Electronic Supplementary Information

Polyethyleneimine modified eggshell membrane as a novel biosorbent for adsorption and detoxification of Cr(VI) from water

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Experimental section

Material

All the needed chemicals were of analytical grade and were purchased from the Chongqing Chemical Reagents Company (Chongqing, China). All the solutions were prepared with ultra pure water. A branched polyethyleneimine (PEI, molecular weight of 25,000) was purchased from Sigma–Aldrich. The solution pH was adjusted using diluted HCl and NaOH solutions. Fresh eggs were purchased from the canteen of Southwest University, and the ESM was obtained easily from the eggshells. Firstly, the ESM was immersed in the 0.5 M nitric acid solution for 30 min in order to remove the residual impurities, and then it was washed with adequate ultra pure water. In succession, the ESM was dried at 80°C and cut into a small piece (about 0.5×0.5 mm) by scissors.

Note that 0.5 M nitric acid solution was used to remove the residual impurities in this work. Although nitric acid is a strong oxidant, the amino groups in ESM in 0.5 M nitric acid solution remain unchanged after the pretreatment. This is attributed to the property of the amino groups. The surface of ESM is generally covered with amino groups. The amino groups belong to basic groups. So, under strong acidic conditions, amino groups were very easily protonated to form the positively charged sites, for example $-NH_3^+$. As soon as $-NH_3^+$ was formed, it is very hard for nitric acid as a strong oxidant to oxidize amino groups. This was confirmed by the results of FT-IR spectra. The following Figure shows the FT-IR spectra of the ESM treated with and without nitric acid. As can be seen, the spectra of the ESM are almost the same as those of the ESM treated with nitric acid. The presence of amines and amides in the ESM and nitric acid treated ESM were found in the this Figure, exhibiting significant peaks at 3300-3500 cm^{-1} (attributed to N-H stretching mode), 1631 cm^{-1} (attributed to N-H bending mode), and 1350-1410 cm^{-1} (attributed to C-N stretching mode). Above results demonstrate that the amino groups of ESM remain unchanged after the pretreatment with nitric acid.

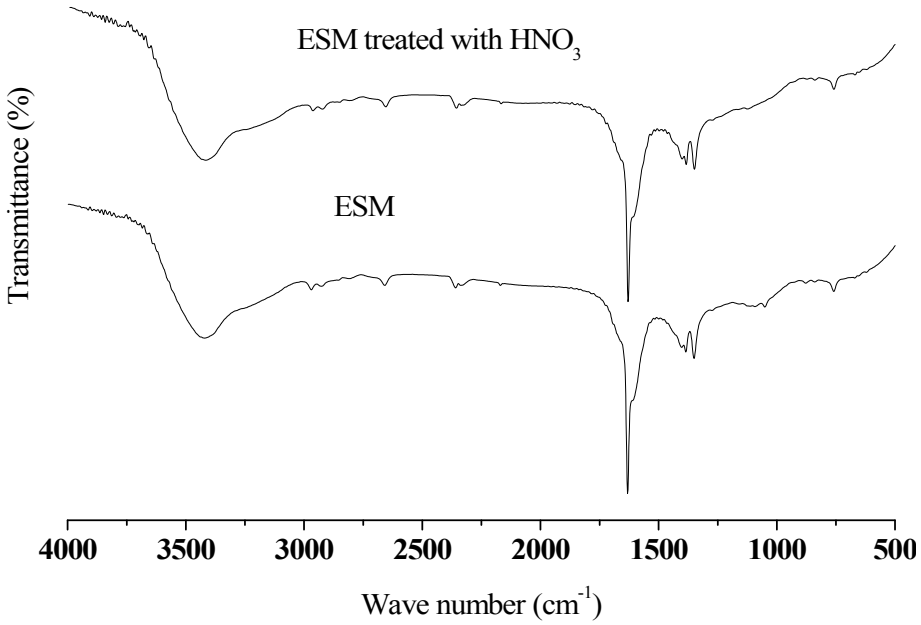

Table S1. The main pore properties of the adsorbents

Biosorbent	Average pore diameter (Å)	Total pore volume (cm^3/g)
ESM	1219.8	1.798E-02
PEI-ESM-10	1042.8	1.377E-02
PEI-ESM-20	1039.6	6.434E-03
PEI-ESM-30	1030.8	3.478E-03
PEI-ESM-40	991.6	3.50E-03

Table S2. The results of element analysis of ESM and PEI modified ESM.

Biosorbent	N%	C%	H%
ESM	14.26	46.18	6.00
PEI-ESM-10	14.34	43.56	7.04
PEI-ESM-20	14.4	43.57	6.87
PEI-ESM-30	14.74	43.20	6.91
PEI-ESM-40	14.84	43.06	6.94

Table S3. The tensile strength and breaking elongation of the adsorbents

Adsorbent	Breaking elongation (%)	Tensile strength (MPa)
ESM	3.26	4.79
ESM-PEI-10	5.80	6.21
ESM-PEI-20	5.69	6.42
ESM-PEI-30	5.28	6.41
ESM-PEI-40	5.27	6.31

Table S4. Comparison of the Langmuir, Freundlich adsorption constants.

Sorbent	Langmuir model			Freundlich model		
	b (L.mg^{-1})	q_{max} (mg.g^{-1})	R^2	n	k	R^2
ESM	0.04	102.00	0.9934	1.82	7.77	0.9483
PEI-ESM-10	0.47	123.46	0.9783	3.22	49.1	0.8730
PEI-ESM-20	0.33	161.29	0.9577	2.28	47.29	0.8734
PEI-ESM-30	0.42	116.28	0.9923	3.00	43.08	0.9177
PEI-ESM-40	0.41	100.00	0.9949	3.89	41.85	0.9033

Table S5. Comparison of the pseudo-first-order, pseudo-second-order adsorption constants.

Sorbent	Pseudo-first-order				Pseudo-second-order		
	q_e * (mg g^{-1})	q_e ** (mgg^{-1})	k_1 (min^{-1})	R^2	q_e ** (mg g^{-1})	v_0 (mg.g^{-1}.min^{-1})	R^2
ESM	48.56	7.89	0.0049	0.8145	47.62	9.87	0.9991
PEI-ESM-10	92.63	28.43	0.0027	0.949	92.59	3.61	0.9992
PEI-ESM-20	97.47	22.06	0.0035	0.8685	96.15	8.8	0.9999
PEI-ESM-30	91.8	16.73	0.0029	0.8407	89.29	10.83	0.9999
PEI-ESM-40	82.98	14.19	0.0022	0.7585	79.37	11.93	0.9999

* experimental; ** calculated

Table S6. Adsorption capacities of various adsorbents for Cr(VI).

Adsorbent	q_{max} (mg/g)	Reference
Surface modified sand	6.24[a]	[1]
Fruits of gular	7.94[b]	[2]
Fe@Fe_2O_3 nanowires	7.78[b]	[3]
Elaeagnus tree leaves	10.94[a]	[4]
Amino starch	12.12[a]	[5]
PEI modified activated carbon	20.05[a]	[6]
Staphylococcus aureus	27.36[a]	[7]
Mesoporous TiO_2	33.9[a]	[8]
Tea and coffee dusts	44.9[a]	[9]
P4VP modified activated carbon	53.7[a]	[10]
Ethylenediamine functionalized Fe_3O_4	61.35[a]	[11]
Strongly Basic Anion Exchange Resins	130[b]	[12]
PEI modified eggshell membrane	161.29[a]	This work

a. Calculated from adsorption isotherm, b. Calculated from kinetics equation

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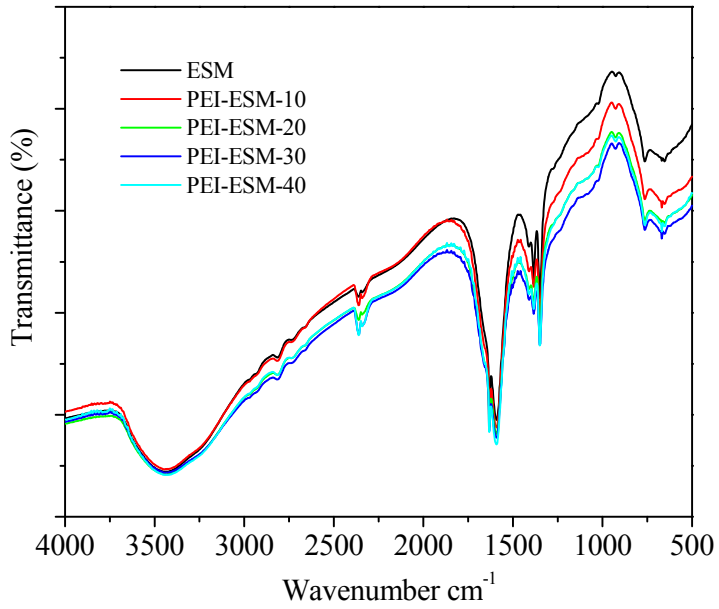

Figure S1. FT-IR spectra of ESM and PEI modified ESM adsorbents.

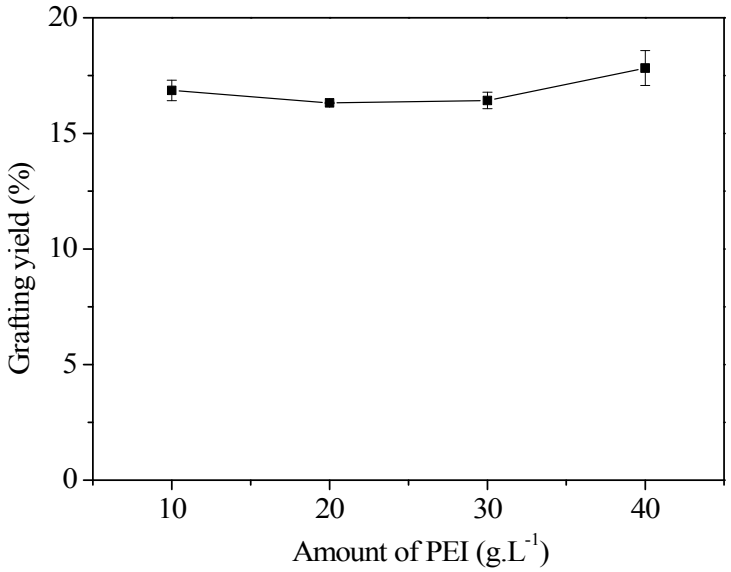

Figure S2. Effect of PEI amount on grafting yield. Experimental conditions: 4 g ESM, 200 mL 1% (w/v) glutaraldehyde, reaction time of 30 min.

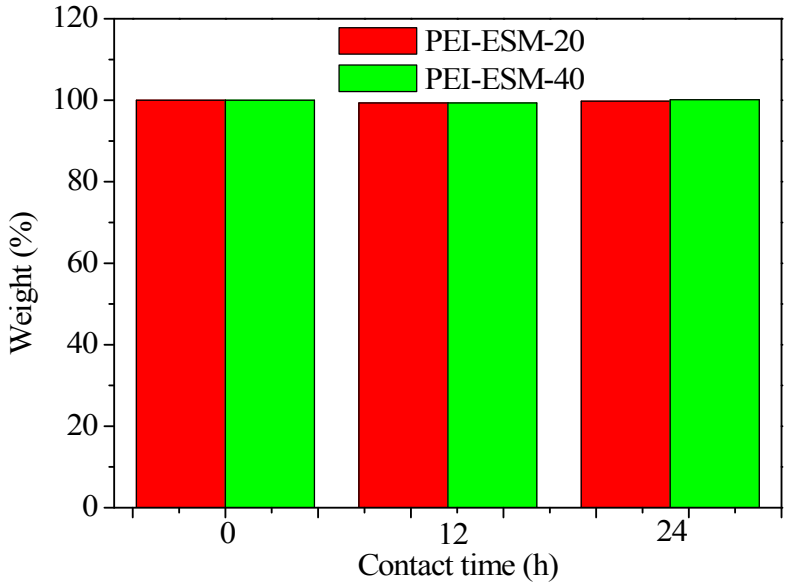

Figure S3. Effect of contact time on weight of the PEI-ESM-20 and PEI-ESM-40 adsorbents in acidic solution (pH=3).

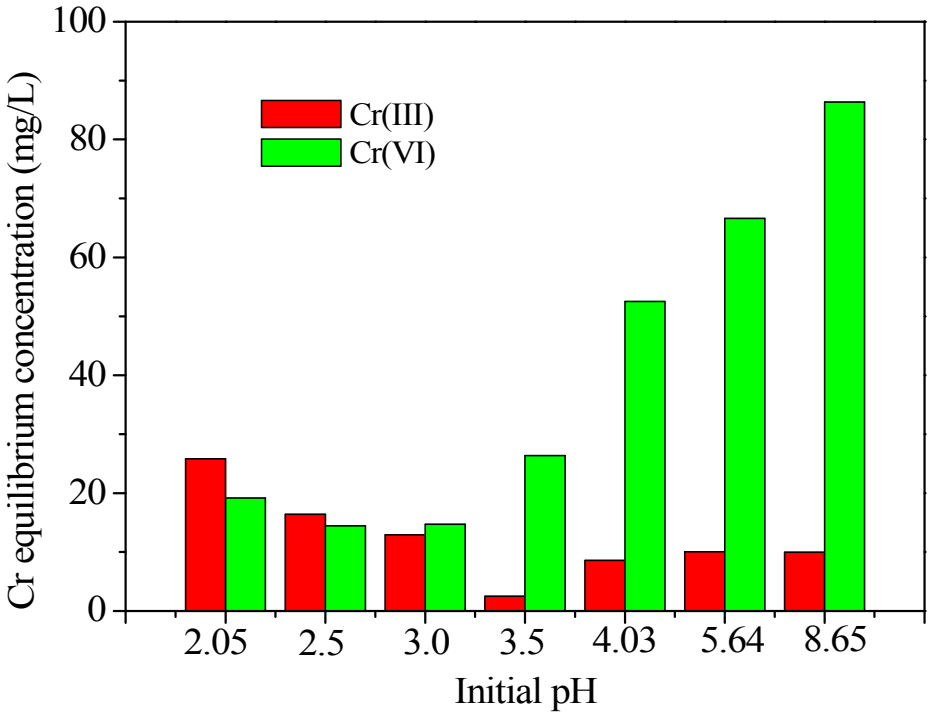

Figure S4. The equilibrium concentration of Cr(III) and Cr(VI) at different initial pH.