ChemComm

Palladium nanoparticle loaded β-cyclodextrin monolith as flow reactor for concentration enrichment and conversion of pollutants based on molecular recognition

Journal:	*ChemComm*
Manuscript ID	CC-COM-10-2020-006684.R1
Article Type:	Communication

COMMUNICATION

Palladium nanoparticle loaded β-cyclodextrin monolith as flow reactor for concentration enrichment and conversion of pollutants based on molecular recognition

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Shunsuke Mizuno[a], Taka-Aki Asoh[a]*, Yoshinori Takashima[bc], Akira Harada[d], and Hiroshi Uyama[a]*

This study reports pollutant remediation by a catalyst-loaded, β-cyclodextrin cross-linked polymer monolith. The monolith enabled removal of the pollutant to a residual concentration with no environmental effect and conversion of the adsorbed pollutant into the useful compound with enriched concentration, allowing for the reuse of adsorption capacity.

With the development of science and technology, aquatic organisms in addition to humans are being adversely affected by various activities such as industry, agriculture, and medicine[1-3]. Therefore, it is necessary to build technology to protect the environment, such as purification of water resources; the environmental pollutant separation that preserves aquatic life and provides safe water is indispensable for the construction of a sustainable society. To address these problems, the development of adsorbent materials has been widely studied. There are many types of substrates for this purpose, such as inorganic materials[4-6], carbon materials[7-13], or polymer materials[14-17], and interactions such as ionic interaction[18, 19], π-π interaction[20, 21], and host-guest interaction[22-24]. Further, a strategy for recovering adsorbed pollutants is also important. In activated carbon, a widely used conventional adsorbent, the regeneration of adsorbability and remediation of pollutants are conducted by pyrolysis at high temperatures. However, treatment at high temperatures requires high energy and thus makes reuse difficult, while processing at low temperatures increases the risk of releasing toxic substances[25-28].

We have devised a new water purification system that uses host-guest interactions to selectively adsorb impurities to concentrate and release them into useful substances. Cyclodextrins are naturally derived cyclic oligosaccharides that recognize hydrophobic molecules with an appropriate size of their inner cavity and form inclusion complexes in water. Among them, β-cyclodextrin (β-CD), composed of seven glucopyranose units, is commonly used as an adsorbent material for water purification because its cavity size is suitable for the inclusion of a variety of organic pollutants. A typical material is a water-insoluble polymer material obtained by directly cross-linking β-CD[29]. However, β-CD cross-linked polymers, represented by polymer beads obtained by reacting β-CD with a cross-linking agent such as epichlorohydrin, have low adsorption efficiency due to their low specific surface area[29-34].

In this study, a monolithic flow reactor with molecular recognition ability was fabricated for the removal of a pollutant to a concentration that does not affect the environment. A palladium nanoparticle-immobilized β-CD cross-linked polymer monolith (**Fig. 1a**) that can convert a pollutant into a useful compound based on molecular recognition was prepared.

The cyclodextrin cross-linked polymer monolith was prepared by a cross-linking reaction between a monochlorotriazine-modified β-CD (MCT-β-CD) and polyethyleneimine (PEI) to form a three-dimensional network structure. MCT-β-CD and PEI were dissolved in water and the resulting solution was poured into a polytetrafluoroethylene (PTFE) tube (inner diameter: 8.0 mm). The cloudy hydrogels were obtained by reaction at 10 °C for 72 h (**Fig. 1b**). The obtained hydrogel was immersed in water, ethanol, and *n*-hexane, consecutively. Finally, a CD monolith was obtained by vacuum drying (diameter: 6.4 mm, height: 12.5 mm). Scanning electron microscopy (SEM) observation revealed that the monolith formed a co-continuous porous structure with a micrometer scale that could pass liquids such as water

---

[a] *Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Yamadaoka 2-1, Suita, Osaka, 565-0871, Japan. E-mail: asoh@chem.eng.osaka-u.ac.jp; uyama@chem.eng.osaka-u.ac.jp*
[b] *Department of Macromolecular Science, Graduate School of Science, Osaka University, 1-1 Machikaneyama-cho, Toyonaka, Osaka 560-0043, Japan. E-mail:*
[c] *Institute for Advanced Co-Creation Studies, Osaka University, 1-1 Machikaneyamacho, Toyonaka, Osaka 560-0043, Japan.*
[d] *The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan.*

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

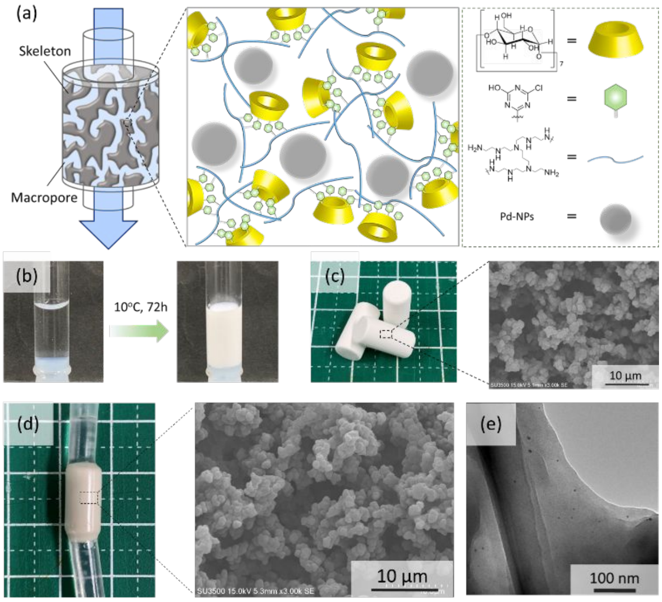


Fig. 1 (a) Schematic illustration of the flow reactor in this study. (b) Fabrication of CD monolith: MCT-β-CD and PEI aqueous solution and cloudy hydrogel resulting from gelation and phase separation, from left to right. (c) Photo of the CD monolith and the macroporous structure by SEM. (d) Photo of the flow reactor and the macroporous structure by SEM. (e) TEM image of the Pd-CD monolith.

and acetone (**Fig. 1c**). Palladium ion was immobilized in the monolith by passing a palladium acetate ($Pd(OAc)_2$) acetone solution through the monolith column at a constant flow rate. Our previous study reported that when a $Pd(OAc)_2$ solution was passed through a polymer monolith possessing PEI moieties, palladium ions were immobilized by complex formation with the contained amino groups. Then, passing a $NaBH_4$ aqueous solution enabled the formation of Pd-NPs with high catalytic activity derived from the porous structure[35]. By passing the $NaBH_4$ aqueous solution, the monolith color changed from pale yellow to gray, suggesting the formation of Pd-NPs. In the SEM images, the macropore sizes before and after the loading of the Pd-NPs are 2.49 µm and 2.38 µm, respectively, and no significant difference was observed for macrospores during the Pd-NPs immobilization process (**Fig. 1c, d**). The size of the Pd-NPs was determined to be 3-4 nm by transmission electron microscopy (TEM) (**Fig. 1e**). Inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements demonstrated that the amount of palladium catalyst immobilized in the monolith was 24.1 µmol/g.

A polymer monolith supporting Pd-NPs was applied to the 4-nitrophenol (4-NP) reduction reaction. It is well known that 4-NP is a representative environmental pollutant and is certified as a priority toxin (by the US Environmental Protection Agency)[36]. However, the reaction to obtain 4-aminophenol (4-AP) from the hydrogenation of 4-NP has been researched as a sustainable reaction that can convert environmental pollutants into pharmaceutical intermediates[35, 37]. A reaction solution prepared by dissolving 4-NP and a hydrogen donor in a phosphate buffer was passed through a Pd-CD monolith. The eluate during the flow reaction was collected in fixed amounts, and each elution sample of the reaction substrate and the product was measured by high-performance liquid chromatography (HPLC). Interestingly, no substrate (4-NP) was detected, and only the product (4-AP) was eluted, indicating that the Pd-CD monolith selectively captured 4-NP and released 4-AP as it would an enzyme. The conversion of the nitro group to an amino group changed the size and polarity of the 4-nitrophenol, which may have changed the affinity for β-CD and thus caused a decrease in adsorbability. Although unreacted 4-NP remained in the monolith, unreacted 4-NP did not elute (Fig. 2a). The adsorption ability of 4-NP and 4-AP for the Pd-CD monolith was confirmed by the breakthrough curve. The difference in the molecular recognition ability of the reaction substrate (4-NP) and the product (4-AP) was clearly observed, as shown in **Fig. 2b, c**. The monolith demonstrated good adsorption efficiency for 4-NP. In the UV-Vis spectra, the 4-NP peak was barely detected in the eluate of the first 20 mL, and the elution gradually appeared as the volume increased. For 4-AP, a small amount of adsorption was observed in the first stage of the flow; however, the elution amount and the initial concentration became almost equal immediately. Therefore, the monolith does not have sufficient adsorption ability toward 4-AP, unlike that for 4-NP. The effect of molecular recognition

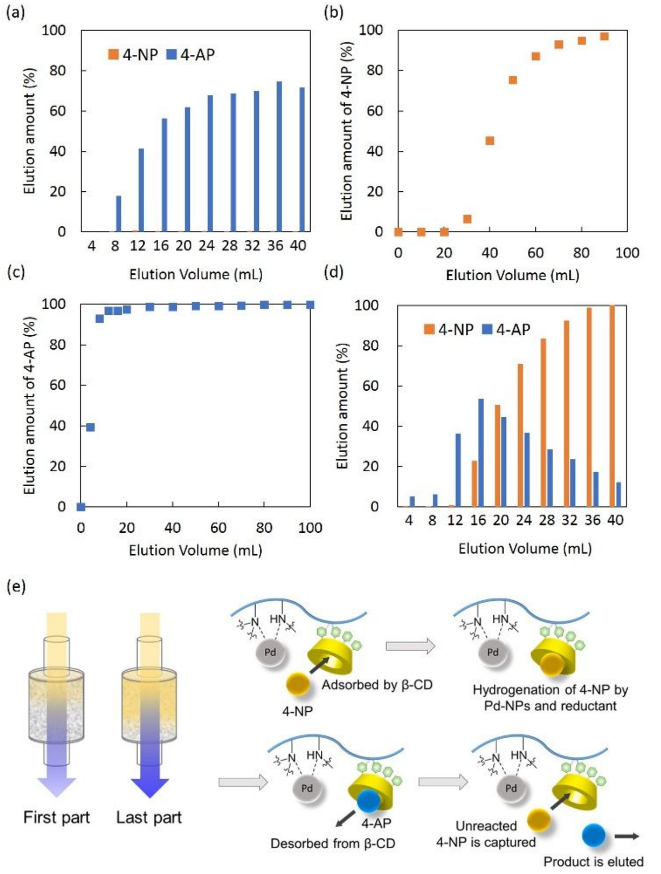


Fig. 2 (a) The elution amounts of 4-NP and 4-AP during the 4-NP reduction in the flow system. Breakthrough curves of (b) 4-NP and (c) 4-AP adsorption by the Pd-CD monolith. (d) The elution amounts of 4-NP and 4-AP when using Ad-COOH as an inhibitor. (e) Proposed mechanism of the effect of the molecular recognition.

on the flow reaction was investigated using a competitor of the host-guest interaction. A recognition inhibitor, 1-adamantanecarboxylic acid (Ad-COOH), which has a higher affinity for β-CD than that of 4-NP[38], was added to the reaction solution. In the presence of a 20 eq. inhibitor, elution of 4-NP was observed as the flow reaction progressed. The amount of produced 4-AP increased at an early stage; this is probably due to the adsorption of both 4-NP and Ad-COOH. Following this, the 4-AP production decreased at the same time that the elution of 4-NP was initiated owing to the influence of the inhibitor **(Fig. 2d)**. Because Ad-COOH did not have a significant influence on the reaction, it is clear that the reaction was suppressed unless 4-NP was captured by β-CD. Therefore, the reaction efficiency was high due to the capture of the substrate by molecular recognition, and not only was the unreacted substrate not eluted, but further, the product was efficiently released after the reaction. Consequently, it is an efficient system that does not interfere with the continuous reaction. From these results, it could be suggested that the inside of the flow reactor that performs such molecular recognition becomes a reaction field where only the reaction substrate exists at a high concentration, which assists the collision between the substrate and catalyst. It has been reported that the formation of inclusion complexes with β-CD improves the efficiency of the hydrogenation reaction of 4-NP[39]. Since the present Pd-CD monolith was designed to have palladium nanoparticles and β-CDs in the vicinity, the reduction reaction was expected to proceed by the mechanism shown in **Fig. 2e**.

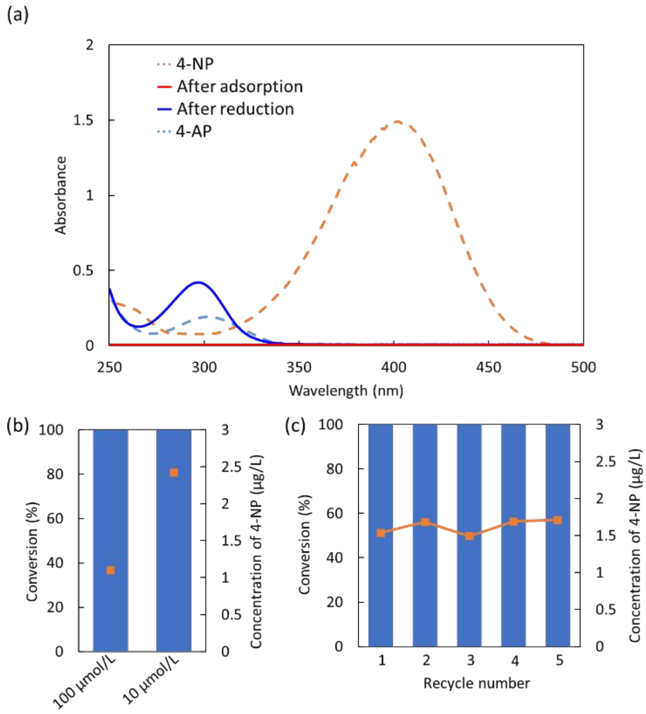


Fig. 3 (a) UV-vis spectra of eluate after adsorption of 4-NP (red line), eluate after reduction (blue line), and 0.1 mmol/L (alkali state) of 4-NP and 4-AP as standards (orange and pale blue dotted lines, respectively). (b) Conversion and the concentration of remaining 4-NP during the stepwise adsorption/reduction of 4-NP. (c) Reusability of the flow reactor: conversion and the concentration of remaining 4-NP in one adsorption/reduction cycle.

By using the clathrate property, product concentration in addition to an efficient reaction is possible. After a large amount of a dilute substrate is passed into the monolith and completely trapped within, a hydrogen donor dissolved in a small amount of water is passed through. As a result, the released product is concentrated. As such, in addition to 4-NP conversion to 4AP, enriched 4-AP can be obtained. When 4-NP aqueous solution (concentration: 100 μmol/L) was passed through the Pd-CD monolith, a yellow adsorption layer derived from 4-NP was clearly observed. No 4-NP peak was observed in the resulting UV-vis spectrum (**Fig. 3a**). The 4-NP concentration in the eluate was determined to be approximately 1.1 μg/L by HPLC. The predicted no effect concentration (PNEC) of 4-NP was reported as 6.9 μg/L[40], thus, this is the concentration with no adverse effect on living things. When testing lower concentrations of 4-NP aqueous solution (concentration: 10 μmol/L), the 4-NP concentration in the eluate was 2.4 μg/L, which was also well below the PNEC (**Fig. 3b**). When the aqueous $NaBH_4$ solution was passed through, the adsorbed 4-NP was reduced by the supported palladium catalyst, and only the 4-AP peak was detected by UV-Vis spectroscopy (**Fig. 3a**). The amount of 4-AP in the reducing agent aqueous solution was almost the same with respect to the initial amount of 4-NP (**Fig. 3b**). The results demonstrated that 4-AP can be enriched to 10 times the initial concentration of 4-NP with a small amount of reducing agent compared to conventional continuous flow reactions. Additionally, the reusability was confirmed by performing this adsorption and reduction process for 5 cycles. During the reusability test, the conversion rate of the reduction reaction was maintained, and it should be noted that the concentration of 4-NP in the eluate was 1.5–1.7 μg/L (**Fig. 3c**). From these results, it was concluded that a new environmentally friendly remediation system was created that can adsorb sufficient 4-NP such that the residual concentration has no effect on the environment, and can convert the 4-NP to 4-AP completely in a concentrated state with the regeneration of the adsorption ability. In practical applications, target molecules must be selectively adsorbed from various impurities. Although molecular recognition improves reactivity, it is a future task to selectively capture targets from contaminant and convert them into useful chemicals.

In conclusion, a flow reaction system that differentiates the reaction substrate and product in the treatment of 4-NP was constructed using a Pd-NP-immobilized cyclodextrin cross-linked polymer monolith. A Pd-NP-loaded β-CD polymer monolith was successfully prepared; the resulting flow reactor was able to independently perform adsorption and reduction of 4-NP. Using this technology, 4-NP concentration in wastewater can be reduced to a concentration that does not affect the environment, and the enrichment of 4-AP can be achieved by a small amount of reducing agent. In this study, the adsorption capacity was restored by the reduction reaction and exhibited reusability for 5 cycles. This flow reaction system provides a novel strategy to favor the reaction progress by molecular recognition and the construction of a highly efficient pollutant treatment that does not affect the environment.

Conflicts of interest

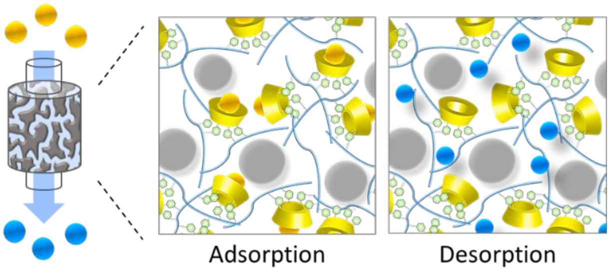
There are no conflicts to declare.

Acknowledgements

This work was supported by JSPS KAKENHI (Grant Numbers 20H02797, 19H02778) and JST-Mirai Program (JPMJMI18E3). We would like to express our appreciation to CycloChem Co., Ltd for the β-CD derivative.

Notes and references

1 R. P. Schwarzenbach, T. Egli, T. B. Hofstetter, U. von Gunten and B. Wehrli, *Annu. Rev. Environ. Resour.*, 2010, **35**, 109–136.
2 K. E. Murray, S. M. Thomas and A. A. Bodour, *Environmental Pollution*, 2010, **158**, 3462–3471.
3 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.
4 A. Walcarius and L. Mercier, *Journal of Materials Chemistry*, 2010, **20**, 4478–4511.
5 P. Z. Ray and H. J. Shipley, *RSC Advances*, 2015, **5**, 29885–29907.
6 S. S. Gupta and K. G. Bhattacharyya, *Advances in colloid and interface science*, 2011, **162**, 39–58.
7 A. Bhatnagar, W. Hogland, M. Marques and M. Sillanpää, *Chemical Engineering Journal*, 2013, **219**, 499–511.
8 J.-Q. Jiang and S. M. Ashekuzzaman, *Current Opinion in Chemical Engineering*, 2012, **1**, 191–199.
9 A. Dąbrowski, P. Podkościelny, Z. Hubicki and M. Barczak, *Chemosphere*, 2005, **58**, 1049–1070.
10 D. Mohan and C. U. Pittman Jr, *Journal of hazardous materials*, 2006, **137**, 762–811.
11 A. Demirbas, *Journal of hazardous materials*, 2009, **167**, 1–9.
12 X. Ren, C. Chen, M. Nagatsu and X. Wang, *Chemical Engineering Journal*, 2011, **170**, 395–410.
13 D. Mohan, A. Sarswat, Y. S. Ok and C. U. Pittman Jr, *Bioresource technology*, 2014, **160**, 191–202.
14 B. Pan, B. Pan, W. Zhang, L. Lv, Q. Zhang and S. Zheng, *Chemical Engineering Journal*, 2009, **151**, 19–29.
15 M. Sajid, M. K. Nazal, N. Baig and A. M. Osman, *Separation and Purification Technology*, 2018, **191**, 400–423.
16 G. Sharma and B. Kandasubramanian, *Journal of Chemical & Engineering Data*, 2020, **65**, 396–418.
17 A. Ramazani, M. Oveisi, M. Sheikhi and F. Gouranlou, *Current Organic Chemistry*, 2018, **22**, 1297–1306.
18 G. Z. Kyzas, J. Fu and K. A. Matis, *Materials*, 2013, **6**, 5131–5158.
19 J. Lipnizki, B. Adams, M. Okazaki and A. Sharpe, *Filtration+ Separation*, 2012, **49**, 30–33.
20 Z. N. Garba, W. Zhou, I. Lawan, W. Xiao, M. Zhang, L. Wang, L. Chen and Z. Yuan, *Journal of environmental management*, 2019, **241**, 59–75.
21 J. O. Eniola, R. Kumar and M. A. Barakat, *Environmental Science and Pollution Research*, 2019, 1–14.
22 S. A. A. Razavi, M. Y. Masoomi and A. Morsali, *Inorganic chemistry*, 2018, **57**, 11578–11587.
23 H. Ju, X. Zhou, B. Shi, X. Kong, H. Xing and F. Huang, *Polymer Chemistry*, 2019, **10**, 5821–5828.
24 A. Zhang, C. Chen, Y. Ji, S. Liu and S. Guo, *Journal of Chemical & Engineering Data*, 2018, **63**, 1578–1587.
25 M. J. Lashaki, M. Fayaz, H. (Helena) Wang, Z. Hashisho, J. H. Philips, J. E. Anderson and M. Nichols, *Environ. Sci. Technol.*, 2012, **46**, 4083–4090.
26 H. Lyu, Y. He, J. Tang, M. Hecker, Q. Liu, P. D. Jones, G. Codling and J. P. Giesy, *Environmental Pollution*, 2016, **218**, 1–7.
27 E. Çalışkan, J. M. Bermúdez, J. B. Parra, J. A. Menéndez, M. Mahramanlıoğlu and C. O. Ania, *Journal of Environmental Management*, 2012, **102**, 134–140.
28 T. Dutta, T. Kim, K. Vellingiri, D. C. W. Tsang, J. R. Shon, K.-H. Kim and S. Kumar, *Chemical Engineering Journal*, 2019, **364**, 514–529.
29 N. Morin-Crini and G. Crini, *Progress in Polymer Science*, 2013, **38**, 344–368.
30 N. Morin-Crini, P. Winterton, S. Fourmentin, L. D. Wilson, E. Fenyvesi and G. Crini, *Progress in Polymer Science*, 2018, **78**, 1–23.
31 A. Alsbaiee, B. J. Smith, L. Xiao, Y. Ling, D. E. Helbling and W. R. Dichtel, *Nature*, 2016, **529**, 190–194.
32 E. E. Leonhardt, M. A. B. Meador and K. L. Wooley, *Chemistry of Materials*, 2018, **30**, 6226–6230.
33 H. Li, B. Meng, S.-H. Chai, H. Liu and S. Dai, *Chemical science*, 2016, **7**, 905–909.
34 Z. Wang, S. Guo, B. Zhang, J. Fang and L. Zhu, *Journal of Hazardous Materials*, 2020, **384**, 121187.
35 Z.-T. Xie, T.-A. Asoh and H. Uyama, *Carbohydrate Polymers*, 2019, **214**, 195–203.
36 M. Zbair, Z. Anfar and H. A. Ahsaine, *RSC Adv.*, 2019, **9**, 5756–5769.
37 H. Koga, N. Namba, T. Takahashi, M. Nogi and Y. Nishina, *ChemSusChem*, 2017, **10**, 2560–2565.
38 M. V. Rekharsky and Y. Inoue, *Chem. Rev.*, 1998, **98**, 1875–1918.
39 J. Tang, Z. Shi, R. M. Berry and K. C. Tam, *Ind. Eng. Chem. Res.*, 2015, **54**, 3299–3308.
40 X. Du, X. Li, T. Luo, N. Matsuur, K. Kadokami and J. Chen, *Procedia Environmental Sciences*, 2013, **18**, 882–889.31



Palladium nanoparticles immobilized β-cyclodextrin cross-linked polymer monolith was prepared to apply the flow reactor. The flow reactor not only adsorbed pollutants to the residual concentration with no environmental effect, but also converted them into concentrated useful substances.