The effect of nano zero-valent iron on chain elongation

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HIGHLIGHTS:

- 5 g/L NZVI can improve caproate production by 100%.
- NZVI can improve H_2 production and prevent pH to decrease.
- *Oscillibacter Marseille-P3260* was found promoted by NZVI.

BACKGROUND: Fermentation to produce the medium chain carboxylates (MCCAs) is known as chain elongation (CE) [1]. Nano zero-valent iron (NZVI) enhance anaerobic digestion by acting as electron donor or pH buffer. Currently, the effect of NZVI on CE is not clear. However, it can be hypothesized that NZVI can promote chain elongation by following reasons: firstly, NZVI oxidation can result in Fenton-like reaction and promote ethanol upgrading. Secondly, NZVI can provide additional electron donors [2]; Lastly, NZVI can prevent pH decreasing to some extent [3]. In addition, As the reducing bacterium play an important role in CE [4], the reducing stress of NZVI might help reshape the microbial communities and benefit CE.

The main objective of this paper is to demonstrate the effect of NZVI on CE and explain the process. Different NZVI doses and ethanol to acetate ratios were considered (table 1). Hydrogen generation, pH changes and iron ions analysis help to figure out the role of NZVI during chain elongation. Moreover, 16s mRNA provided the information of microbial communities affected by NZVI.

RESULTS & DISCUSSION: Caproate production was enhanced with NZVI addition. Significant improvement can be observed when the dose was 5g/L or higher (fig. 1a). The highest concentration of caproate among group A was 21.9 mmol/L in A5, which was 36.9% higher than A0. Higher promotion by NZVI was shown in fig. 1b. B5 produced 27.2 mmol/L caproate, which was about 100% higher than B0. Besides, 22.4 mmol/L caproate was gained in C5, such was 47.6% higher than C0.

NZVI can help enhance ethanol consumption. The more NZVI has been added, the less ethanol left. In Fig. 1b., About 17.9 mmol/L ethanol was not used in B0 while merely 4.5 mmol/L ethanol was left in B5, which means 7.4% more ethanol was used when NZVI was added. NZVI oxidation can use dissolved oxygen as electron acceptor, produce hydroxyl radical, which can conduct Fenton-like reaction and oxidized ethanol. More Fe ions were found with higher dose of NZVI. So it can be assumed that NZVI played as activator for ethanol oxidation.

NZVI can promoted hydrogen generation and prevent pH to continuously decrease. NZVI can obviously improve hydrogen production by 50.0% to 71.3% in group A. Also, about 19.9% and 11.2% increase of hydrogen production can be observed in group B and C. Hydrogen production in CE can be caused by NZVI corrosion and ethanol consumption. Besides, pH value in each reactor were maintained nearly or higher than 5.4 with NZVI addition. NZVI corrosion can directly neutralized pH. Moreover, producing longer chain carboxylates with the present of NZVI also increased pH value.

According to 16s mRNA analysis, *Oscillibacter Marseille-P3260* was found unique in CE and being promoted by NZVI. Besides, *Corynebacterium*, a typical iron utilization bacterium was also significantly enriched with NZVI addition. These evidences suggest a potential electron path between NZVI oxidation and chain elongation. Also, reshaped microbial communities could improve ethanol utilization in return.

CONCLUSION: This research clearly demonstrated that chain elongation can be enhanced by NZVI addition. NZVI oxidation can active ethanol oxidation and provide electron indirectly. Meanwhile, NZVI prevented pH to decrease lower than 5.4. Moreover, Chain elongation microbiome can be reshaped by NZVI. The results indicated a new way to optimize chain elongation and a new insight on microbial interaction between chain elongation and iron oxidation.

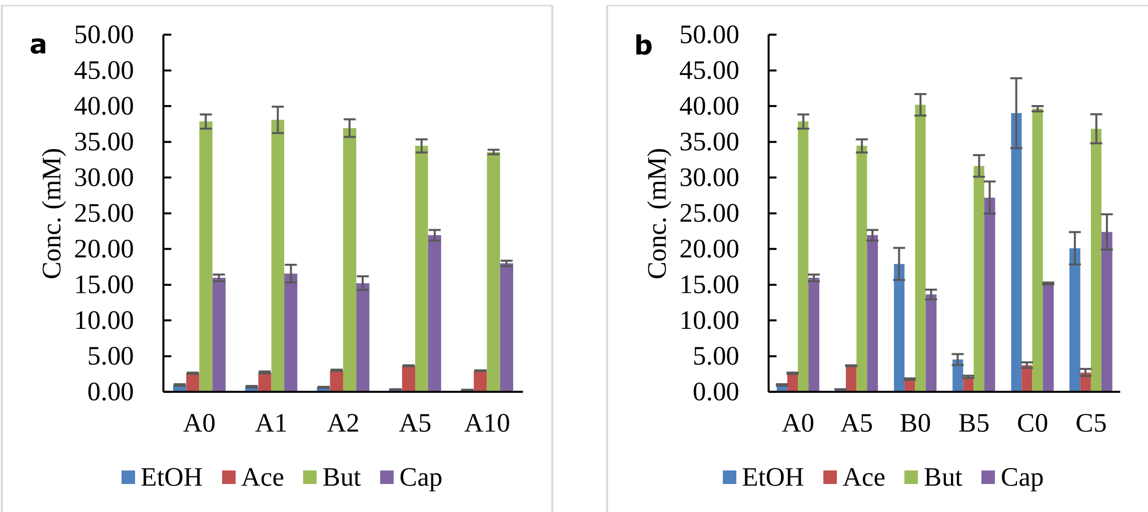

Figure 1. Ethanol and carboxylates concentrations after 14 days.

Table 1. Initial ethanol concentration and NZVI dose.

No.	Group	Mark	Initial ethanol	NZVI dose
1		A0	200 mmol/L	0 mg/L
2		A1	200 mmol/L	100 mg/L
3	A	A2	200 mmol/L	200 mg/L
4		A5	200 mmol/L	500 mg/L
5		A10	200 mmol/L	1000 mg/L
6	B	B0	300 mmol/L	0 mg/L
7		B5	300 mmol/L	500 mg/L
8	C	C0	400 mmol/L	0 mg/L
9		C5	400 mmol/L	500 mg/L

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