Supporting information

We have compared the effect of nZVI and ZVZ on the debromination of BDE-47 (5 mg/L) with the results shown in Fig. S1. In the system with nZVI (100 mg/L), about 35.1% of the BDE-47 was conversion after reaction for 90 min. However, when ZVZ (100 mg/L) was used, approximately 68.3% of the BDE-47 was removed during the 90 min reaction. The result indicated that the conversion of BDE-47 increase 33.2% by ZVZ compared with nZVI. This difference was probably resulted from the ZVZ (ZVZ, $E_H^0 = – 0.76$ V) is a stronger reductant than ZVI ($E_H^0 = – 0.44$ V), due to its higher reduction potential, which was kinetically more reactive and thermodynamically more favorable than ZVI, leading to more rapid and complete dehalogenation (Han et al., 2013; Blotevogel et al., 2018). Similar results were obtained by Tratnyek et al. (Tratnyek et al., 2010) who investigated the reduction dechlorination of CCl_4 by ZVZ and ZVI. Therefore, ZVZ system was adopted for the subsequent research. However, ZVZ was oxidized by water or oxygen easily, forming a Zn(II)(hydr)oxides passivation layer to cover its surface. To enhance the corrosion of ZVZ particles and promote the conversion of BDE-47, organic acids including L-ascorbic acid (AA), oxalic acid (OA), L-tartaric acid (L-TA), malic acid (MA) and succinic acid (SA) were introduced to the ZVZ system. As can be seen from Fig. S2, all of the reductive and non-reductive (SA) organic acids enhanced the conversion of BDE-47, compared with the case of the ZVZ alone. Among these, AA was particularly effective organic acids in terms of promoting the conversion of BDE-47. This could due to the molecular structure of dienol structure and lactone ring in the ascorbic acid, and previous studies have shown that the high reduction and dissolution reactivity of AA (Stone and Morgan, 1984; Kleszczewska, 1999; Zumreoglukaran, 2006). Thus, reduction characteristics of BDE-47 in the system of ZVZ were investigated by addition of AA.

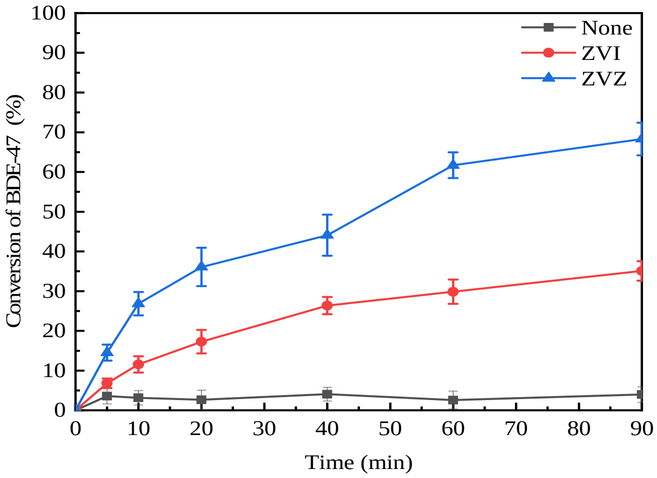

Fig. S1 Effect of different systems on BDE-47 removal (100 mg/L ZVZ, 100 mg/L ZVI, methanol/H_2O = 40/60 (v/v), and pH = 4.00)

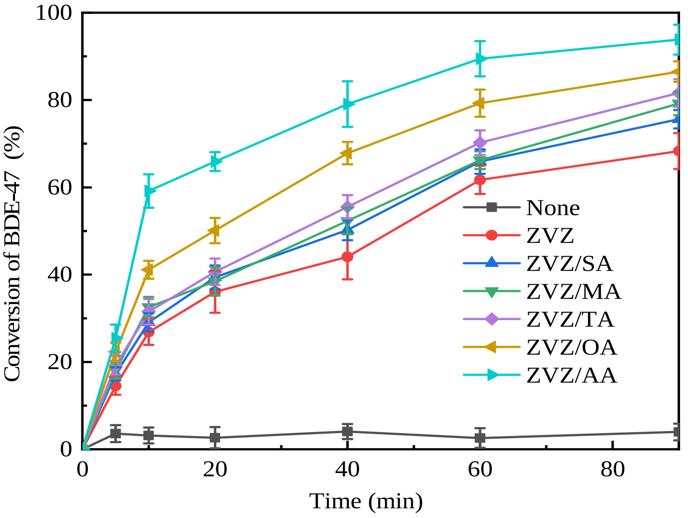

Fig. S2 Effect of different reductive organic acids on BDE-47 removal (100 mg/L ZVZ, 3 mmol/L organic acids, methanol/H_2O = 40/60 (v/v), and pH = 4.00)

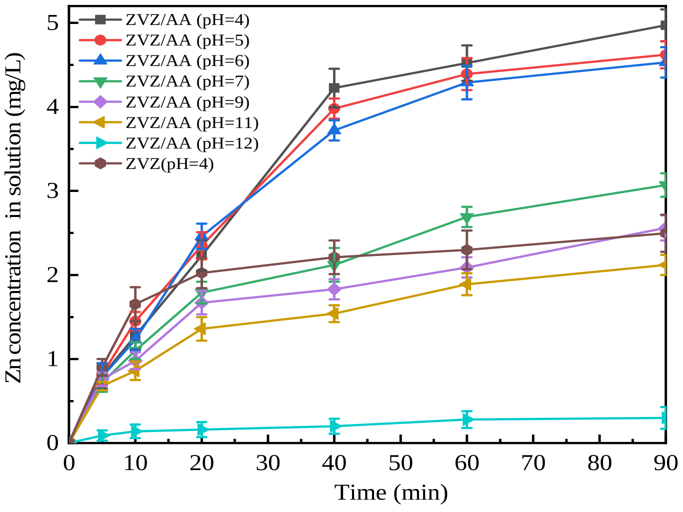

Fig. S3 Zn concentration in solution change during BDE47 degradation (100 mg/L ZVZ, 3 mmol/L AA, methanol/H_2O = 40/60 (v/v))

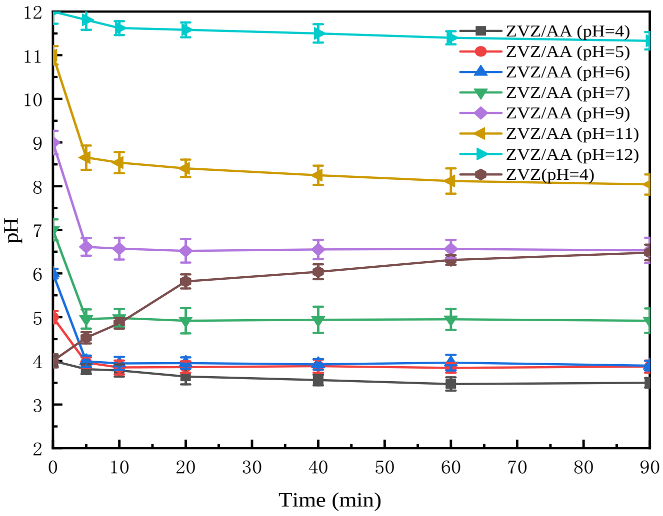

Fig. S4 The change of pH during the reaction (100 mg/L ZVZ, 3 mmol/L AA, methanol/H_2O = 40/60 (v/v))

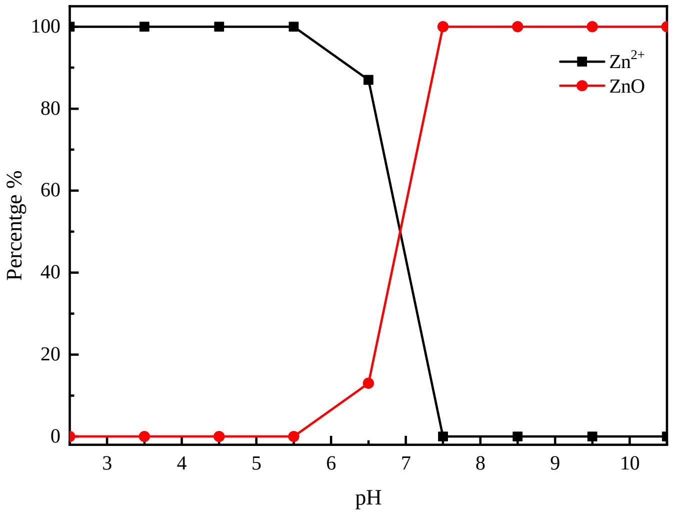

Fig. S5 Species distribution of Zn(II) at a pH range of 2.50 to 11.50

The zeta potential is a significant parameter that associated with the particle electrostatic interactions and stability of ZVZ (Mukherjee et al., 2016). The surface charges of the ZVZ particles were determined, and the results are shown in Fig. S6. The Zeta potential of the ZVZ decreased from 21.33 mV to 15.94 mV with an increasing water proportion in solution from 30% to 60%, it is possible result from the week chelation between methanol and ZVZ, due to the hydroxyl group in methanol, and accelerating the corrosion of ZVZ. However, the observed difference between the Zeta potential of the ZVZ at different water proportion were not significantly influence the removal of the BDE-47.

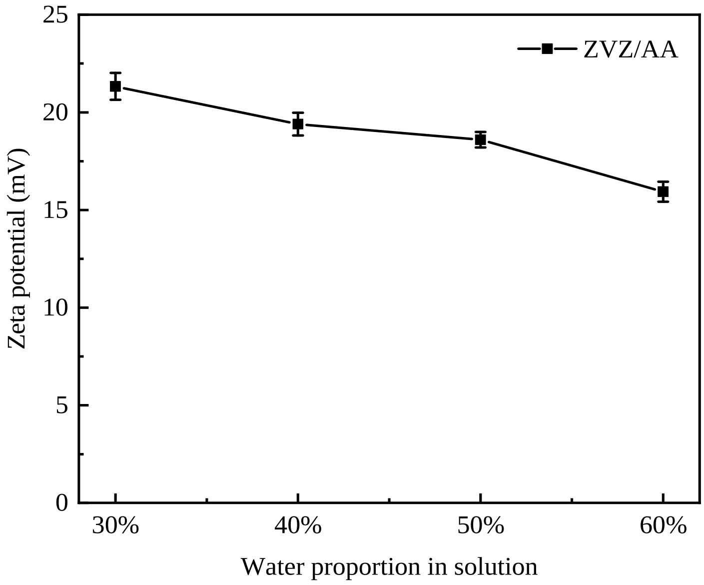

Fig. S6 Effect of water proportion in solution on Zeta potential of ZVZ in the ZAZ/AA system

Figure S7 showed the zeta potential of ZVZ in the ZAZ/AA system in different initial solution pH, and the values in parentheses at the horizontal axis means the solution pH after adding 100 mg/L ZVZ and 3 mmol/L AA into the solution. The zeta potentials of original solution pH = 4.00, 5.00, 6.00, 7.00, 9.00, 11.00, and 12.00 were +15.89, +16.51, +16.23, +6.78, +5.22, –1.10, and –6.91 mV, respectively. During the pH lower than 9.00, the ZVZ carried positive surface charges, while pH was higher than 11.00, the ZVZ possessed a negative charge. Generally speaking, a system has the higher absolute value of zeta potential, and the better the electrostatically stability of the system is (Huang et al., 2009). Figure S7 illustrated the ZVZ in original solution pH = 4.00, 5.00, and 6.00 were the most stable and relatively hard to aggregation among the different pH conditions. While the zeta potentials of ZVZ in the original solution pH = 11.00 are –1.10 mV around to zero, owing to the weaker electrostatic repulsion, the ZVZ could be more susceptible to aggregation, thus decreasing the reactivity of ZVZ in the ZVZ/AA system. Previous studies have shown that the zeta potential taking place at zero with maximum instability and agglomeration (Mukherjee et al., 2016). In addition, these results are consistent with the results of the removal of BDE-47.

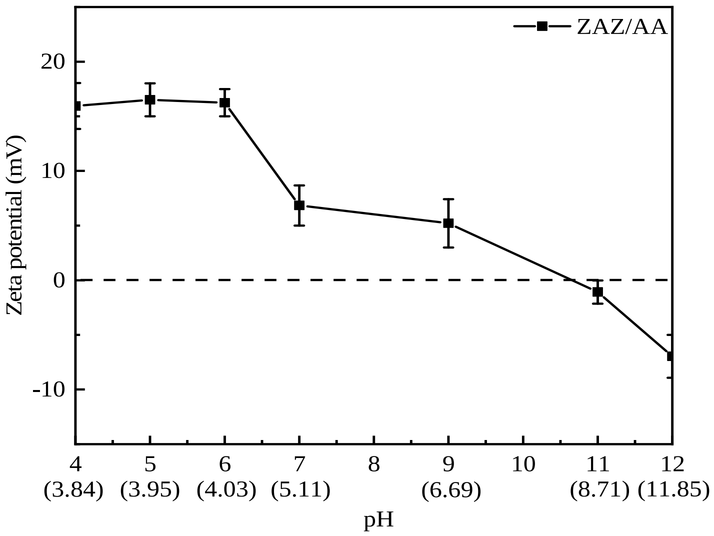

Fig. S7 Effect of solution pH on Zeta potential of ZVZ in the ZAZ/AA system

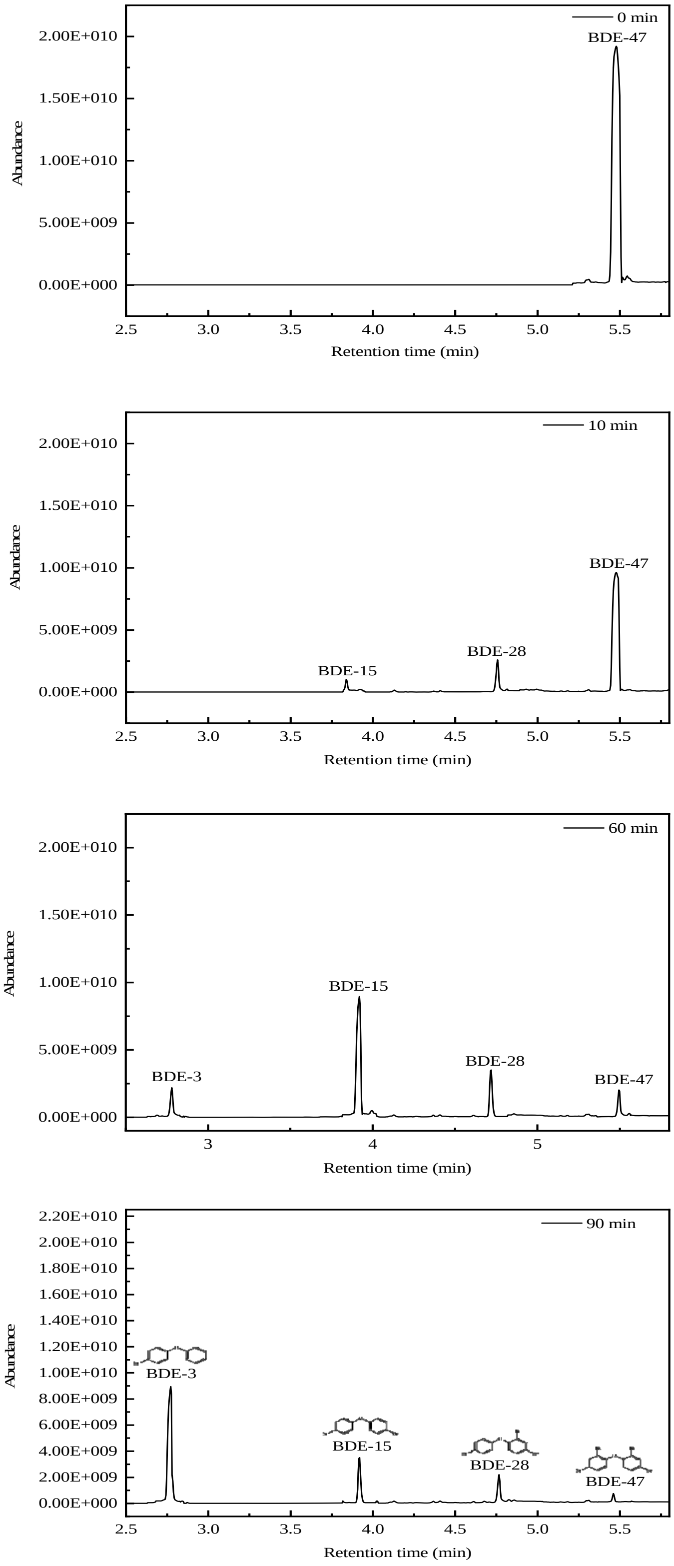

Fig. S8 GC-MS chromatogram results of the intermediates for BDE47 degradation by ZVZ/AA at different time

The reaction kinetics of BDE-47 conversion by different reaction conditions all followed pseudo-first-order kinetics, in the ZVZ/AA system, and the rate constants are summarized in Table S1.

Table S1 Efficiencies and pseudo-first-order kinetic constants for BDE-47 transformation during 90 min reduction using ZVZ/AA system operated by different parameters

Different reaction conditions		Conversion efficiency (%)	Kinetic constants (k, h^{-1})	R^2
different systems	ZVZ	68.3	0.74	0.96
	AA	13.7	0.084	0.93
	ZVZ/AA	93.8	1.78	0.95
water proportion	30%	7.39	0.050	0.90
	40%	46.0	0.37	0.92
	50%	64.8	0.609	0.89
	60%	93.8	1.78	0.95
ZVZ dosage	50 mg/L	75.7	0.91	0.98
	80 mg/L	79.5	0.96	0.92
	100 mg/L	93.8	1.78	0.95
	200 mg/L	94.5	1.85	0.93
AA addition amount	1 mmol/L	74.1	0.87	0.91
	2 mmol/L	82.6	1.06	0.94
	3 mmol/L	93.8	1.78	0.95
	4 mmol/L	94.84	1.89	0.96
original solution pH	4	93.8	1.78	0.95
	5	90.2	1.50	0.91
	6	91.7	1.59	0.93
	7	76.9	0.95	0.94
	9	74.1	0.78	0.97
	11	69.4	0.74	0.97
	12	85.9	1.29	0.92

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