	0.10 MSC-GP	0.0349	148.72	0.9693
4	0.50 MSC-GP	0.0115	24.584	0.9946
5	1.00 MSC-GP	0.0172	75.431	0.9642

Tab. S2 pH value of water with adding MCPA@MSC-GP/SA

No	MCPA@MSC-GP/SA (g)	Content of MSC-GP (g)	pH value
1	0.10	0.05	6.11
2	0.10	0.10	6.22
3	0.10	0.50	6.22
4	0.10	1.00	6.41

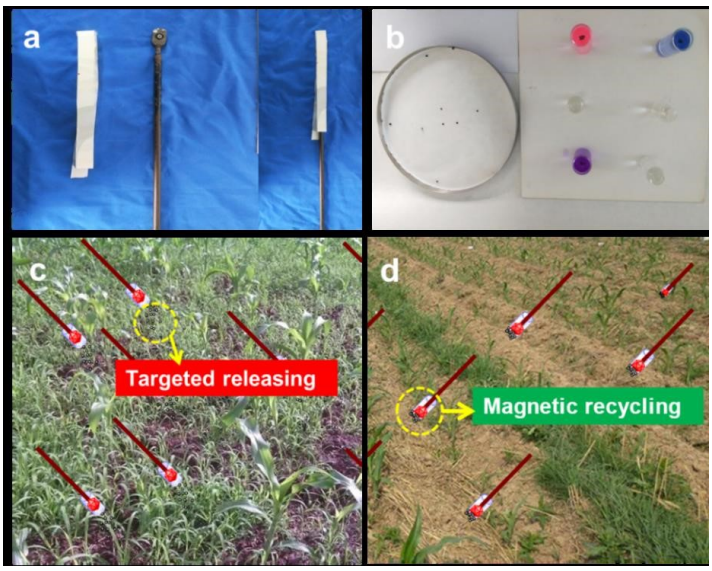

Fig. S3. Simulation of targeted release and recovery of MCPA@MSC-GP/SA

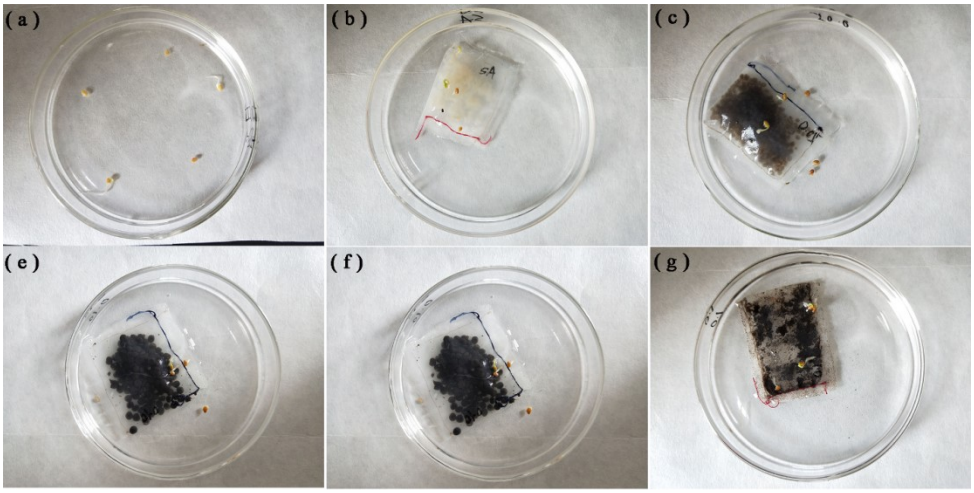

Fig. S4 Seed germination of clover weeds within MCPA@MSC-GP/SA. (a) Blank; (b) MCPA@SA; (c~d) MCPA@MSC-GP/SA with different amount of SC-GP (0.05 g, 0.1 g, 0.5 g, 1.0 g).

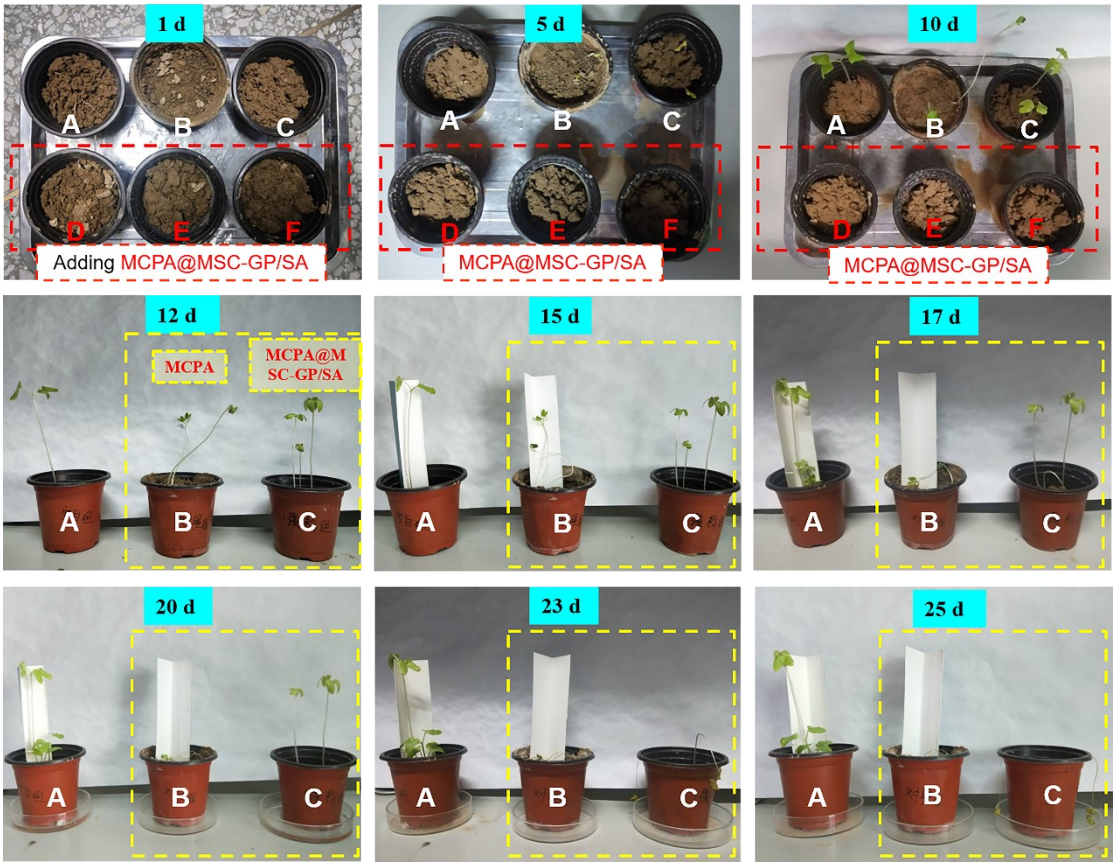

Fig. S5 Effects of slow-release herbicidal on the growth process of morning glory plants (the red frame line in D, E, and F is the group added with MCPA@MSC-GP/SA; the unframed line in A, B, and C is the blank group; in the graphs of the plants growing to 12 d-25 d, A is control, B is the MCPA group, and C is the MCPA@MSC-GP/SA composite.)

Video S1 Simulation of targeted release and recovery of MCPA@MSC-GP/SA

Refenences

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[2] T. Zhou, Y. Wang, S. Huang. Synthesis composite hydrogels from inorganic-organic hybrids based on leftover rice for environment-friendly controlled-release urea fertilizers. Sci Total Environ 615 (2018) 422-430.

[3] Mohammad Bagheri Z, Rahmati A, Hoshyarmanesh P. Synthesis of a novel superabsorbent with slow-release urea fertilizer using modified cellulose as a grafting agent and flexible copolymer. International Journal of Biological Macromolecules, 182 (2021) 1893-1905.