Facile Modification of Polythiophene/TiO$_2$ Composite Using Surfactants in Aqueous Medium for Enhanced Pb(II) Adsorption and Mechanism Investigation

Jie Chen[1], Ning Wang[1], Hongyu Ma[1], Jinwei Zhu[2], Jiangtao Feng[1, *], Wei Yan[1, *]

1 Department of Environmental Science and Engineering, State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Xi'an 710049, PR China

2 Shaanxi Electrical Equipment Institute, Xi'an 710025, PR China

*Corresponding authors:

E-mail: fjtes@mail.xjtu.edu.cn (Jiangtao Feng);

        yanwei@mail.xjtu.edu.cn (Wei Yan)
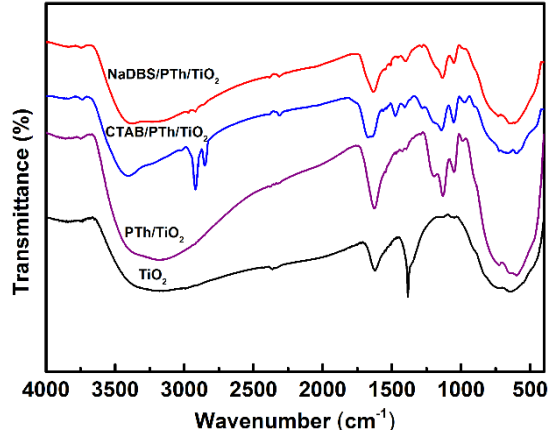
Tel.:   +86-13032912105;

Fax: +86-029-82664731.

Figure *S1.* FT-IR spectra of the TiO_2, PTh/TiO_2, $NaDBS/PTh/TiO_2$ and $CTAB/PTh/TiO_2$ composites in the region between 400 and 4000cm^{-1}
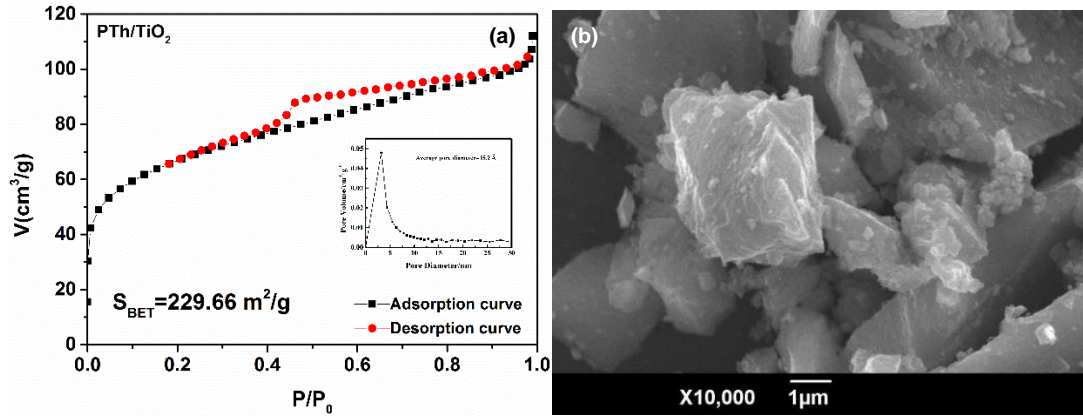

Figure *S2.* Nitrogen gas adsorption-desorption isotherms and pore size distribution (insets) of the PTh/TiO_2 composite (a) and SEM image of the PTh/TiO_2 composite (b)[1].
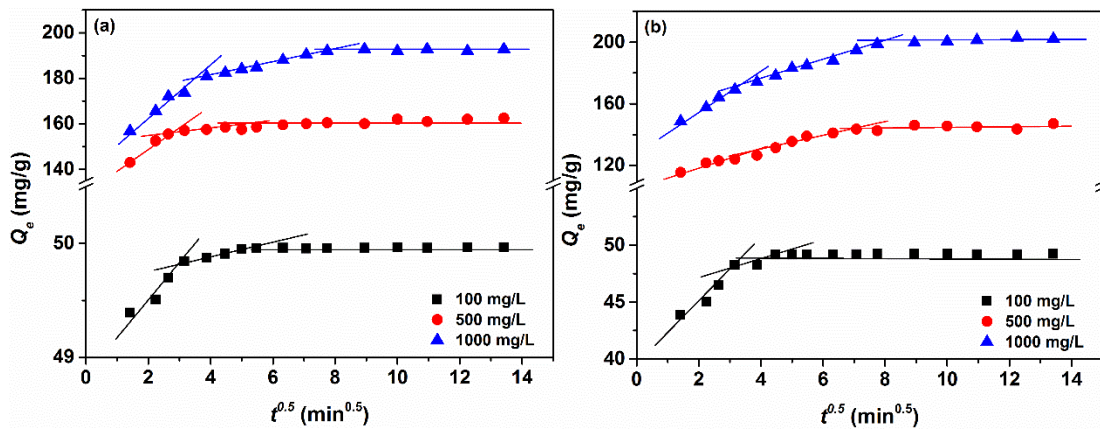

Figure *S3.* Multi-fit of the adsorption kinetic data of $NaDBS/PTh/TiO_2$ (a) and $CTAB/PTh/TiO_2$ composites (b) for Pb^{2+} to Weber-Morris Model.

Table *S1*. Adsorption equilibrium parameters acquired from different models in the adsorption of Pb^{2+} onto PTh/TiO_2 composite at 25ºC[1].

	Langmuir model			Freundlich model		
	q_m (mg/g)	K_L (L/mg)	R^2	n	K_F (mg^{1-n}·L^n/g)	R^2
25°C	151.52	0.0075	0.991	0.44	7.80	0.985
35°C	170.36	0.011	0.995	0.43	10.54	0.957
45°C	173.61	0.025	0.997	0.30	26.04	0.859
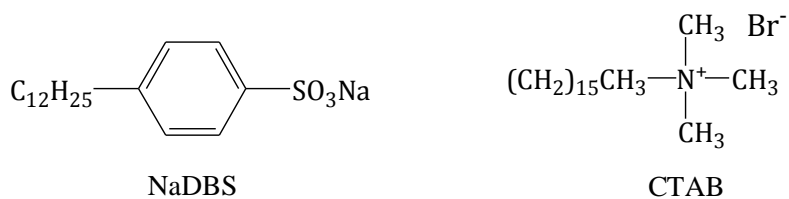
Scheme *S1* Surfactants used and their formulas.

Additional experiments

S1 Effect of the adsorbent dose

S1.1 Experiments

A certain amount of composites with the dosage ranging from 0.5 to 3.0 g/L were added in 100 mg/L of Pb^{2+} solution (20 mL) with pH=6.0, and the mixture was stirred with 200 rpm of agitation speed for 24 h at 25°C. Then the mixture was centrifuged at 4000 rpm for 6 min. The supernatant was analyzed to determine the concentration of Pb^{2+}.

S1.2 Results and discussion

The effect of adsorbent dosage on the adsorption capacity and the cost of operation are the important factors in the engineering application. The results of dosage effect on the Pb^{2+} adsorption are shown in **Figure *S4***. The removal amount increases fast at first and then reach a plateau after 2.0, while the adsorption capacities decrease with the dosage increase. This is due to the fact that there are increasing adsorption sites for adsorption as the dosage increase, resulting in better removal efficiency[2]. However, the increasing dosage leads to a decrease in average amount of adsorbate on adsorbents if the initial ion concentration was constant, causing the decrease of adsorption capacity. Taking all things into consideration, 2 g/L was applied in whole studies.
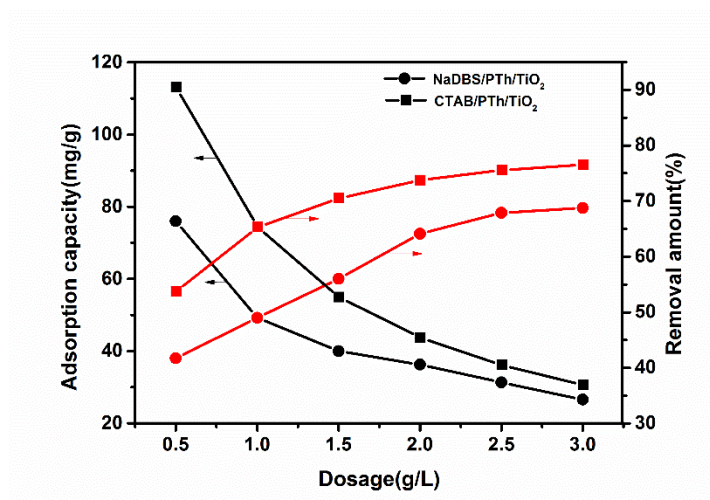

Figure *S4*. Effect of dose on the adsorption capacity and removal amount of Pb^{2+} onto the NaDBS/PTh/TiO$_2$ and CTAB/PTh/TiO$_2$ composite.

S2. Effect of the agitation speed

S2.1 Experiments

20 mL 100 mg/L of Pb^{2+} solution at pH=6.0 was mixed with 0.04 g of adsorbent, and stirred with the agitation speed ranging from 150 to 300 rpm for 24 h at 25°C. Then the mixture was centrifuged, and the Pb^{2+} residual concentration in the solution was analyzed and calculated.

S2.2 Results and discussion

The boundary layer thickness, which has a great impact on the adsorption kinetic, increased with the initial concentration, while the increased agitation would decrease the boundary layer resistance and influent the mass transfer[2]. Low (100 mg/L) and high (1000 mg/L) initial concentrations of Pb^{2+} were applied to investigate the effects for mass transfer on the adsorption capacities of both composites. The results are shown in **Figure S5**. The adsorption capacities increase with agitation speed, indicating that the external mass transfer influences the adsorption capacities of Pb^{2+}. If the agitation speed is lower than 200 rpm, the adsorption capacities increase drastically with the enhancement of the agitation speed. While there is little influence on adsorption capacities with the agitation speed over 200 rpm. Therefore the optimal 200 rpm was used in the following studies.
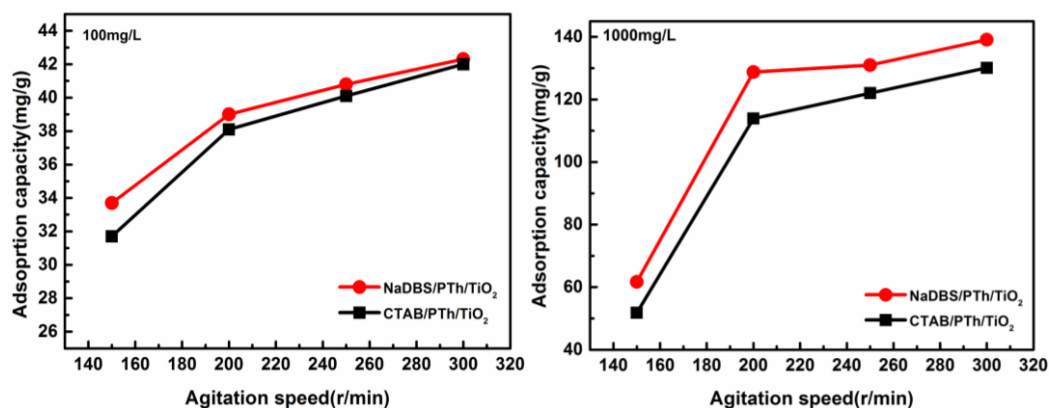

Figure S5. Effects of agitation on the adsorption capacity of Pb^{2+} onto the NaDBS/PTh/TiO$_2$ and CTAB/PTh/TiO$_2$ composites.

S3 Effect of the ionic strength

S3.1 Experiments

The effect of ionic concentration (0-0.3 mol/L) on the adsorption was carried out by adding different amounts of $NaNO_3$ into the 100 mg/L of Pb^{2+} solution at pH=6.0, respectively. Then 0.04 g of composite was stirred with the solution at the agitation speed of 200 rpm for 24 h at 25°C. The analysis and calculation methods of Pb^{2+} residual concentration were the same as those presented above.

S3.2 Results and discussion

Reality sewage contains a variety of ions influencing the adsorption behavior. In this study, the ionic circumstance was created by adding different concentrations of $NaNO_3$ into the Pb^{2+} solution. The effect of the ionic strength is depicted in **Figure *S6***, and it shows that the Pb^{2+} adsorption capacities of both composites decrease with the increase of the ionic strength. The influence of the ionic strength on the activity coefficients and competition adsorption may explain this phenomenon in this system[3]. Meanwhile, the thickness of the electrical double layer (EDL), greatly on which the charge on the surface of a hydrated adsorbent is relied, decreases as ionic strength increases, leading to a reduction in adsorption through electrostatic attraction[4]. It can be noted that $CTAB/PTh/TiO_2$ is more intensely affected. It may be because CTAB have a longer alkyl chain, and the EDL of $CTAB/PTh/TiO_2$ would be thus influenced more intensely.
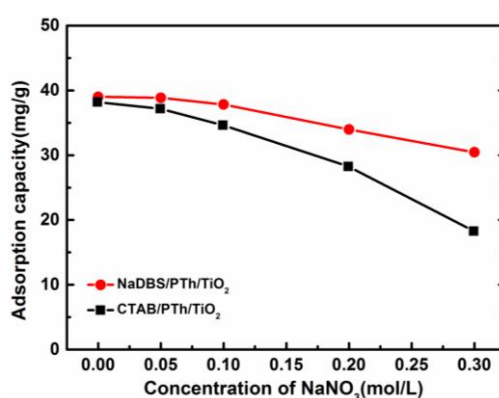

Figure *S6*. Effect of the ionic strength on the adsorption capacity of Pb^{2+} onto the $NaDBS/PTh/TiO_2$ and $CTAB/PTh/TiO_2$ composites.

S4 Feasibility investigation for the composites adsorbing other divalent heavy metals

S4.1 Experiments

0.04 g of composites were suspended in 20 mL 1000 mg/L of Pb^{2+}, Cu^{2+}, Co^{2+}, Cd^{2+}, Zn^{2+} solution, respectively, and the pH range is fixed at 5.0 to eliminate the effect of heavy metal precipitation on the adsorption. The mixture was stirred with 200 rpm of the agitation speed for 24 h at 25°C. Then the mixture was centrifuged at 4000 rpm for 6 mins at the agitation speed of 200 rpm. The supernatant was analyzed to determine the concentration.

S4.2 Results and discussion

The objective of adsorption capacity investigation for other divalent heavy metals is to evaluate the feasibility of using the surfactants modified composites as an adsorbent for removing the toxic heavy metals from aqueous solution. The results on a molar basis in **Figure *S7*** depicted that both composites owned the considerable adsorbability for Pb^{2+}, Cu^{2+}, Co^{2+}, Cd^{2+} and Zn^{2+}. Larger adsorption capacity of CTAB modified PTh/TiO_2 was found, suggesting the unique advantage of CTAB modification for adsorption. It can be noted that the adsorption capacities were in the order of $Pb^{2+}> Cu^{2+}> Co^{2+}> Cd^{2+}>Zn^{2+}$, and the adsorption affinity of heavy metals is tentatively related to their properties such as hydrated radius, softness and electronegativity[5].
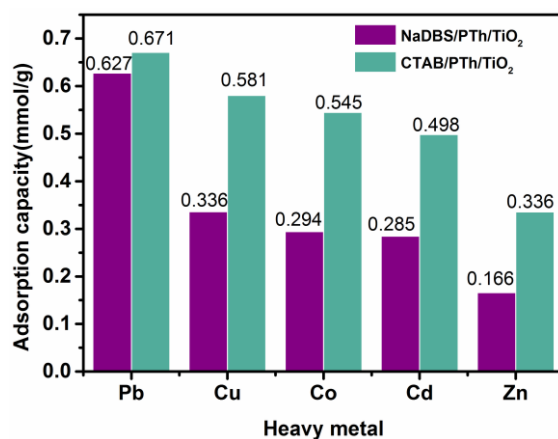

Figure *S7*. Adsorption capacity of Pb^{2+}, Cu^{2+}, Co^{2+}, Cd^{2+} and Zn^{2+} onto the NaDBS/PTh/TiO_2 and CTAB/PTh/TiO_2 composites

References

1.   Chen, J.; Feng, J. T.; Yan, W., Facile synthesis of a polythiophene/TiO$_2$ particle composite in aqueous medium and its adsorption performance for Pb(II). *RSC Adv.* **2015,** 5, 86945-86953.

2.   Ho, Y. S.; McKay, G., Sorption of dye from aqueous solution by peat. *Chem. Eng. J.* **1998,** 70, 115-124.

3.   Zhao, D. L.; Feng, S. J.; Chen, C. L.; Chen, S. H.; Xu, D.; Wang, X. K., Adsorption of thorium(IV) on MX-80 bentonite: Effect of pH, ionic strength and temperature. *Appl. Clay Sci.* **2008,** 41, 17-23.

4.   Weng, C. H.; Sharma, Y. C.; Chu, S. H., Adsorption of Cr(VI) from aqueous solutions by spent activated clay. *J. Hazard. Mater.* **2008,** 155, 65-75.

5.   Zhong, L.; Peng, X.; Song, L.; Yang, D.; Cao, X.; Sun, R., Adsorption of Cu^{2+} and Ni^{2+} from aqueous solution by arabinoxylan hydrogel: Equilibrium, kinetic, competitive adsorption. *Sep. Sci. Technol.* **2013,** 48, 2659-2669.