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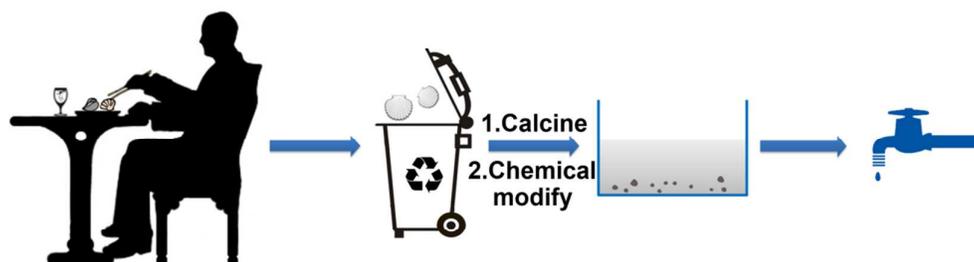
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Graphical Abstract

A new high-efficiency adsorbent (PDA-CaCO₃) is fabricated via simple thermal calcination ostracean shells and chemical modification with dopamine. Importantly, it can be easily regenerated by low-cost reagents, and exhibited high adsorption capacity after multiple adsorption-desorption cycles.



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COMMUNICATION

Mussel-Inspired Synthesis of Polydopamine-Functionalized Calcium Carbonate as Reusable Adsorbents for Heavy Metal Ions**Chengyong Li,^{*abc} Zhong-ji Qian,^d Chunxia Zhou,^{ab} Weiming Su,^b Pengzhi Hong,^{ab} Shucheng Liu,^{ab} Lei He,^a Zhimeng Chen^a and Hongwu Ji^{*abc}**⁵ Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

Abstract: A new high-efficiency adsorbent (PDA-CaCO₃) is fabricated via simple thermal calcination ostracean shells and chemical modification with dopamine. The adsorption capacity for Pb(II) and Cd(II) was 336.32 and 175.48 mg g⁻¹, respectively. Importantly, it can be easily regenerated by low-cost reagents, and exhibited high adsorption capacity after multiple adsorption-desorption cycles.

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Recently, water pollution by heavy metals has become a serious environmental issue and received significant attention because of their detrimental impacts on the environment and human health.¹⁻² For a few decades, a variety of technologies have been exploited to remove of heavy metals including chemical precipitation,³ adsorption,⁴ membrane filtration,⁵ and biological treatment.⁶ Among these methods, adsorption is one of the most effective and widely used approaches due to its relatively low cost, easy operation, and fewer harmful secondary products.⁷ Various kinds of adsorbents, including porous carbon,⁸⁻⁹ silica,¹⁰ metal oxides,¹¹⁻¹⁴ and polymer resins,¹⁵ have demonstrated their potential applications for removal of a range of heavy metals. Belonging to a class of catecholamines with excellent biocompatibility, dopamine can be spontaneously polymerized into poly dopamine (PDA) and form adhesive coatings on a wide range of substrates, which was inspired by the properties of adhesive proteins in marine mussels.¹⁶ There are abundant functional groups especially catechol groups of PDA, which are expected to be the active sites for heavy metals ions through electrostatic, bidentate chelating, or hydrogen bonding interactions. Considering these fascinating properties of dopamine, including self-polymerization and strong adhesion, PDA coating nanomaterials were widely used for adsorption of metal ions. Recently, nanofibrous polydopamine complex membranes were applied in adsorption of Lanthanum

(III) ions.¹⁷ Polydopamine coated natural zeolites were used to removal copper ions.¹⁸ However, the performance of the traditional adsorbent materials is limited by their relatively low density of specific surface areas or adsorption active sites. Meanwhile, the preparing processes of many adsorbents are complicated, which increase the operational cost in their practical applications.

In this manuscript, we report the preparation of calcium carbonate functionalized with PDA and its application for removing of heavy metal ions. Pb(II) and Cd(II) are chose as the target mental ions, which seriously influence human health. Pb(II) and Cd(II) are chronic poison, which can accumulate continually entering into the body and will show toxic effects after a certain time. Pb(II) can damage the human central nervous, hematopoietic and the digestive system. In addition, Pb(II) plays negative effects on children's health and intellectual development. Cd(II) can damage the function of kidney and lung. In our experiments, PDA-CaCO₃ was successfully prepared by a simple chemistry modification procedure in this work. The abundant functional groups especially catechol groups of PDA is expected to be the active sites for heavy metals ions through electrostatic, bidentate chelating, or hydrogen bonding interactions. We found that the resultant PDA-CaCO₃ exhibits improved adsorption capacities toward different kinds of heavy ions compared with pure CaCO₃. In addition, the raw material (CaCO₃) was obtained by calcined waste ostracean shells in this work. Ostracean shells are a sustainable natural resource since thousands of ostracean are consumed every year, generating abundant ostracean shells as waste. Ostracean shells are natural composites consisting of highly mineralized chitin, protein and bioceramic CaCO₃. Using simple thermal calcination in air, the chitin and protein organic components in the shells can be removed to form pure CaCO₃ framework containing hollow channels, which is the key factor to adsorbents. Of equal importance is that the material can be regenerated by low-cost HCl to desorb the heavy ions and maintains high adsorption capacities after multiple cycles.

To demonstrate the universal presence of these nanopore structures in ostracean shells, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to

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study the microstructures of the samples. The SEM image in Fig.1(a) shows a typical 3D morphology of the pure CaCO_3 fabricated from ostracean shells. As shown, it clearly reveals the interconnected network with the porous structure of the pure CaCO_3 . The disordered wormhole-like nanopores with diameter distribution of 20-100 nm can be seen clearly. A similar porous morphology was observed for modified with polydopamine (PDA- CaCO_3) (Fig.1b), which indicates that PDA is uniformly coated on the surface of CaCO_3 due to the strong affinity during the polymerization process. TEM images show that the sharp of pure CaCO_3 (Fig.1c) is different to each other due to the complicated structure of ostracean shells. In addition, the size is variable. There are many nanopores (Fig.1c) observed in TEM image, which is accorded with SEM image (Fig.1a). As shown in Fig. 1d, the microstructure is not changed after PDA modified. Specific surface area plays an important role on the absorption. PDA- CaCO_3 and pure CaCO_3 possess almost the same specific surface areas, which were measured to be 321.6 and 330.5 $\text{m}^2 \text{g}^{-1}$, respectively (Fig.S1).

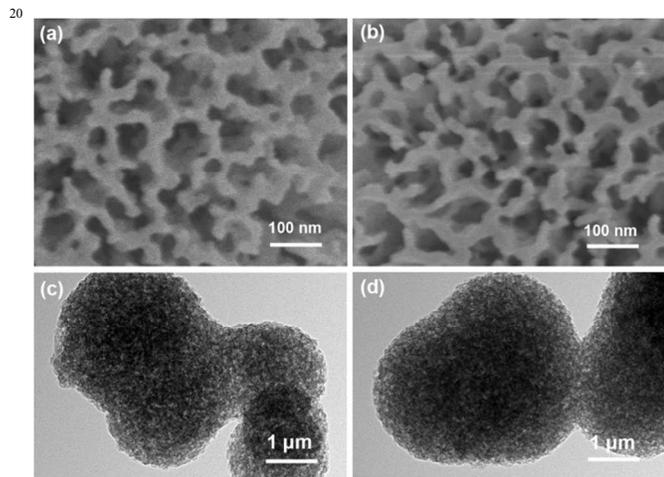


Fig.1 SEM and TEM images of pure CaCO_3 (a, c) and PDA- CaCO_3 (b, d).

In order to further confirm the successful modification, the compositional change of CaCO_3 before and after modified by dopamine was examined by IR (Fig.S2) and XPS (Fig.S3). Due to the water absorption in pure CaCO_3 (blue line), there are two obvious absorption band ($3000\text{-}3600 \text{ cm}^{-1}$ and $1400\text{-}1600 \text{ cm}^{-1}$) caused by hydroxyl group. However, these two absorption band disappear after modified with dopamine. The absorption of water is becoming difficultly due to the protection of dopamine. The characteristic absorption bands of dopamine can be observed. First, the sharp absorption around 3640 cm^{-1} is phenol hydroxyl group. Second, the two broad absorption bands between 3600 cm^{-1} and 3400 cm^{-1} (left inset) are caused by amino group. In addition, the characteristic absorption bands of aromatic rings are observed (right inset, $1600\text{-}1400 \text{ cm}^{-1}$). The results of XPS measurement show there is a new peak of N1s emerges in PDA- CaCO_3 , compared with pure CaCO_3 , which should arise from PDA on the surface of CaCO_3 (Fig.S3).

To evaluate the effect of pH values on the adsorption of Pb(II) and Cd(II) onto PDA- CaCO_3 , we conducted batch experiments in a series of solutions with the same initial concentrations and pH values adjusted from 3.0 to 6.0 (Fig.2). From the result, it can be

found that the maximum removal of Pb(II) is greatly higher than Cd(II). In acidic solutions (pH value lower than 3.0), CaCO_3 is not stable. Thus, absorption experiments were not carried out when solution pH is less than 3.0. Meanwhile, the species of surface functional groups on PDA- CaCO_3 were protonized with positively charged surface, and the adsorption capacities of metal ions were low due to the electrostatic repulsion. With increasing pH values, the surface charges of PDA- CaCO_3 became more negative, and the adsorption capacities of Pb(II) or Cd(II) dramatically increased in the range of pH values from 3.0 to 6.0. When pH exceeded 6, metals hydroxides could be formed due to the formation of the precipitation of heavy metals hydroxides. In this condition, the removal mechanism of metal ions will become more complicated, and it will be difficult to distinguish between the adsorption and precipitation of metal ions removed from solutions.

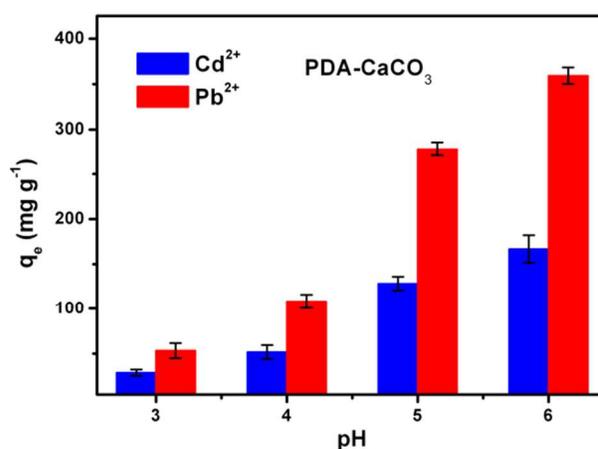


Fig.2 Effects of pH values on the adsorption capacities of Cd(II) and Pb(II) on PDA- CaCO_3 .

As is well known, solution pH is one of the most important factors affecting the surface charges of the adsorbents, which is fatal to adsorption characteristics. In order to confirm above views, zeta-potentials of samples in the solution under different pHs were investigated (Fig.S4). The zeta-potentials of pure CaCO_3 ($<10 \text{ mV}$) are much smaller than the ones of PDA- CaCO_3 and decrease with increasing pH. The isoelectric point of PDA- CaCO_3 is between 4 and 5. Above the isoelectric point, the surfaces of the PDA- CaCO_3 are negatively charged due to the ionization of oxygen functional groups. When solution $\text{pH} < 4$, the species of surface functional groups on PDA- CaCO_3 were protonized with positively charged surface, and the adsorption capacities of metal ions were low due to the electrostatic repulsion. With increasing pH values, the surface charges of PDA- CaCO_3 became more negative, and the adsorption capacities of Pb(II) or Cd(II) dramatically increased in the range of pH values from 3.0 to 6.0.

The equilibrium isotherm plays a fundamental role in describing the interactive behavior between solutes and adsorbent. We then compared the adsorption capacities of PDA- CaCO_3 and CaCO_3 at pH 6.0 by equilibrium adsorption isotherm studies. The adsorption capacities of the two adsorbents progressively increased with increasing concentrations of metals ions, and finally

reached the saturation states (Fig.3). These adsorption data were fitted into the Langmuir isotherm model, suggesting that the adsorption of metal ions took place at the functional groups or binding sites. From the fitting results, we obtained the maximum adsorption capacities of Pb(II) and Cd(II) onto PDA-CaCO₃ were 336.32 and 175.48 mg g⁻¹, showing a significant improvement relative to that of pure CaCO₃ (73.20 and 37.78 mg g⁻¹). The relatively higher adsorption capacity of Pb(II) should possibly arise from the higher binding affinity of phenolic group to Pb(II) compared with Cd(II).¹⁹

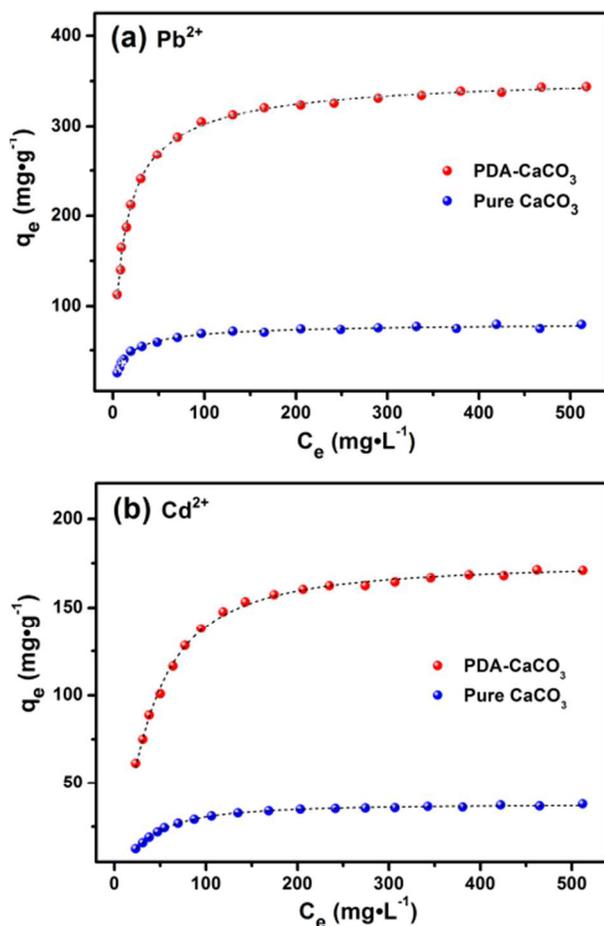


Fig.3 Adsorption behaviors of Pb(II) (a) and Cd(II) (b) on PDA-CaCO₃ and pure CaCO₃. Adsorption isotherm curving was fitting by Langmuir isotherm model.

The adsorption kinetics of Pb(II) or Cd(II) was examined by using the metal ion concentration of 100 mg L⁻¹ at pH 6.0, and the samples were collected at different time intervals up to 10 h. The amount of Pb(II) or Cd(II) adsorbed onto PDA-CaCO₃ and CaCO₃ increased sharply within the initial 100 min, then rose slowly, and reached equilibrium in 200 min (Fig.4). The pseudofirst order and pseudosecond order kinetic models were employed to fit the experimental data, respectively. The kinetic model parameters were obtained from fitting the results and presented in Table S1. On the basis of the value of r^2 , it is clear that the pseudosecond order kinetic model provides a better correlation in contrast to the pseudofirst order model for adsorption of Pb(II) or Cd(II) onto CaCO₃ and PDA-CaCO₃. The pseudosecond

order model is based on the assumption that chemisorption is the rate determining step, which further confirms the adsorption mechanism in our system.

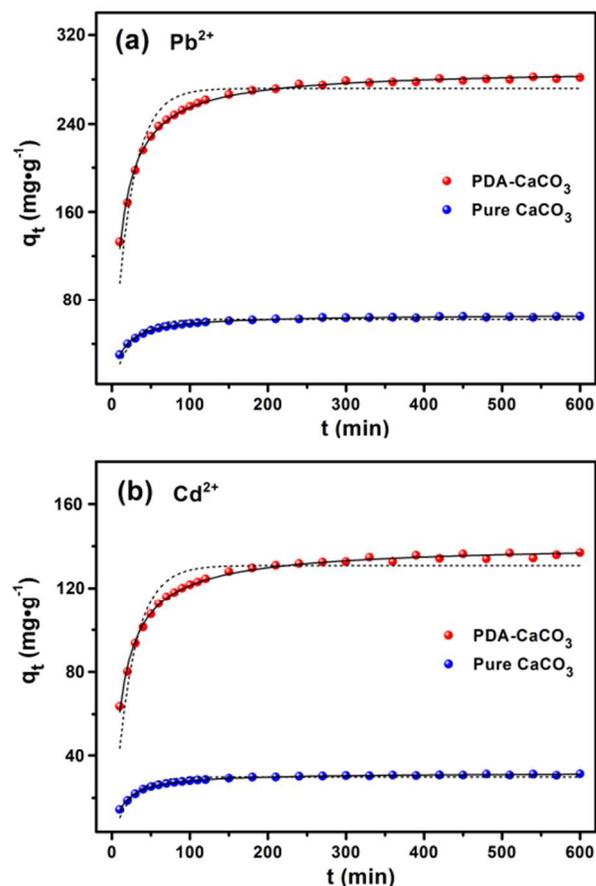


Fig.4 Adsorption kinetic plots and curving fitting by pseudo-first-order (dot line) and pseudo-second-order (solid line) kinetic models of Pb(II) and Cd(II) on PDA-CaCO₃ and CaCO₃.

XPS was employed to analyze the existing forms of Pb(II) or Cd(II) on PDA-CaCO₃ (Fig.S5). The high resolution Pb 4f spectrum can be fitted into two peaks, which appear at 138.8 eV (Pb 4f_{7/2}) and 143.7 eV (Pb 4f_{5/2}). In Pb(OH)₂, the Pb 4f_{7/2} peak appears at 138.4 eV, indicating the complexation of Pb(II) onto PDA-CaCO₃ and no precipitation occurs at pH 6.0. The Cd 3d_{5/2} spectrum shows a main band centering at 405.4 eV, accompanied by a secondary one at higher binding energy, which can be assigned to Cd 3d_{3/2} at 412.2 eV, whereas the characteristic energy of Cd(OH)₂ shows a main band centering at 404.6 eV. Thus, adsorption process may involve the interactions of Pb(II) and Cd(II) species with the oxygen and nitrogen function groups such as amine, amino, et al. on the adsorbents.^{17, 18}

The regeneration and reuse of adsorbents is a crucial factor for assessing their potential for practical applications. 1 mM HCl solutions can be used as the desorption agent to recover Pb(II) and Cd(II) from the adsorbents. The decrease of adsorption capacity of PDA-CaCO₃ and pure CaCO₃ could possibly result from reduced stability of the PDA coating or CaCO₃ in strong acid. However, the adsorption capacities of regenerated PDA-CaCO₃ were still much higher than those of CaCO₃ after ten re-

peated adsorption and desorption cycles, and more than 80% of its adsorption capacities were retained (Fig.5a). Therefore, PDA-CaCO₃ offers the possibility for easy recycle and reuse for the removal of heavy metal ions. However, the adsorption capacity of pure CaCO₃ for Pb(II) and Cd(II) were decreased to 67.5% and 63.2% after tenth regeneration, respectively (Fig.5b). In order to confirm the stability of adsorbents, PDA-CaCO₃ after regeneration for the first and the tenth time was observed by TEM. As shown in Fig.S6, there is no significant change after regeneration.

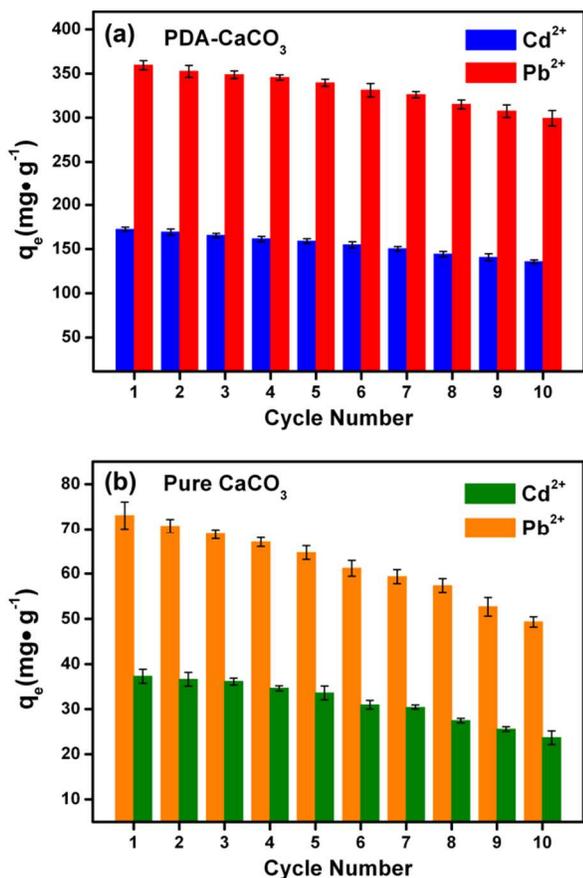


Fig. 5 Adsorption capacities of PDA-CaCO₃ (a) and pure CaCO₃ (b) as a function of repeated adsorption-desorption cycles for the removal of Pb(II) and Cd(II).

In conclusion, a new high efficiency adsorbent (PDA-CaCO₃) is fabricated via simple thermal calcination ostracean shells and chemical modification with dopamine. The adsorption capacity of PDA-CaCO₃ for Pb(II) and Cd(II) was greatly enhanced in comparison with pure CaCO₃. Importantly, it can be easily regenerated by low-cost reagents, and exhibited high adsorption capacity after multiple adsorption-desorption cycles.

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Notes and references

- R. P. Schwarzenbach, B. I. Escher, K. Fenner, T. B. Hofstetter, C. A. Johnson, U. von Gunten and B. Wehrli, *Science*, 2006, **313**, 1072-1077.
- R. P. Schwarzenbach, T. Egli, T. B. Hofstetter, U. von Gunten and B. Wehrli, *Annu. Rev. Env. Resour.*, 2010, **35**, 109-136.
- M. McDonald, I. Mila and A. Scalbert, *J. Agric. Food. Chem.*, 1996, **44**, 599-606.
- S. Dai, M. C. Burleigh, Y. H. Ju, H. J. Gao, J. S. Lin, S. J. Pennycook, C. E. Barnes and Z. L. Xue, *J. Am. Chem. Soc.*, 2000, **122**, 992-993.
- V. Dushenkov, P. B. A. N. Kumar, H. Motto and I. Raskin, *Environ. Sci. Technol.*, 1995, **29**, 1239-1245.
- H. Eccles, *Trends Biotechnol.*, 1999, **17**, 462-465.
- I. Ali, *Chem. Rev.*, 2012, **112**, 5073-5091.
- J. Gong, T. Liu, X. Wang, X. Hu and L. Zhang, *Environ. Sci. Technol.*, 2011, **45**, 6181-6187.
- Y. X. Zhang, Z. L. Liu, B. Sun, W. H. Xu and J. H. Liu, *RSC Advances*, 2013, **3**, 23197-23206.
- A. M. Liu, K. Hidajat, S. Kawi and D. Y. Zhao, *Chem. Commun.*, 2000, 1145-1146.
- J. S. Hu, L. S. Zhong, W. G. Song and L. J. Wan, *Adv. Mater.*, 2008, **20**, 2977-2982.
- Y. X. Zhang, X. Y. Yu, Z. Jin, Y. Jia, W. H. Xu, T. Luo, B. J. Zhu, J. H. Liu and X. J. Huang, *J. Mater. Chem.*, 2011, **21**, 16550-16557.
- Y. X. Zhang, Y. Jia, Z. Jin, X. Y. Yu, W. H. Xu, T. Luo, B. J. Zhu, J. H. Liu and X. J. Huang, *CrystEngComm*, 2012, **14**, 3005-3007.
- Y. X. Zhang and Y. Jia, *Appl. Surf. Sci.*, 2014, **290**, 102-106.
- A. Duran, M. Soyulak and S. A. Tuncel, *J. Hazard. Mater.*, 2008, **155**, 114-120.
- H. Lee, S. M. Dellatore, W. M. Miller and P. B. Messersmith, *Science*, 2007, **318**, 426-430.
- G. Hong, L. Shen, M. Wang, Y. Yang, X. Wang, M. Zhu and B. S. Hsiao, *Chem. Eng. J.*, 2014, **244**, 307-316.
- Y. Yu, J. G. Shapter, R. Popelka-Filcoff, J. W. Bennett and A. V. Ellis, *J. Hazard. Mater.*, 2014, **273**, 174-182.
- D. G. Kinniburgh, C. J. Milne, M. F. Benedetti, J. P. Pinheiro, J. Filius, L. K. Koopal and W. H. Van Riemsdijk, *Environ. Sci. Technol.*, 1996, **30**, 1687-1698.