Electronic Supplementary Material (ESI) for RSC Advances.

Determination of Fe^0/GO composite ratio

Experiment methods

250mL of acclimated activated sludge (8.50g /L) was added to each of the seven anaerobic reactors, and the Fe^0/GO composite ratios were set as 7:1, 5:1, 2:1, 1:1, 1:2, 1:5, 1:7, and 1.0g/L of Fe^0/GO composite was added. Adjust the pH value of the influent to about 7.0, set the temperature at 40℃, and the treatment period was 24h. The pH value of influent and effluent, gas production and COD_{Cr} removal rate in each cycle were measured to determine the appropriate composite ratio of Fe^0/GO.

Analysis methods

pH values were determined by pH meter (PHS-3C/501, INESA, China) with composite electrodes. COD_{Cr} concentration was determined by COD analyzer (DR1010, HACH, USA). The produced gas volume was measured by the drainage method.

Results and discussion

As can be seen from Fig.S1,S2 and S3, when Fe^0:GO was 5:1, the effluent pH of the system was about 7.6, no serious acid accumulation was caused, the maximum gas production was stable at about 530mL, and the maximum COD_{Cr} removal rate in the system was about 84%. Compared with other composite ratios, the organic wastewater treatment effect in the system was the best under this ratio. When the composite ratio was 2:1, the treatment effect of the anaerobic system was second only to 5:1. However, when the ratio of Fe^0:GO was too high, a large amount of Fe^0 was deposited at the bottom of the system, which was not conducive to the treatment of wastewater by microorganisms. Therefore, when Fe^0:GO was 7:1, the treatment effect of microorganisms on wastewater in the system was weakened. However, when the proportion of GO was significantly higher than that of Fe^0, the gas production and COD_{Cr} removal rate of the system were significantly reduced, which may be attributed to two aspects: one was the adsorption of methane by GO itself. Gadipelli et al. found that graphene-based materials had a strong adsorption effect on methane molecules, thus the adsorption site of GO was occupied, which was not conducive to the adsorption of GO on microorganisms and pollutants in wastewater, thus further inhibiting the biochemical reaction in the reactor.[36] On the other hand, the thickness of GO sheets was at the nanometer level, and long-term exposure can cause damage to microbial cells. Therefore, a large amount of GO can have a negative impact on the entire anaerobic system.[37] So the suitable composite ratio of Fe^0/GO was 5:1.

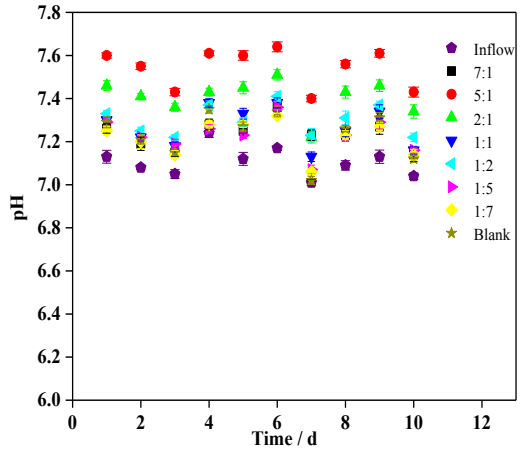

Fig.S1 Changes of pH value

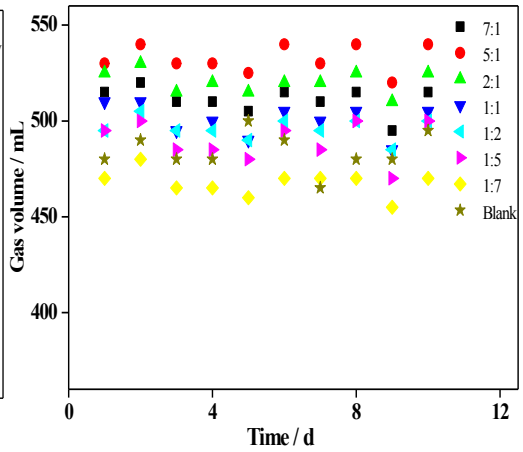

Fig.S2 Changes of gas production

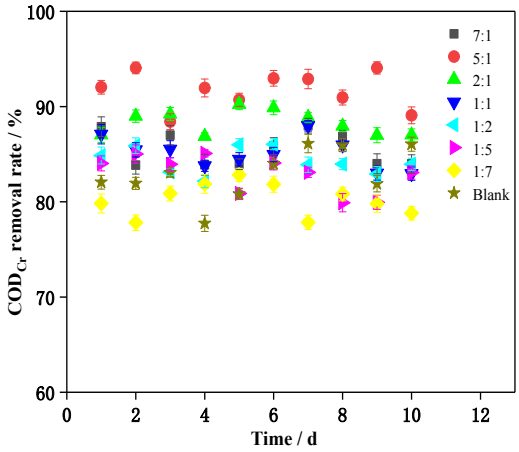

Fig.S3 Changes of removal rate of COD_{Cr}

Determination of dosage of Fe^0/GO composite

Experiment methods

With 5:1 as the composite ratio of Fe^0/GO, 7 reactors were set with Fe^0/GO dosage of 0.2, 0.4, 0.6, 0.8, 1.0, 1.2 and 1.4 g/L, respectively. The operating conditions of the systems were consistent with the determination of the composite ratio. The pH value of influent and effluent, gas production and COD_{Cr} removal rate of each cycle were measured to determine the appropriate Fe^0/GO dosage.

Analysis methods

pH values were determined by pH meter (PHS-3C/501, INESA, China) with composite electrodes. COD_{Cr} concentration was determined by COD analyzer (DR1010, HACH, USA). The produced gas volume was measured by the drainage method.

Results and discussion

As can be seen from Fig.S4,S5, and S6, when Fe^0/GO dosage was 1.2 g/L, the effluent pH of the system was about 7.5, the gas production was stable at about 540 mL, and the COD_{Cr} removal rate was about 92%. Compared with the dosage, the system had the best treatment effect on organic wastewater under this dosage. When Fe^0/GO dosage was 1.0 g/L, the wastewater treatment effect was also relatively good. When the dosage was 0.2-0.6 g/L, the effluent pH was low, and the removal rate of gas production and COD_{Cr} in the effluent was at a medium or low level. This was because the Fe^0/GO dosage was too small, and the electron transfer in the anaerobic system cannot be fully improved and the adsorption process cannot be promoted, so the COD_{Cr} removal rate and gas production were relatively low. However, when Fe^0/GO dosage was 1.4 g/L, the treatment effect of wastewater in the system was weakened. In addition to cell damage caused by nano GO sheets, excessive Fe^0 also had adverse effects on the anaerobic system. Excessive Fe^0 can produce a large amount of Fe^{2+}. Studies have shown that high concentration of Fe^{2+} can inhibit the activity of microorganisms and decrease the concentration of dehydrogenase (dehydrogenase was one of the key enzymes for microorganisms to degrade organic pollutants to obtain energy), leading to a decrease in the degradation ability of microorganisms to pollutants.[38] Therefore, when Fe^0/GO dosage was 1.2 g/L, the anaerobic system had the best treatment effect on high concentration organic wastewater.

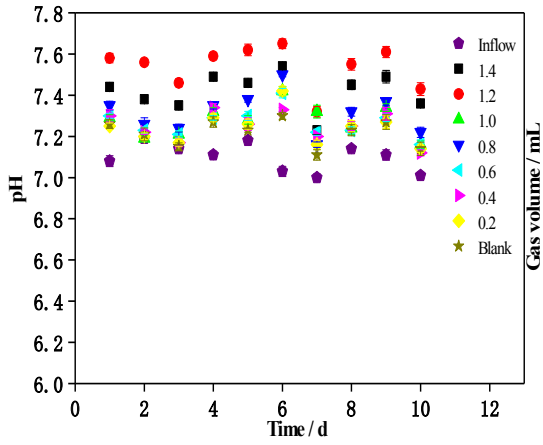

Fig.S4 Changes of pH value

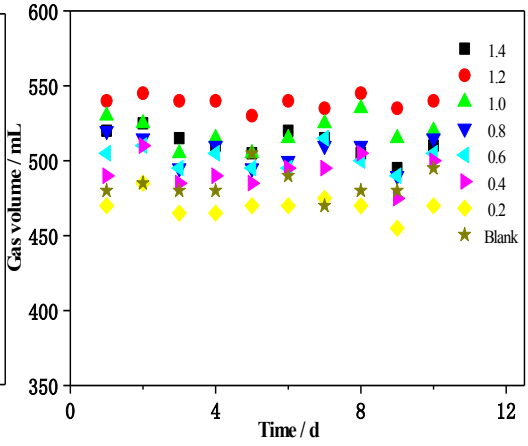

Fig.S5 Changes of gas production

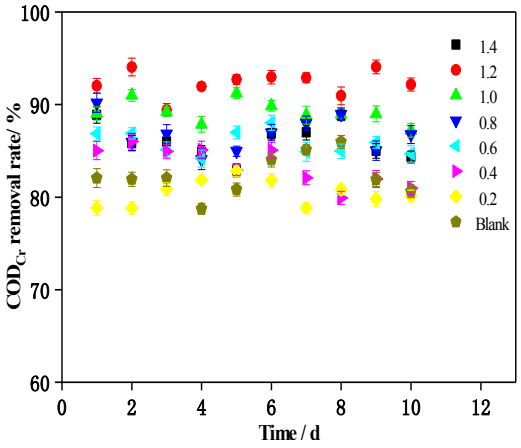

Fig.S6 Changes of removal rate of COD_{Cr}