Supplementary Material

One-pot Synthesis of Highly Active Ni/Fe Nano-bimetal by Simultaneous Ball Milling and In-situ Chemical Deposition

▪ Shuo-Shuo Zhang [a, †], Ning Yang [a, †], Shou-Qing Ni [a, *], Vinothkumar Natarajan [b], Hafiz Adeel Ahmad [a], Shiping Xu [a], Xu Fang [c], Jinhua Zhan [b, *]

▪ [a] *Shandong Provincial Key Laboratory of Water Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Shandong University, No. 27 Shanda South Road, Jinan 250100 Shandong, PR China*

▪ [b] *Key Laboratory for Colloid & Interface Chemistry of Education Ministry, Department of Chemistry, Shandong University, Jinan 250100, PR China*

▪ [c] *State Key Laboratory of Microbial Technology, Shandong University, Jinan 250100, PR China*

▪ [†] Shuo-Shuo Zhang and Ning Yang contributed equally to this work and share the first authorship.

▪ *Corresponding author：Shou-Qing Ni, E-mail: sqni@sdu.edu.cn. Phone and Fax numbers: + 86-531-88365660. Jinua Zhan, E-mail: jhzhan@sdu.edu.cn. Phone and Fax number: + 86-531-88365017.

Summary

Text S1. Materials

Text S2. Preparation of iron sponge and Ni/Fe bimetal prepared by chemical solution deposition (CSD) and ball milling (BM).

Text S3. Characterization of Ni/Fe bimetal

Fig. S1. Relationship between $\ln(C/C_0)$ and time as a function of milling time (Ni content = 25 *wt* %) on the dechlorination of 4-CP.

Fig. S2. Effect of milling time on the X-ray diffraction peaks of the Ni/Fe materials.

Fig. S3. TEM image of Ni/Fe-B&C.

Fig. S4. EDS analysis of the Ni/Fe-B&C.

Fig. S5. Effect of Ni/Fe dosage on the k_{obs} and k_m in the dechlorination kinetics.

Fig. S6. Effect of 4-CP concentration on the k_{obs} and k_c in the dechlorination kinetics.

Fig.S7. (a) Concentration of dissolved Fe and Ni ion in solution and (b) the total loss and respective loss rate of Fe, Ni after 10-cycle dechlorination reaction at different initial pH. (Reaction condition: Ni/Fe dose = 1 g/10mL, 4-CP concentration = 20 mg/L, Ni content = 20 wt%, each reaction time = 30 min)

Text S1. Materials

Iron sponge (>98%) was obtained from Hanbang water purification material factory (Gongyi, Henan, China). Nickel (>99%) powder was obtained from Aladdin Reagent Co., Ltd. (Shanghai). Ethanol and HPLC grade methanol was purchased from Fu Yu Fine Chemical Co., Ltd. (Tianjin, China). 4-CP (>99%) was procured from Lark Technology Co., Ltd. (Beijing, China). All the other reagents used in the experiments were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Methanol was GR grade while other chemicals used were AR grade.

Text S2. Preparation of iron sponge and Ni/Fe bimetal prepared by chemical

solution deposition (CSD) and ball milling (BM).

Pretreatment of iron sponge

3.0 g iron sponge briquette was charged into stainless steel (SS) milling pot (100 mL) with several steel balls (90g, 6 mm size). Ball milling process was performed in a planetary ball mill (QM-3SP2, Nanjing University Instrument, China) consisting of four grinding jars at a rotation speed of 270 rpm and duration of 2 h with ambient air. The obtained black powder was stored in centrifugal tubes with N_2 for future use.

Ni/Fe bimetal prepared by CSD

5g iron sponge powder prepared before was added into 50 mL of H_2SO_4 solution at pH 1.0 in a 100-mL flask and put it on a shaker at 220 rpm for 15 min. After this, the powder was washed with DI water (50 mL, pre-aerated by N_2 for 15 min) for three times. Finally, the powder treated by acid was mixed with 50 mL $NiCl_2$ ethanol solution (10 g Ni/L) and constantly shaken in a rotary shaker (220 rpm) at 25ºC for 4 h. Then, the obtained powder was separated and washed three times with deoxygenated DI water. The reaction occurs as follows;

$$Fe^0(s) + Ni^{2+}(aq) \rightarrow Fe^{2+}(aq) + Ni^0(s) \quad (1)$$

Ni/Fe bimetal prepared by BM

Different proportions of nickel powder and iron sponge powder have been poured into grinding jars with 30 g steel balls per 1 g mixture. By a planetary ball mill, mixed powders were milled at a rotation speed of 270 rpm without inert gas

protection for 2 h. The prepared powders were deposited in a centrifugal tube with N_2.

Text S3. Characterization of Ni/Fe bimetal

The scanning electron microscopy (SEM, JSM-6700F, JEOL, Japan) and energy dispersive X-ray spectroscopy (EDS, INCA X- Sight, Oxford Instruments, UK) was used to characterize the morphology and surface elemental composition of the Ni/Fe bimetallic particles prepared by BM and B&C. X-ray diffraction (XRD) analysis was performed to examine the changes of crystal before and after B&C. The Ni/Fe bimetal particles were supported on a carbon-coated Cu-grid to carry out morphological studies using a transmission electron microscopy (TEM, JEM-1011, JEOL, Japan). The electrochemical measurement (cyclic voltammetry) was carried out in a conventional three-electrode cell using a CHI 660D electrochemical work station at room temperature.

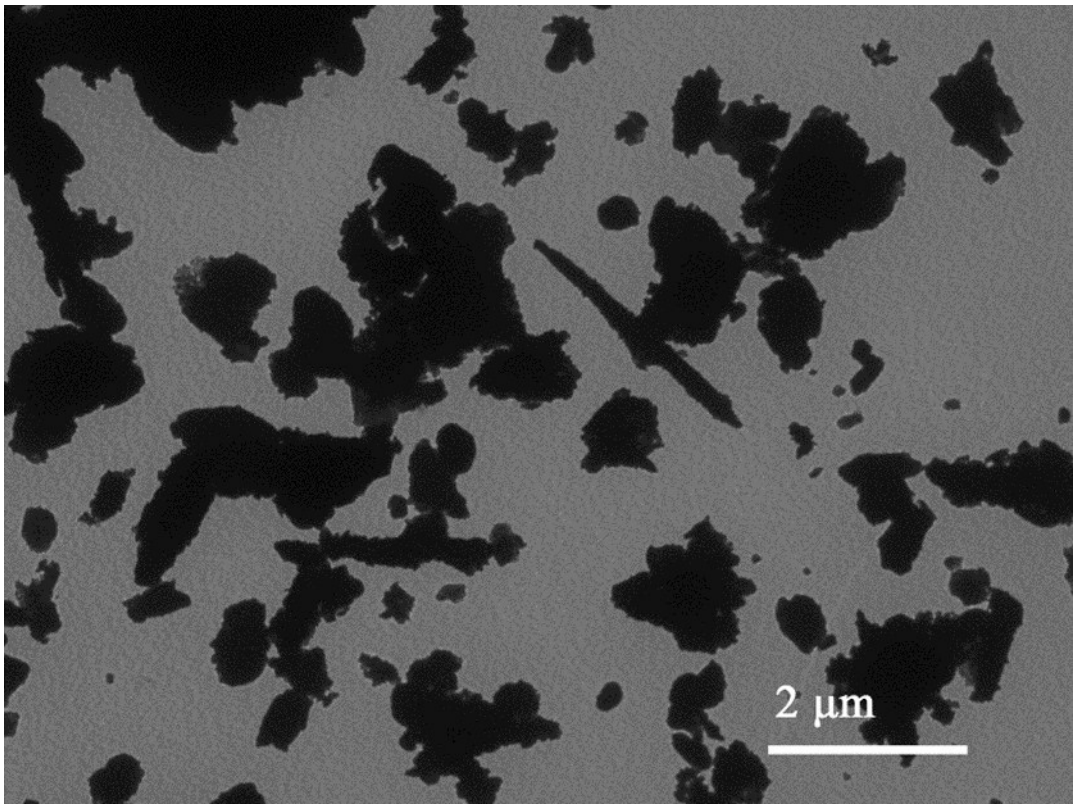


Fig. S1. TEM image of Ni/Fe-B&C.

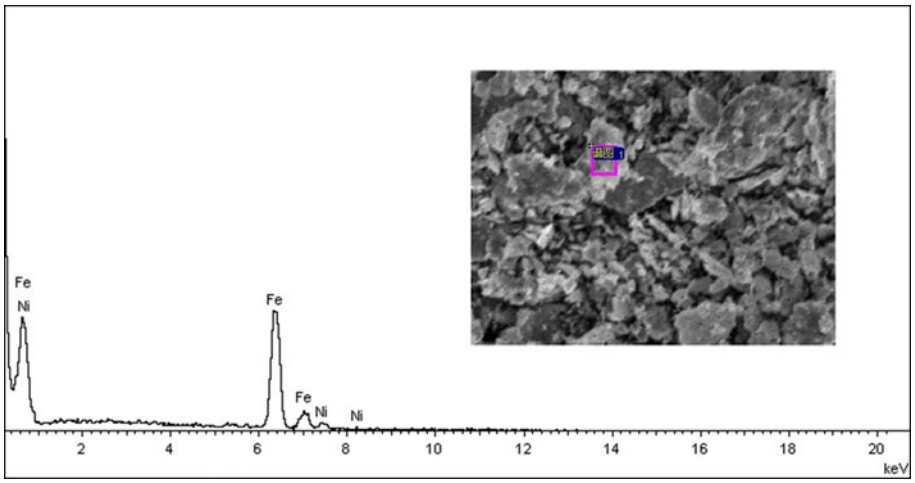


Fig. S2. EDS analysis of the Ni/Fe-B&C.

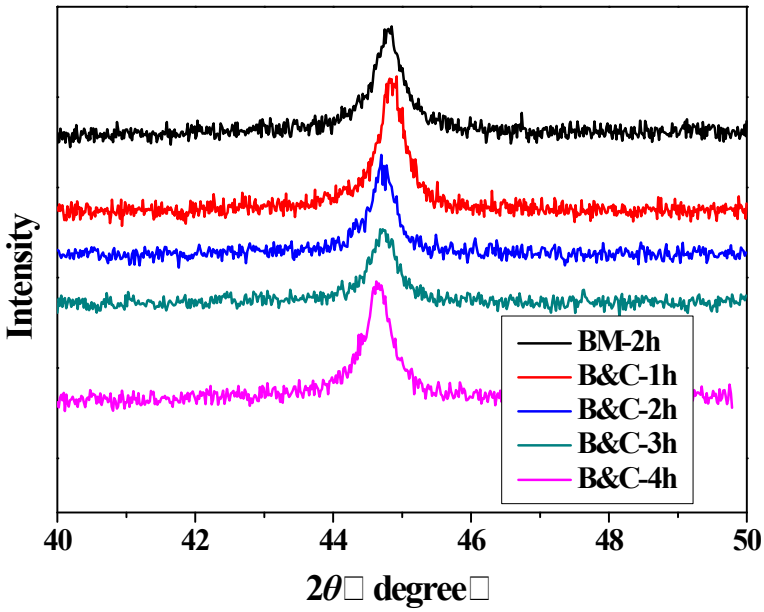


Fig. S3. Effect of milling time on the X-ray diffraction peaks of the Ni/Fe materials.

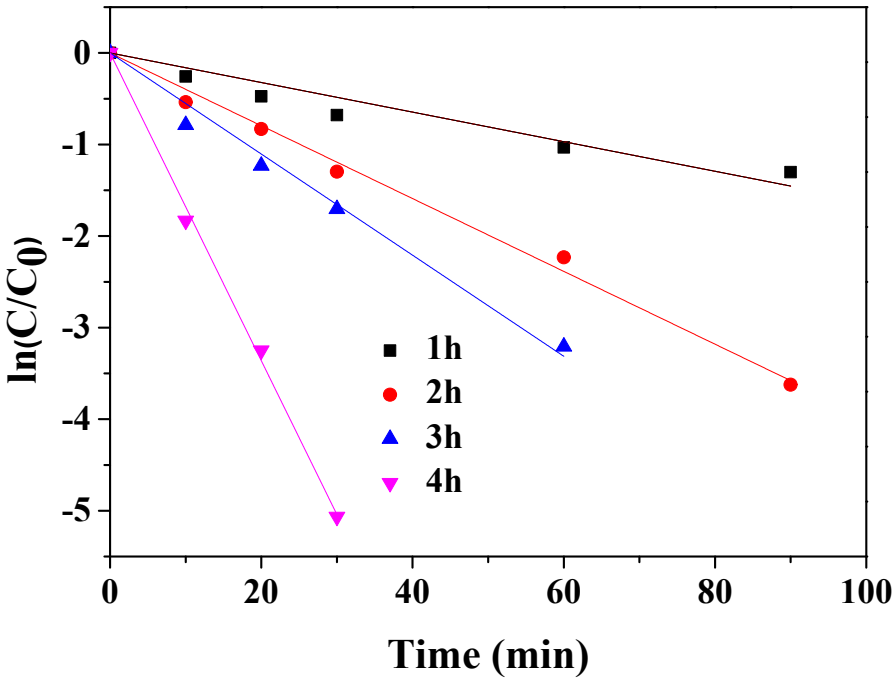


Fig. S4. Relationship between $\ln(C/C_0)$ and time as a function of milling time (Ni content = 25 *wt* %) on the dechlorination of 4-CP.

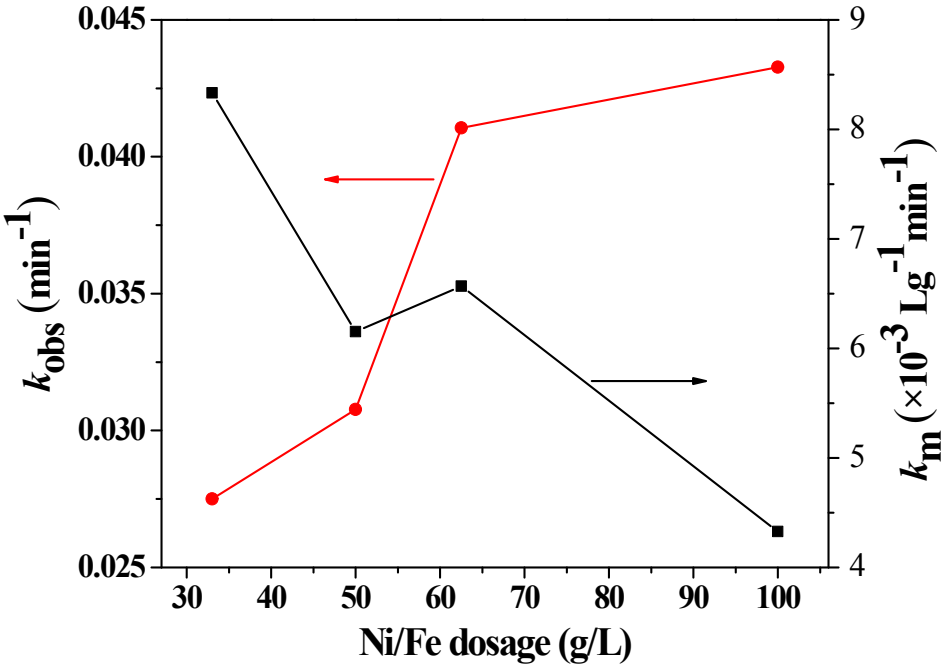
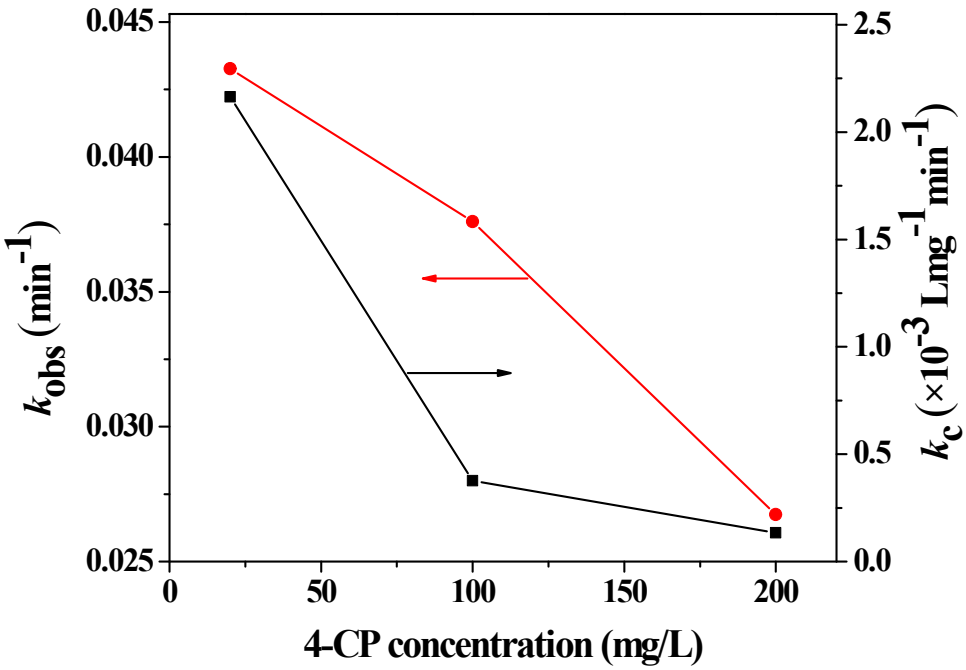


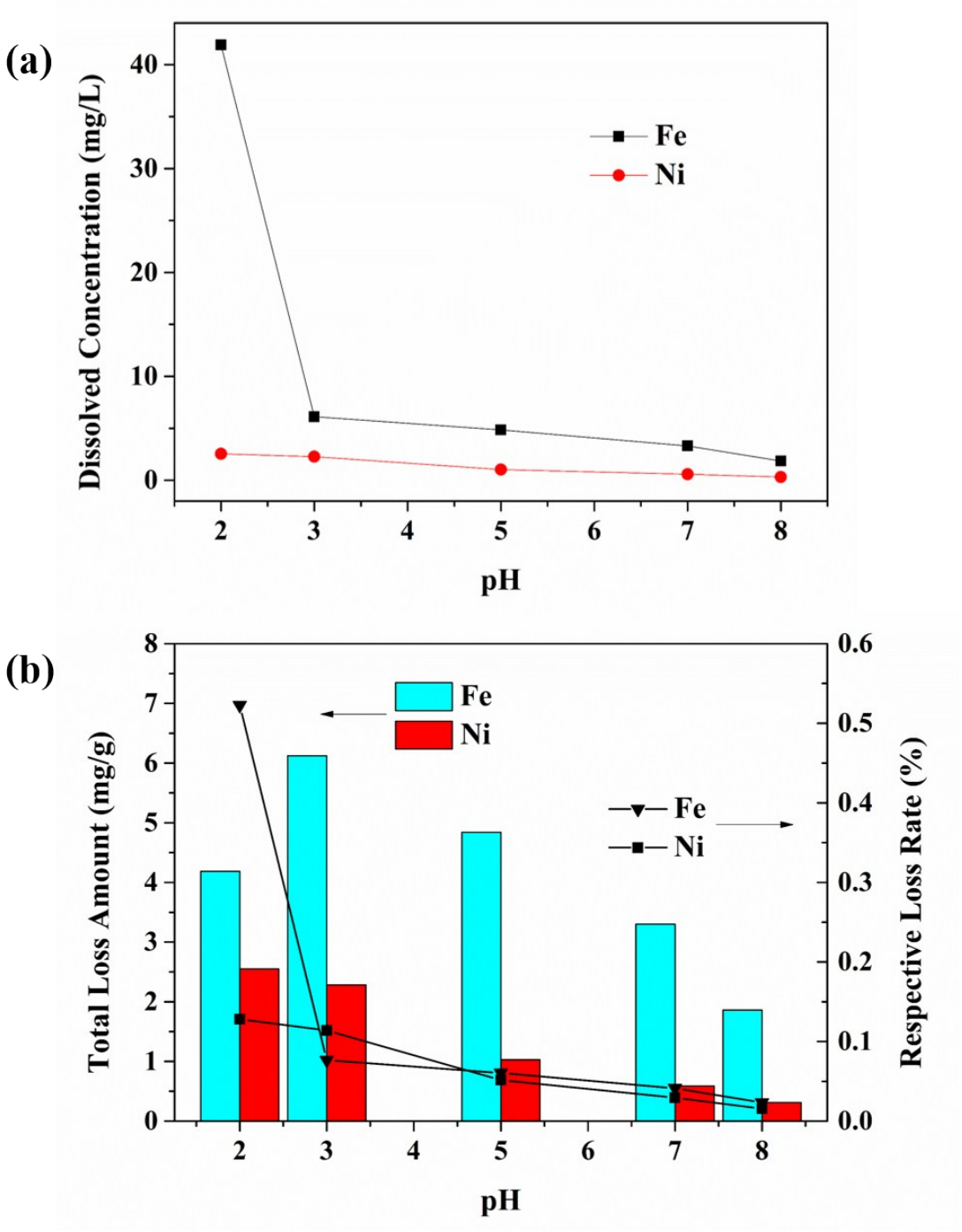
Fig. S5. Effect of Ni/Fe dosage on the k_{obs} and k_m in the dechlorination kinetics.



154

155 **Fig. S6.** Effect of 4-CP concentration on the k_{obs} and k_c in the dechlorination kinetics.

156



157

158 **Fig. S7.** (a) Concentration of dissolved Fe and Ni ion in solution and (b) the total loss
159 and respective loss rate of Fe, Ni after 10-cycle dechlorination reaction at different
160 initial pH. (Reaction condition: Ni/Fe dose = 1 g/10mL, 4-CP concentration = 20
161 mg/L, Ni content = 20 wt%, each reaction time = 30 min)