Research article

Reuse of recalcitrant-rich anaerobic effluent as dilution water after enhancement of biodegradability by Fenton processes

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ABSTRACT

Anaerobic digestion is used to treat effluents with a lot of organics, such as molasses distillery wastewater (MDW) which is the effluent of bioethanol production from molasses. The raw MDW requires a lot of dilution water before biodigestion, while the digested MDW has high level of recalcitrants which are problematic for its discharge. This study investigated ferric coagulation, Fenton, Fenton-like (with ferric ions as catalyst) processes and their combinations on the biodegradability of digested MDW. The Fenton and Fenton-like processes after coagulation increased the MDW biodegradability defined by (BOD_5/COD) from 0.07 to (0.4–0.6) and saved 50% of H_2O_2 consumed in the classic Fenton process. The effluent from coagulation coupled to a Fenton-like process was used as dilution water for the raw MDW before the anaerobic digestion. The process was stable with volumetric loading of approx. 2.7 g COD/L/d. It resulted in increased overall biogas recovery and significantly decreased the demand for the dilution water.

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1. Introduction

Many kinds of industrial wastewater contain a high level of organic pollutants, up to dozens of g/L chemical oxygen demand (COD). When applicable, anaerobic digestion is mostly applied to treat the wastewater due to its high energy efficiency by the recovery of biogas (Chan et al., 2009). For the molasses distillery wastewater (MDW), the first challenge in anaerobic digestion is the requirement of high volumes of dilution water. For example, an alcohol distillery of average size with its feedstock as molasses, can release dozens of tons of organic rich effluent or MDW (Arimi et al., 2014). The MDW has a dark color and high COD (50–100 g/L). Due to this high COD and the presence of recalcitrants, a high dilution rate (up to 10) is required prior to anaerobic digestion (Jimenez et al., 2003; Harada et al., 1996). The anaerobically digested MDW still has high remnant COD (1–2 g/L) and dark color mainly consisting of melanoidins and related compounds which make its

disposal problematic. This necessitates some further treatment prior to its disposal (Neves et al., 2006; Pant and Adholeya, 2007; Riaño et al., 2014). The low biodegradability and dark color of the remnant COD after anaerobic digestion is caused by organic recalcitrants (Mohana et al., 2007). Therefore, further treatment is required to enhance the biodegradability for the subsequent biological treatment. On the other hand, it is also reasonable to re-use the treated anaerobic effluent of MDW as the dilution water so that the clean water requirement is reduced and the energy recovery from the organics is maximized.

The use of AOPs is the most common choice for treatment of toxic wastewater or those with recalcitrants. The most applied AOP methods are the Fenton, (Arimi et al., 2014; Ma and Xia, 2009; Oller et al., 2011), and ozonation (Battimelli et al., 2010) processes. Their applications as pre-treatment and post-treatment in various types of wastewaters are reviewed (Oller et al., 2011). However, AOPs are expensive especially if they are used on wastewaters containing high COD (Cañizares et al., 2009). This is caused by the non-selectivity of AOPs, which requires high quantities of chemicals to oxidize the organic matrix. The strategy that is currently applied to reduce this limitation of high cost is combining AOPs with biological methods. The AOP enhance the biodegradability of the effluent before the bulk COD is eliminated by biological methods (Oller et al., 2011). The use of AOPs prior to biological processes is also
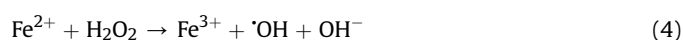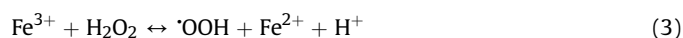
possible where the effluent is biodegradable but has high re-calcitrants, which require enhancement of biodegradability prior to the final biodigestion.

The Fenton process is one of the commonly applied AOPs and it involves oxidation by the highly reactive radicals formed by the reaction of ferrous ions and hydrogen peroxide as shown in Equations (1) and (2) below:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \ ^{\cdot}OH + OH^- \qquad (1)$$

$$^{\cdot}OH + RH \rightarrow R^{\cdot} + H_2O \qquad (2)$$
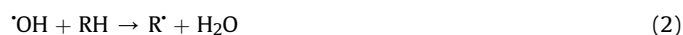
The ferrous ions are converted to ferric ions and the vice versa during the process (Deng and Englehardt, 2006). Most of the COD loss by Fenton processes occurs when the ferric sludge (oxy-hydroxides) precipitates out with some organics. The COD removal is maximized by optimizing ferric coagulation after the Fenton process through adjustment of pH. However, the coagulation after Fenton removes the oxidized organics, which could be used for the biogas production as a result of enhanced biodegradability. A re-use or biological process would be a prudent option if the Fenton effluent has substantial COD.

The Fenton process has several advantages over other AOP processes in that the process in deed does not require expensive initial installations. Most of the process costs are associated with the purchase of the chemicals including hydrogen peroxide. The optimum ratio of hydrogen peroxide to COD feed was reported as 2 (Bautista et al., 2007). It is possible to reduce the requirement of hydrogen peroxide and ferrous catalyst by the elimination of some COD before Fenton process through ferric coagulation pre-treatment. The remnant iron after coagulation can be used further as a catalyst in a process called "Fenton-like process", in order to produce radicals with hydrogen peroxide as in Equations (3) and (4) follows:

$$Fe^{3+} + H_2O_2 \leftrightarrow \ ^{\cdot}OOH + Fe^{2+} + H^+ \qquad (3)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \ ^{\cdot}OH + OH^- \qquad (4)$$

In comparison to ferrous iron, ferric iron is a more effective coagulant in the removal of melanoidin colorants and COD from the industrial wastewater (Arimi et al., 2015), and the process has an optimal pH at acid values (4–5). This implies that after ferric coagulation only a small pH change is required to obtain the optimal pH condition for the Fenton processes. The enhancement of biodegradability of wastewater by treatment with the Fenton process has been reported for several wastewaters: chip board effluent (de Souza et al., 2006), poultry manure wastewater (Yetilmezsoy and Sakar, 2008), textile wastewater (Kang et al., 2002), pharmaceutical wastewater (Tekin et al., 2006) and olive oil mill wastewater (Khoufi et al., 2006). The enhancement of biodegradability of landfill leachate by pre-treatment with Fenton process was also reported (Deng and Englehardt, 2006).

There is however no documentation on biodegradability enhancement of recalcitrants by pretreatment with ferric coagulation followed by Fenton-like oxidation using the remnant ferric ions as catalyst. The possible re-use of Fenton treated wastewater as dilution water for biological digestion has also not been reported. This study used MDW to understand deeper the performance of combined ferric coagulation and Fenton/Fenton-like processes on recalcitrants' removal in organic wastewater. The remnant metal ions, COD removal and biodegradability changes were studied. The possibility of Fenton treated effluent as a source of dilution water for raw MDW before anaerobic digestion was also investigated.

2. Methodology and materials

2.1. Materials

The source of the raw MDW was Nordzucker AG, Braunschweig, Germany. It had high COD (600 g/L) as a result of prior concentration through evaporation by the suppliers. Hydrogen peroxide (w/v 35%), sodium hydrogen sulfite (w/v 39%), and hydrogen chloride (w/v 32%) were all purchased from Merck KGaA, Darmstadt, Germany. The following other chemicals were also reagent grade and purchased from the same company: ferric chloride hexahydrate ($FeCl_3.6H_2O$), sodium hydroxide, and ferrous chloride heptahydrate ($FeSO_4 \cdot 7H_2O$).

2.2. Anaerobic digestion

The pre-concentrated MDW was anaerobically digested as explained in (Arimi et al., 2015) after it was diluted to COD 10–12 g/L with tap water before adding the following trace nutrients: calcium, nickel, cobalt, molybdate, zinc, manganese and copper salts. The main parameters of digested MDW included: COD 1000–1300 mg/L, BOD_5 60–150 mg/L, conductivity 4–5 mS/cm, and pH 7–8.

2.3. Direct Fenton

The digested MDW had its pH adjusted to 3 using sulfuric/hydrochloric acid, after which several volumes of 100 mL were measured and transferred into labeled beakers of 200 mL. Hydrogen peroxide (2 g/L) and different amounts of $FeSO_4 \cdot 7H_2O$ was added into each beaker. In the second experiment, each beaker had 168 mg/L Fe^{2+} in form of $FeSO_4 \cdot 7H_2O$ plus different amount of H_2O_2 (0.6–2.33 g/L) added. All the beakers were stirred with a magnetic stirrer at 60 RPM at room temperature. After 4 h reaction, excess 39% sodium hydrogen sulfite (volume equal to 30% H_2O_2 used) was added to eliminate the unreacted H_2O_2. The stirring was stopped and the beaker content allowed to sediment down. The clarified water was adjusted to pH 5 using 10 M NaOH. The liquid was again allowed to stand still for more coagulation to take place. The clarified top layer was decanted and analyzed for COD and BOD_5.

2.4. Coagulation plus classic Fenton or Fenton-like oxidation

The pH of anaerobically digested MDW was adjusted to 5 with sulfuric acid, and 120 mL samples were put in 200 mL beakers. To allow more iron to be introduced later as a catalyst in Fenton or Fenton-like process, half of the optimal coagulant dose (half the value that produced maximum COD removal): 112 mg/L Fe^{3+} in form of $FeCl_3$ was used in the first step of coagulation. The coagulant was spiked into each beaker which was immediately stirred at 500 RPM with a magnetic stirrer for 3 min. The stirring speed was decreased to 60 RPM for 20 min. The mixture was allowed to stand still for 30 min for the precipitation to take place. The upper clear liquid was decanted, 100 mL of which was transferred into a separate 200 mL beaker with pH adjusted to 2.5–3 and used for the classic Fenton or Fenton-like process.

In the classic Fenton experiment, 33.6 mg/L Fe^{2+} was added to each of 100 mL sample with varying amount of H_2O_2 (166.5–1665 mg/L). Varying amounts of Fe^{2+} (5.6, 11.2, 22.4, 33.6, 44.8, 56.2 g/L) were also added into separate 200 mL beakers with a constant amount of 1 g/L H_2O_2. The beakers were stirred at 120 RPM for 3 h. The pH was re-adjusted to 5 with 10 M NaOH and the reaction was also stopped by adding three drops of sodium hydrogen sulfite. In Fenton-like experiment, the Fe^{3+} was added as