Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information (SI) on

Carboxymethyl cellulose modified magnetic bentonite composite for efficient enrichment of radionuclides

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1. Models of adsorption kinetics

The kinetic results were modeled by the pseudo-first-order and pseudo-second-order rate equations, showing as follows:[1]

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303}t \tag{1}$$

$$\frac{t}{Q_t} = \frac{1}{2K'Q_e^2} + \frac{t}{Q_e} \tag{2}$$

where Q_e (mg·g^{-1}) and Q_t (mg·g^{-1}) are the amount of radionuclides enriched at equilibrium and specific time t (h). k_1 (h^{-1}) and K' (g·mg^{-1}·h^{-1}) are the kinetic rate constants of two equations, respectively.

2. Langmuir and Freundlich isotherm models

Langmuir adsorption isotherm model assumes that the adsorbent surfaces provide homogeneous binding sites and equivalent adsorption energies, and there is no interaction between adsorbed species.[2] It is always applied to describe monolayer adsorption behavior in different systems, and can be expressed in the following form:

$$\frac{C_e}{Q_s} = \frac{1}{K_L Q_{s,\max}} + \frac{C_e}{Q_{s,\max}} \tag{3}$$

where Q_s (mg·g^{-1}) is the amount of enriched radionuclides on CMC-*g*-MB composite, $Q_{s,max}$ (mg·g^{-1}) is the maximum of enriched radionuclides per unit weight of CMC-*g*-MB composite on the complete monolayer coverage, K_L (L·mg^{-1}) is the Langmuir adsorption coefficient implying adsorption enthalpy and varies with temperatures.

As an empirical equation, Freundlich isotherm model is based on the adsorption behavior occurred on heterogeneous surfaces, and is expressed by Eq. (4):

$$log\ Q_s = log\ K_F + \frac{1}{n} log\ C_e \tag{4}$$

where K_F (mg^{1-n}·L^n·g^{-1}) is the Freundlich adsorption coefficient correlated with adsorption capacity and $1/n$ is an index of isotherm non-linearity correlated with to the adsorption intensity at specific temperatures.[3]

3. Adsorption thermodynamics

The adsorption amounts of Cs(I), Sr(II) and Co(II) on CMC-*g*-MB composite increase as the temperature increases from 298 K to 338 K. Thermodynamic parameters including average standard enthalpy change (ΔH^0), standard entropy change (ΔS^0) and standard Gibbs free energy change (ΔG^0) of radionuclide adsorption on CMC-*g*-MB composite are calculated from the temperature-dependent adsorption isotherms. ΔG^0 is expressed as the following function:

$$\Delta G^0 = -\mathrm{RT} \ln K^0 \tag{5}$$

where R is the ideal gas constant (8.314 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$), K^0 is the adsorption equilibrium constant standing for the adsorption abilities of CMC-*g*-MB composite towards radionuclides. The values of $\ln K^0$ can be obtained by plotting $\ln K_d$ versus C_e for radionuclide adsorption and then extrapolating C_e to zero (Fig. S5).

ΔH^0 and ΔS^0 can be achieved the slope and intercept of the plots of $\ln K^0$ versus $1/T$ by Eq. (6):

$$\Delta S^0 = -\left(\frac{\partial G^0}{\partial T}\right)_P \tag{6}$$

$$\ln K^0 = \frac{\Delta S^0}{\mathrm{R}} - \frac{\Delta H^0}{\mathrm{RT}} \tag{7}$$

Linear plots of $\ln K^0$ versus $1/T$ for Cs(I), Sr(II) and Co(II) adsorption on CMC-*g*-MB composite are shown in Fig. S5D.

Table S1. Parameters for kinetic models.

Model	Parameters	Cs(I)	Sr(II)	Co(II)
Pseudo first order	k_1 (h^{-1})	0.217	0.220	0.215
	Q_e ($mg \cdot g^{-1}$)	74.6	59.2	38.9
	R^2	0.948	0.946	0.953
Pseudo second order	K' ($g \cdot mg^{-1} \cdot h^{-1}$)	0.016	0.012	0.031
	Q_e ($mg \cdot g^{-1}$)	79.7	62.5	40.2
	R^2	0.999	0.999	0.999
	$Q_{e,exp}$[a)] ($mg \cdot g^{-1}$)	80.5	63.0	41.1

[a)] $Q_{e,exp}$ is the experimental value of adsorption capacity.

Table S2. Parameters simulated from Langmuir and Freundlich models.

Experimental conditions		Langmuir model			Freundlich model		
		$Q_{s,max}$ ($mg \cdot L^{-1}$)	K_L ($L \cdot mg^{-1}$)	R^2	K_F ($mg^{1-n} \cdot L^n \cdot g^{-1}$)	1/n	R^2
CMC-*g*-MB							
Cs(I)	298 K	80.5	0.468	0.996	29.9	0.319	0.899
	318 K	87.7	0.497	0.995	33.0	0.321	0.929
	338 K	96.7	0.508	0.998	36.4	0.333	0.966
Sr(II)	298 K	63.0	0.299	0.995	19.9	0.336	0.936
	318 K	71.2	0.285	0.996	21.3	0.359	0.945
	338 K	81.4	0.302	0.999	24.5	0.370	0.948
Co(II)	298 K	41.1	0.373	0.991	16.1	0.271	0.910
	318 K	49.7	0.327	0.994	17.3	0.302	0.948
	338 K	64.8	0.272	0.996	19.9	0.343	0.963
MB							
Cs(I)	298 K	48.5	0.250	0.991	13.7	0.368	0.904
Sr(II)	298 K	39.5	0.070	0.996	5.60	0.483	0.957
Co(II)	298 K	26.3	0.065	0.986	3.37	0.505	0.930

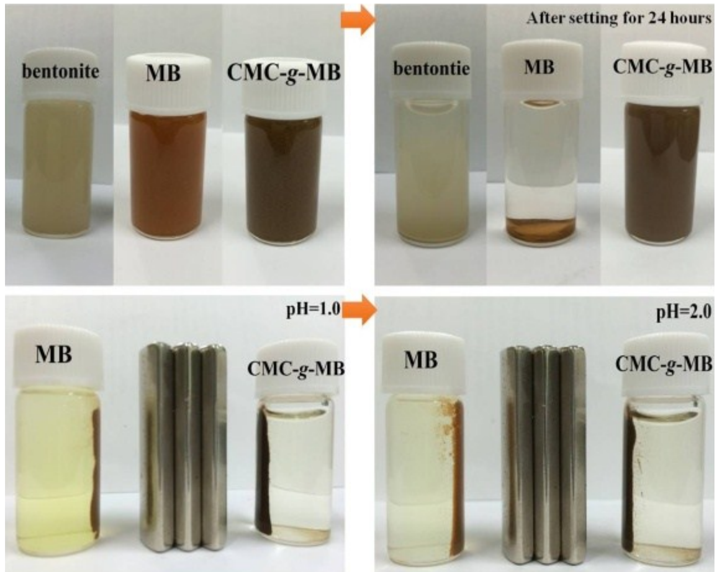

Fig. S1. Dispersion images of bentonite, MB and CMC-*g*-MB composite (settling for 24 hours), and stability evaluation of MB and CMC-*g*-MB composite in acid conditions.

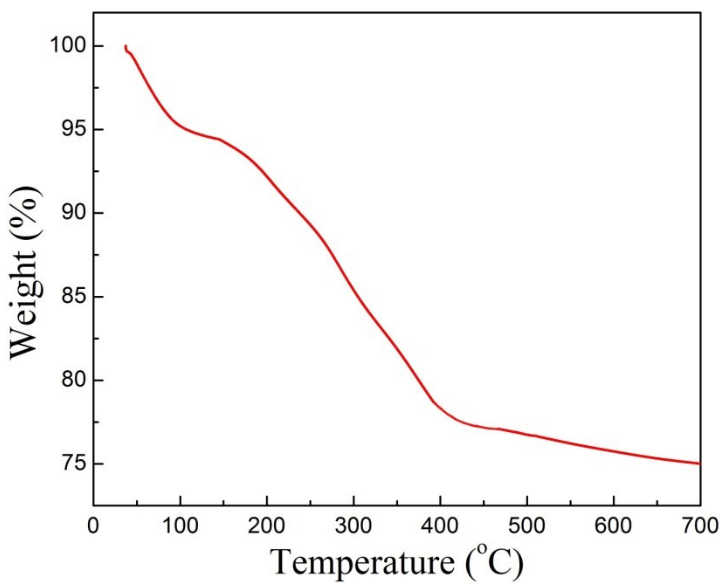

Fig. S2. Typical TGA curve of CMC-*g*-MB composite.

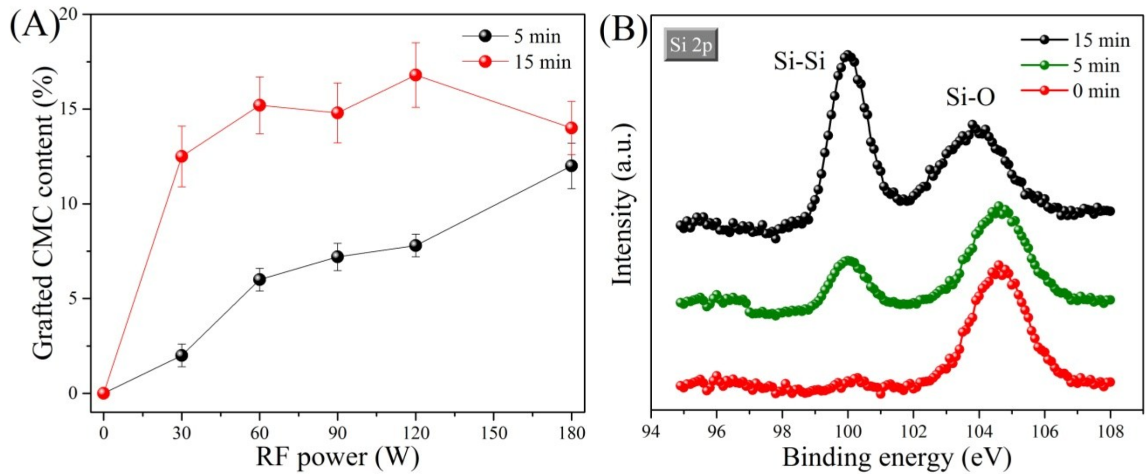

Fig. S3. Influences of RF power and time on the CMC grafting content (A); XPS Si 2p spectra of CMC-*g*-MB composite treated with different duration times of RF plasma (B).

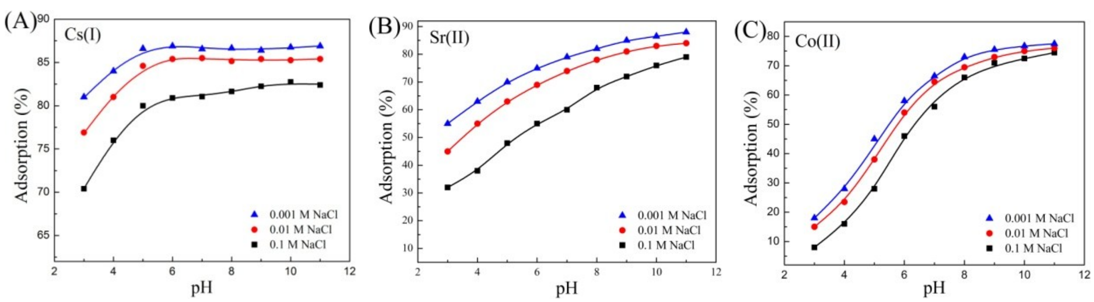

Fig. S4. Effect of pH on Cs(I), Sr(II) and Co(II) adsorption with different ionic strengths. $m/V = 0.5$ g·L^{-1}, $T = 298$ K, $C_{initial} = 20$ mg·L^{-1} for all cations.

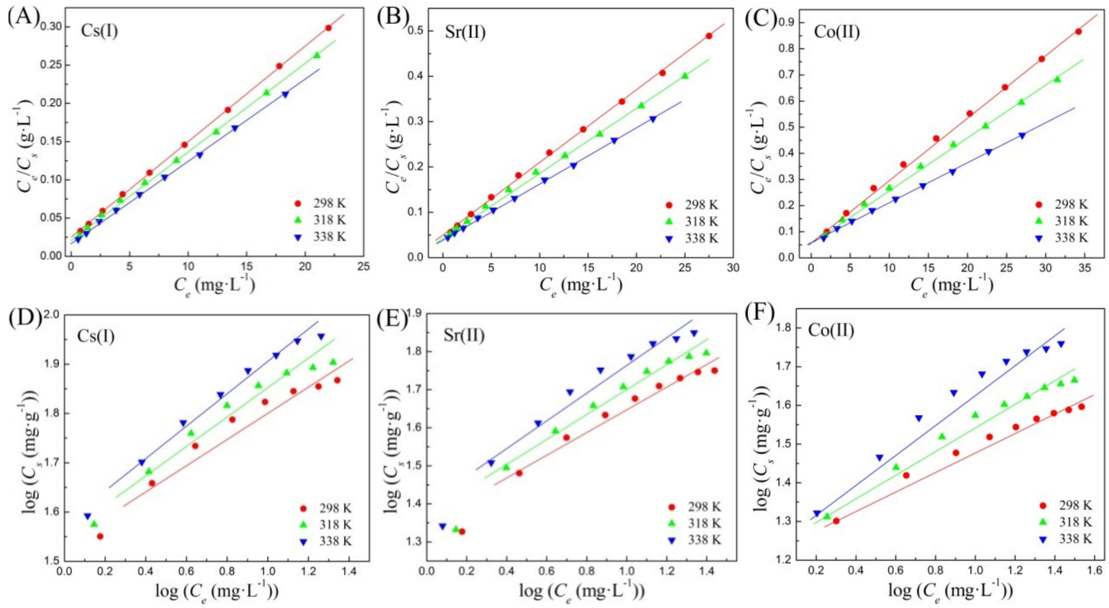

Fig. S5. Langmuir isotherms of Cs(I) (A), Sr(II) (B), Co(II) (C) and Freundlich isotherms of Cs(I) (D), Sr(II) (E), Co(II) (F) adsorption on CMC-*g*-MB composite at different temperatures, $pH = 6.0 \pm 0.1$, $m/V = 0.5$ g·L^{-1}, $I = 0.01$ M NaCl.

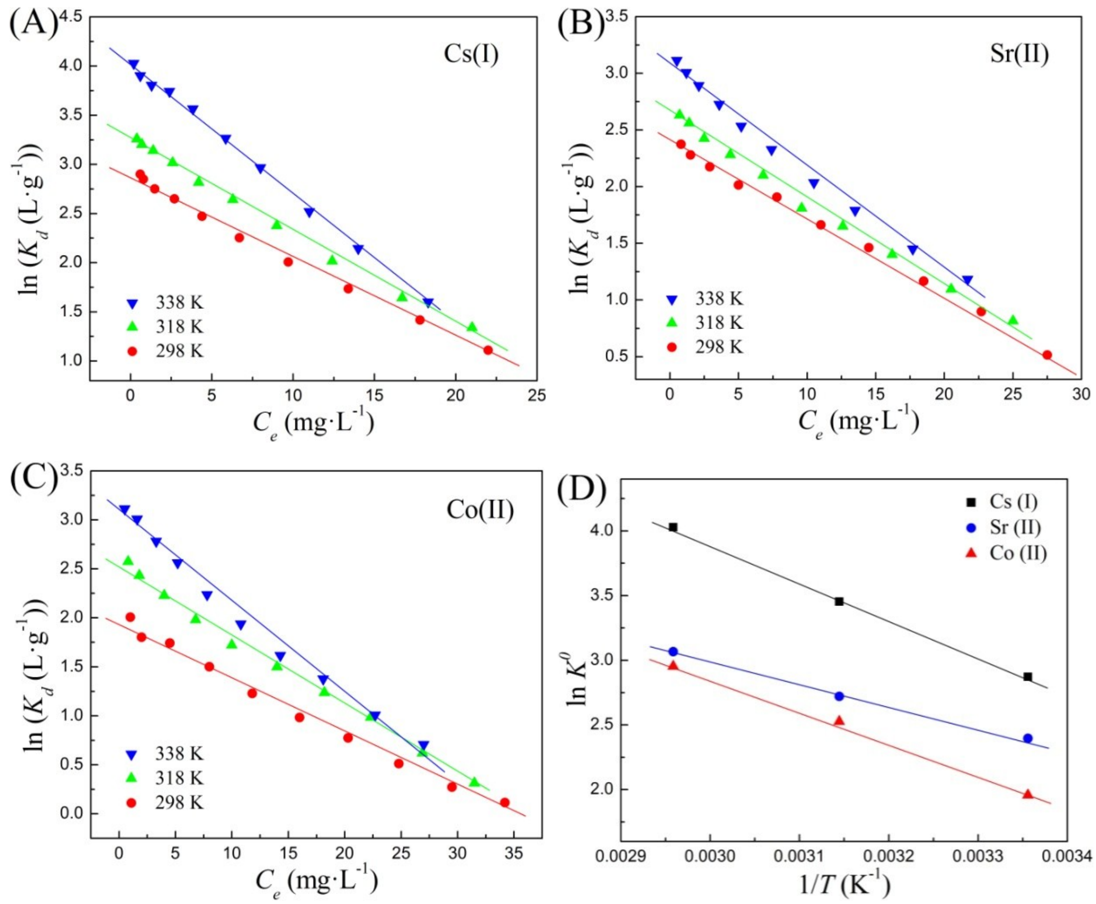

Fig. S6. Linear plots of lnK_d versus C_e for the adsorption of Cs(I) (A), Sr(II) (B) and Co(II) (C). Linear plots of lnK^0 versus 1/T for the radionuclide adsorption (D). pH = 6.0 ± 0.1, m/V = 0.5 g·L^{-1}, I = 0.01 M NaCl.

References

1. Y. S. Ho and G. McKay, *Process Biochem.*, 1999, **34**, 451–465.

2. C. H. Wu, *J. Hazard. Mater.*, 2007, **144**, 93–100.

3. F. A. Digiano, G. Baldauf, B. Frick and H. *Sontheimer, Chem. Eng. Sci.*, 1978, **33**, 1667–1673.