Electronic Supplementary Information

Polyethylenimine/grapefruit peel hybrid biosorbent for removal of toxic CdTe quantum dots from water

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Adsorption kinetics

Two kinetic models, namely pseudo-first-order (eq 1)[1] and pseudo-second-order (eq 2)[2], were used to describe the adsorption behavior.

$$\ln(q_e - q_t) = \ln q_e - kt \qquad (1)$$

$$t/q_t = 1/v_0 + t/q_e \qquad (2)$$

where q_e (mg/g) and q_t (mg/g) represent the adsorption capacity at equilibrium and at time t, k is the pseudo-first-order adsorption rate constant, and v_0 is the initial adsorption rate (mg g^{-1} h^{-1}). The regression coefficient values (R^2) and related parameters obtained from pseudo-first-order and pseudo-second-order models are shown in Table S2.

Adsorption isotherms

The isotherm data were fitted by the Langmuir (eq 3)[3] and Freundlich (eq 4)[4] isotherms according equations as follows:

$$1/q_e = 1/q_{max} + (1/q_{max}b)\,(1/C_e) \qquad (3)$$

$$\log q_e = \log k + (1/n) \log C_e \qquad (4)$$

where q_e (mg/g) and q_{max} (mg/g) are the equilibrium adsorption capacity and the maximum adsorption capacity, C_e (mg/L) is the concentration of solution at equilibrium, b is the constant related to energy of adsorption, k and n are the constants of Freundlich adsorption. The parameters of the Langmuir and Freundlich models calculated from the adsorption isotherms are listed in Table S3.

References

1. M. Najafi, Y. Yousefi, A. A. Rafati, *Sep. Purif. Technol.,* 2012, **85**, 193–205.

2. L. Wang,; X. L. Wu, W. H. Xu, X. J. Huang, J. H. Liu, A. W. Xu, *ACS App. Mater. Interfaces,* 2012, **4**, 2686–2692.
3. Z. Yu, X. Zhang, Y. Huang, *Ind. Eng. Chem. Res.*, 2013, **52**, 11956–11966.
4. J. Wang, L. Zhao, W. Duan, L. Han, Y. Chen, *Ind. Eng. Chem. Res.,* 2012, **51**, 13655–13662.

Table S1. Nitrogen content of GP and PEI-GP by the XPS analysis

Biosorbent	Nitrogen content (at. %)
GP	4.29
PEI-GP-0.8	7.13

Table S2. The relevant parameters of the pseudo-first-order and the pseudo-second-order kinetics

Adsorbents	$q_{e,exp}$ (mg g^{-1})	Pseudo-first-order			Pseudo-second-order		
		$q_{e,cal}$ (mg g^{-1})	k (h^{-1})	R^2	$q_{e,cal}$ (mg g^{-1})	v_0 (mg g^{-1} h^{-1})	R^2
PEI-GP-0.2	173.24	85.51	0.2234	0.8714	177.31	234.19	0.9991
PEI-GP-0.4	280.83	121.58	0.1634	0.8973	288.18	336.70	0.9996
PEI-GP-0.6	377.07	271.66	0.2632	0.8578	400.00	275.48	0.9971
PEI-GP-0.8	431.84	392.06	0.2338	0.9844	478.47	195.70	0.9961
PEI-GP-1.0	356.03	251.72	0.2448	0.9766	383.14	243.31	0.9970

Table S3. Freundlich isotherm and langmuir isotherm parameters for adsorption of CdTe DQs onto PEI-GP

Adsorbents	Langmuir			Freundlich		
	b (L/mg)	q_{max} (mg/g)	R^2	n	k	R^2
PEI-GP-0.2	-0.0023	-62.933	0.3998	0.552	0.006	0.9542
PEI-GP-0.4	-0.0004	-342.466	0.3409	0.707	0.104	0.9555
PEI-GP-0.6	-0.0001	-1080.66	0.1722	0.806	0.374	0.9396
PEI-GP-0.8	-0.0001	-1078.76	0.2388	0.790	0.403	0.9434
PEI-GP-1.0	-0.00009	-1546.42	0.2138	0.835	0.600	0.9713

Table S4. Concentrations of K^+, Na^+, Ca^{2+} and Mg^{2+} in the tested water samples

Water sample	K^+ (mg/L)	Na^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)
ultra pure water	not detected	not detected	not detected	not detected
tap water	2.30	11.9	56.0	12.2
wastewater	12.2	59.0	74.7	13.1

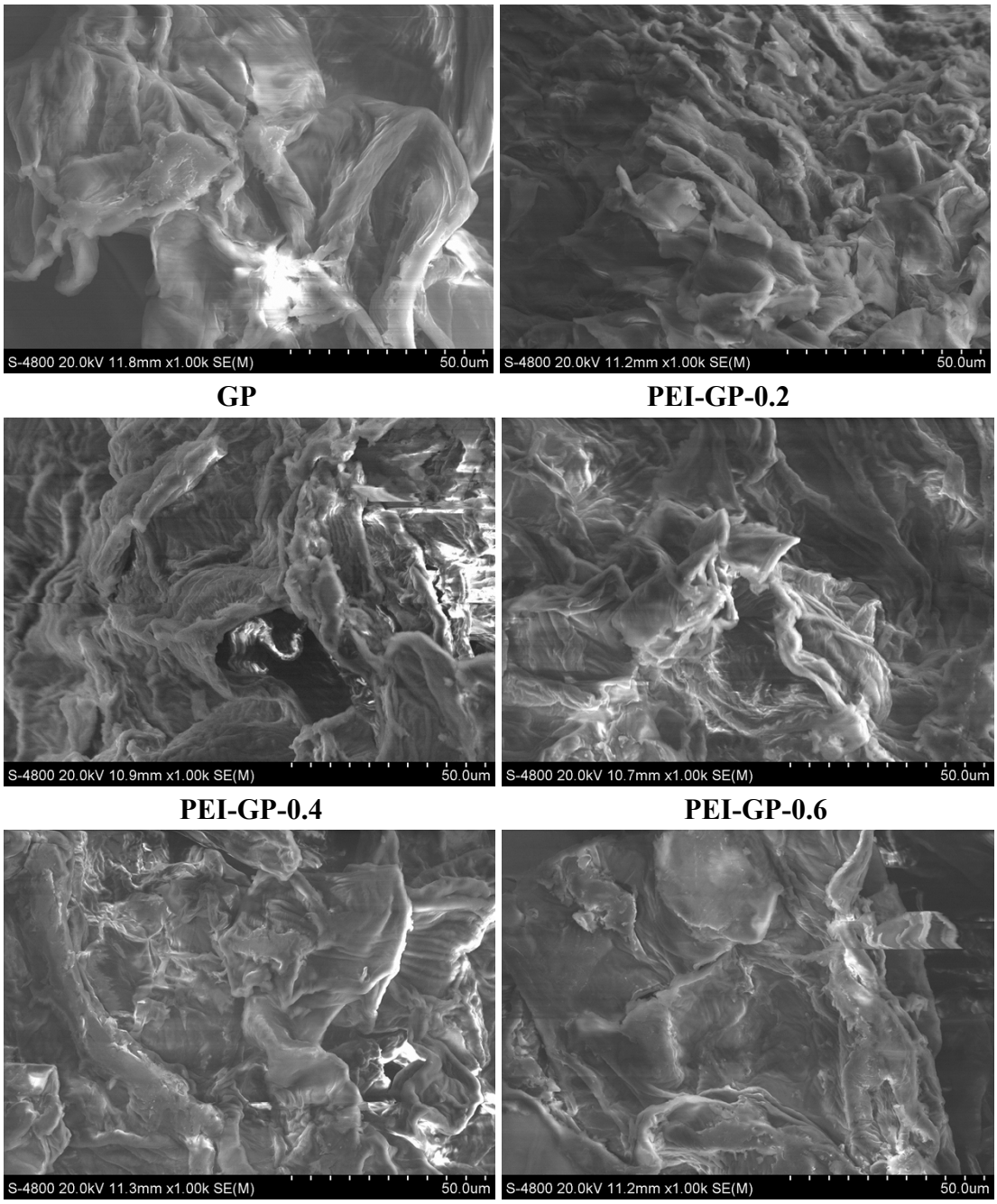


Figure S1. SEM images of GP and PEI-GP with different PEI content

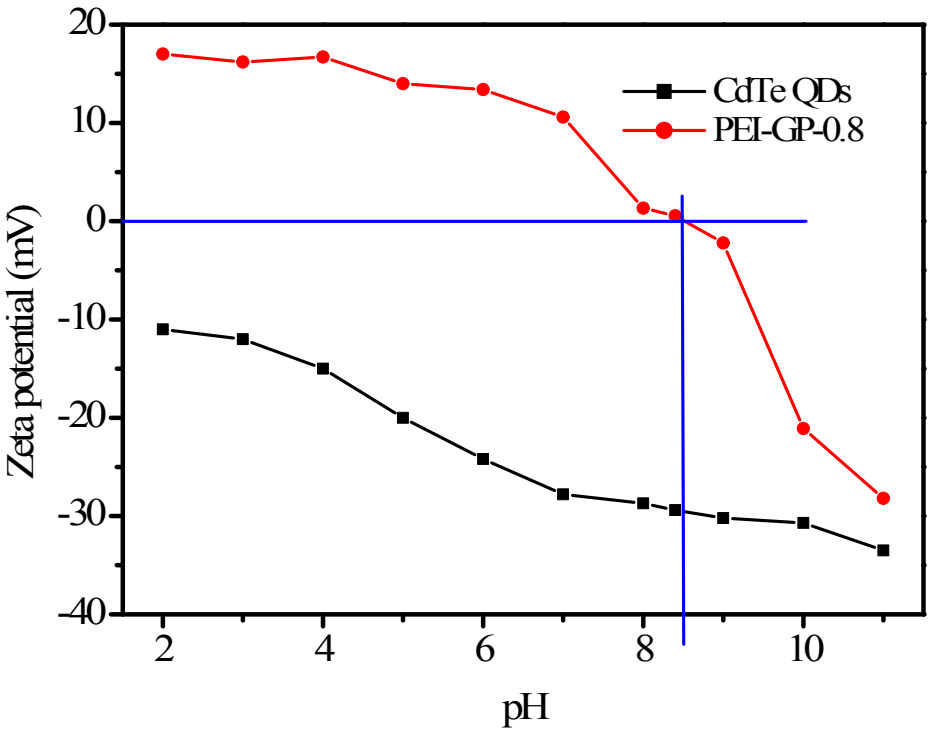


Figure S2. The effect of solution pH on the zeta potential of CdTe QDs and PEI-GP-0.8 adsorbent

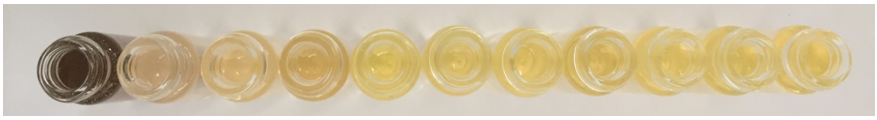
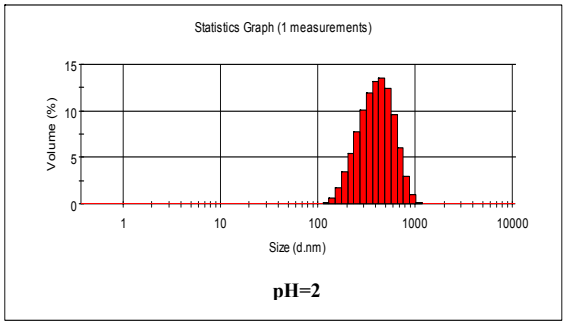
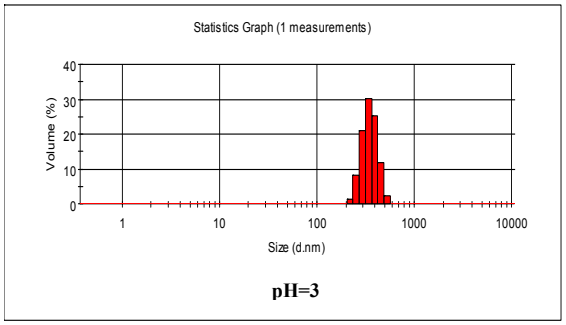


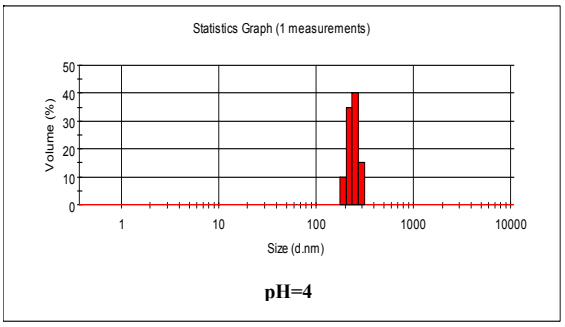
Figure S3. Images of CdTe QDs under different solution pH ranging from 2 to 11 (from *left* to *right*: 2, 3, 4, 5, 6, 7, 8, 8.4, 9, 10, and 11)



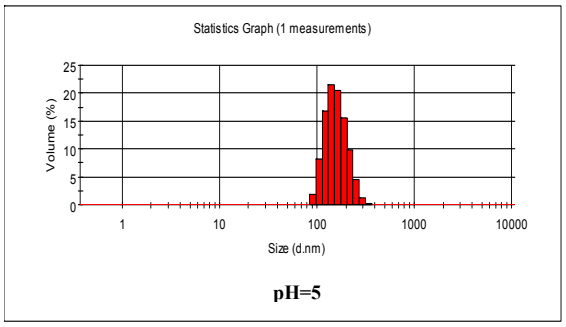
pH=2



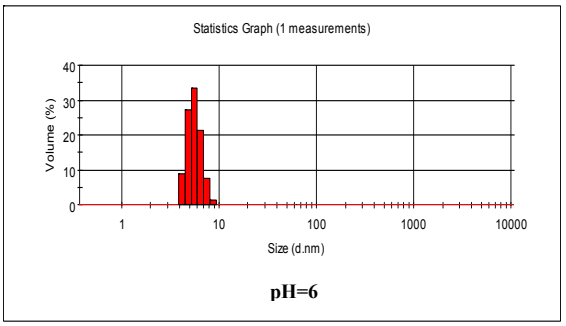
pH=3



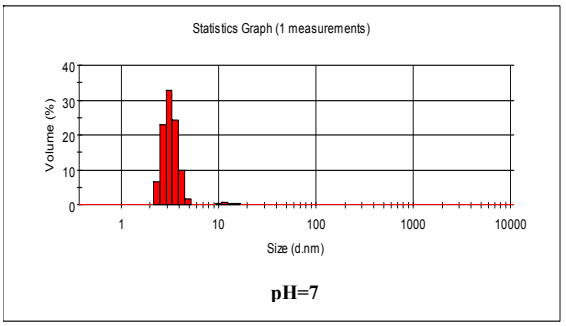
pH=4



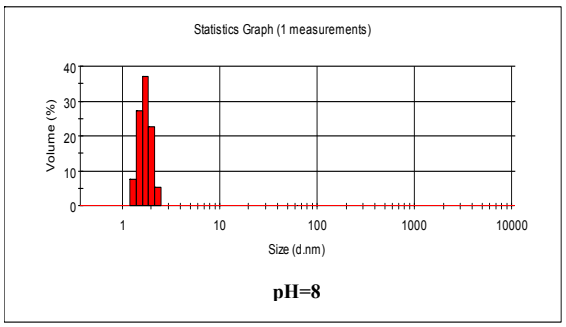
pH=5



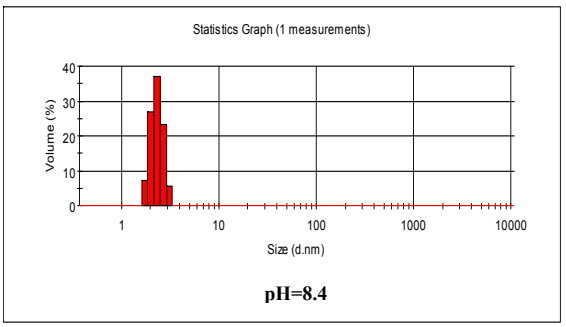
pH=6



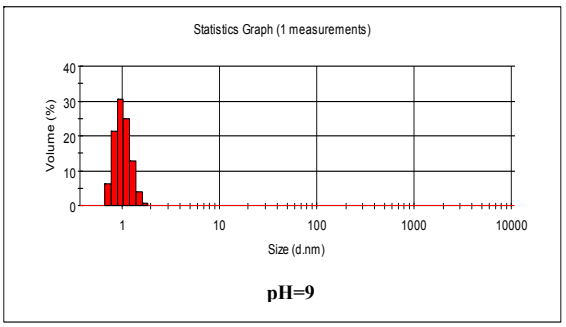
pH=7



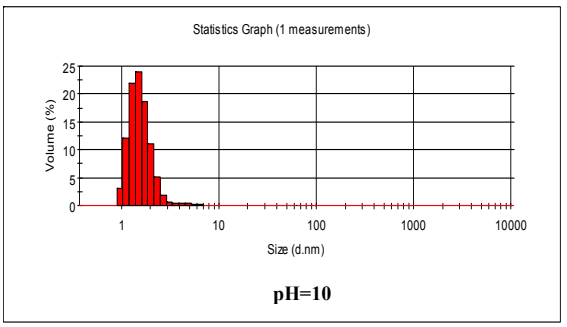
pH=8



pH=8.4



pH=9



pH=10

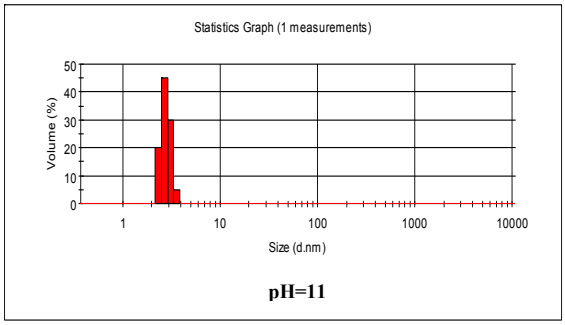


Figure S4. Hydrodynamic diameter distributions of CdTe QDs under different solution pH ranging from 2 to 11.

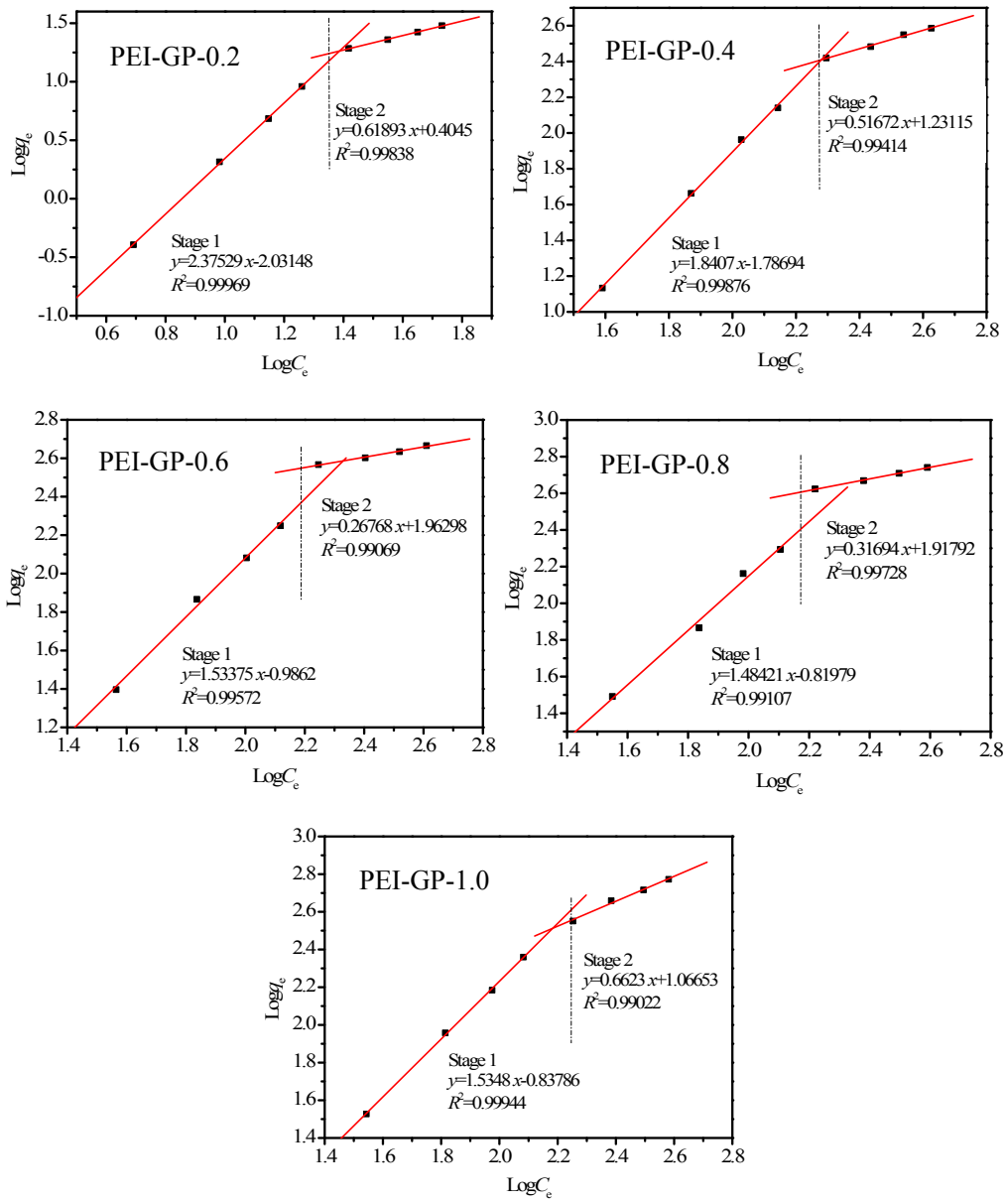


Figure S5. The absorption isotherm model of CdTe QDs onto PEI-GP adsorbents by Freundlich model fitting

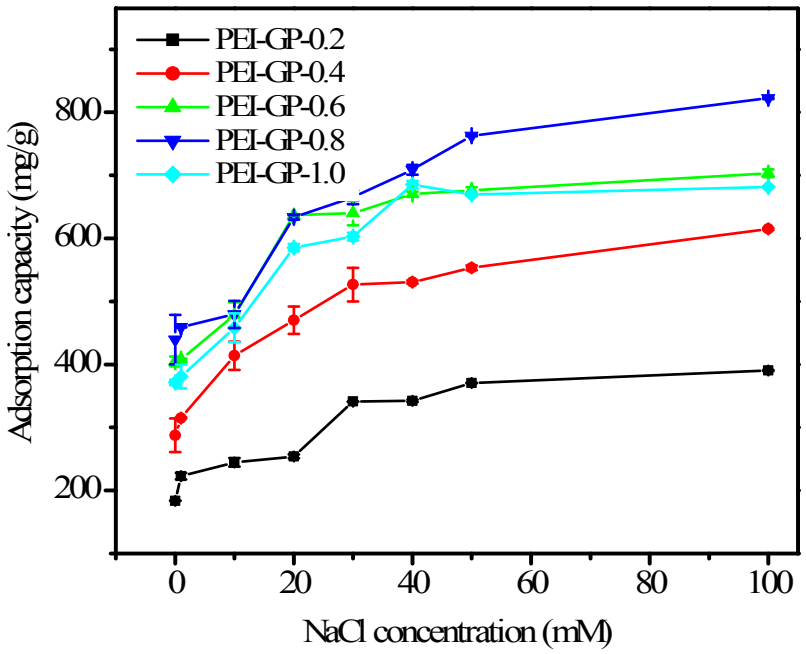


Figure S6. Effect of NaCl concentration on the adsorption of CdTe QDs onto PEI-GP

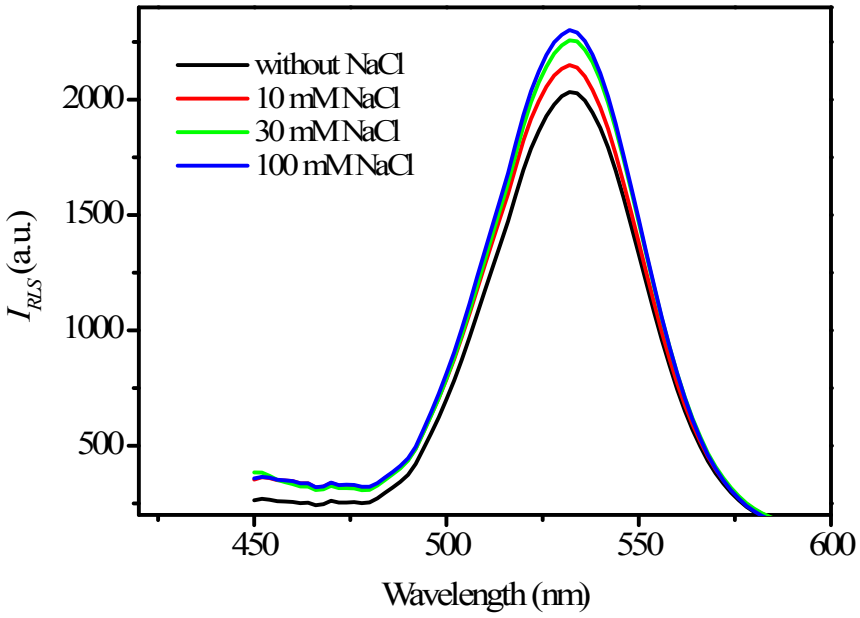
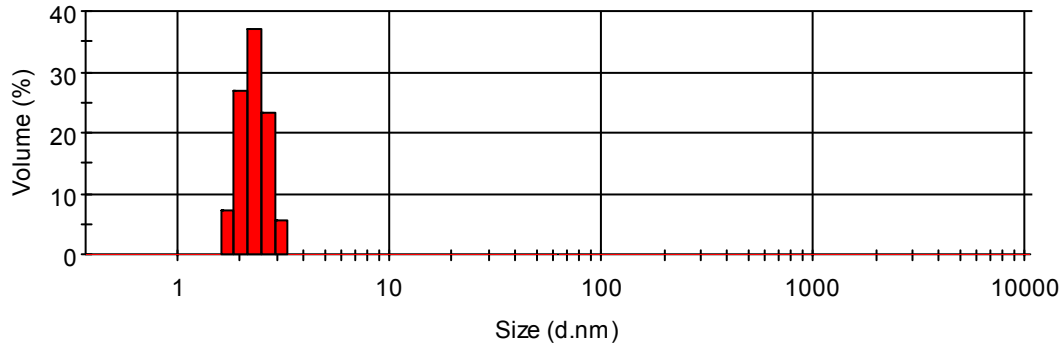
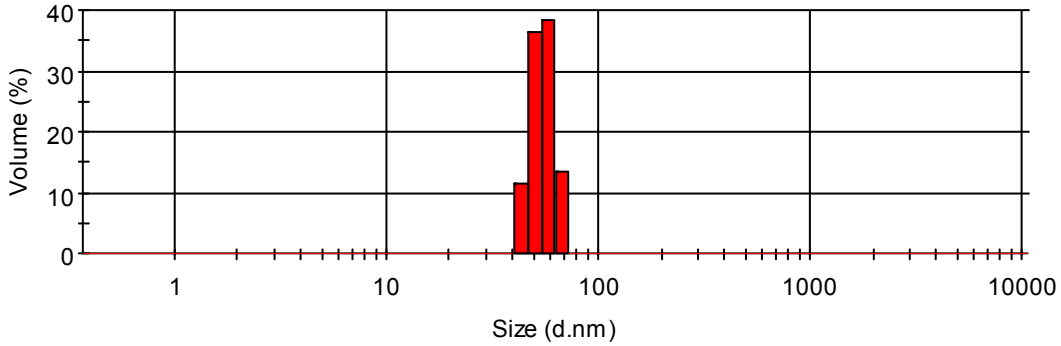


Figure S7. RLS spectra of CdTe QDs in the presence of various concentrations of NaCl.

QDs (A)



100 mM NaCl (B)



1 mM $CaCl_2$ (C)

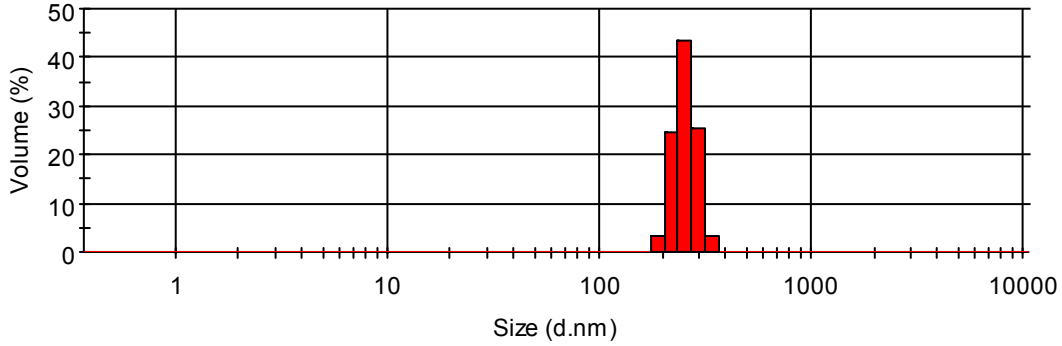


Figure S8. Hydrodynamic diameter distribution of CdTe QDs (A) in the presence of 100 mM NaCl (B) and 1 mM $CaCl_2$ (C).

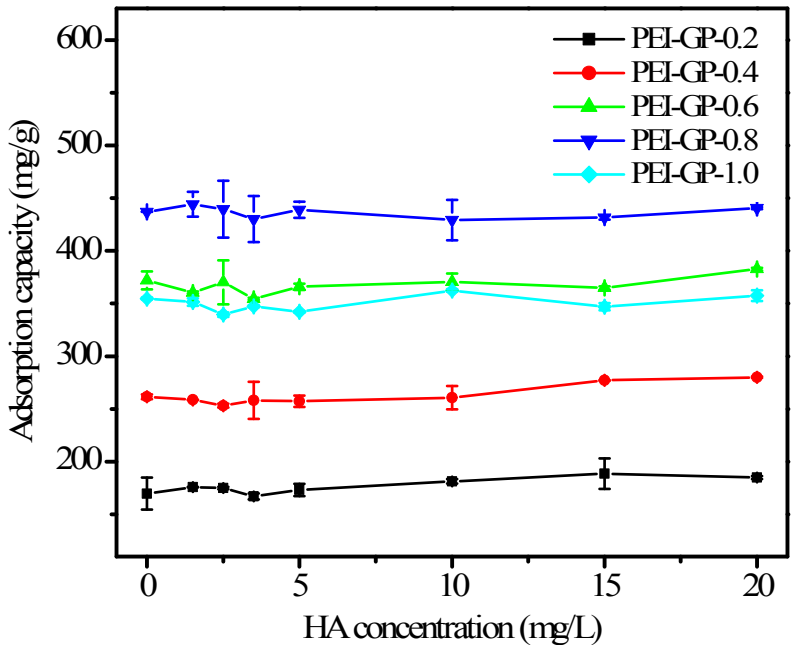


Figure S9. Effect of HA concentration on the adsorption of CdTe QDs onto PEI-GP.

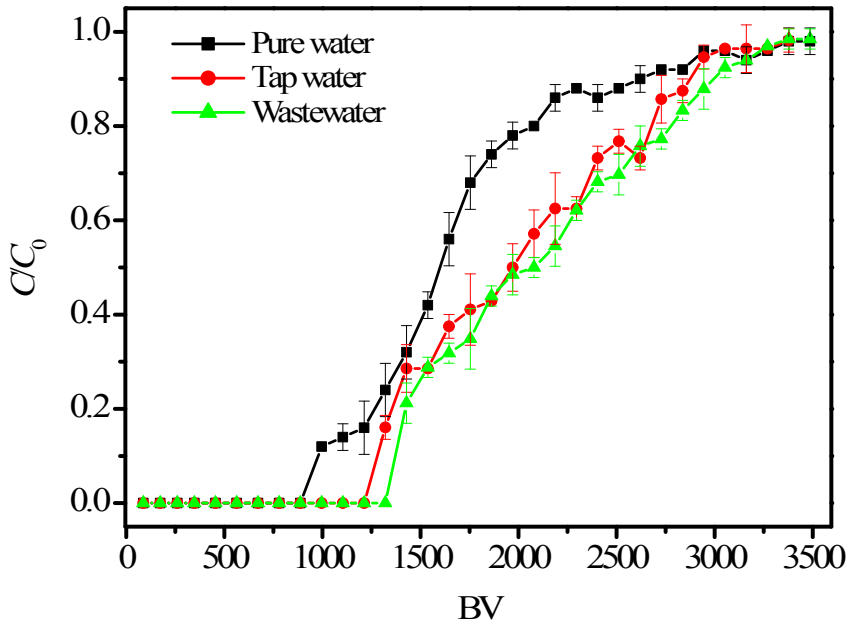


Figure S10. Breakthrough curves for PEI-GP mini-column for biosorption of CdTe QDs in pure water, tap water and wastewater.