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Original Research

# Modified natural zeolite as heterogeneous Fenton catalyst in treatment of recalcitrants in industrial effluent☆

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ABSTRACT

Industrial effluents with high recalcitrants should undergo post-treatment after biological treatment. The aim of this study was to use cheap and abundantly available natural materials to develop heterogeneous Fenton catalysts for the removal of colored recalcitrants in molasses distillery wastewater (MDW). The pellets of zeolite, which is naturally available in many countries, were modified by pre-treatment with sulphuric acid, nitric acid and hydrochloric acid, before embedding on them the ferrous ions. The effects of pH and temperature on heterogeneous Fenton were studied using the modified catalysts. The sulphuric acid-ferrous modified catalysts showed the highest affectivity which achieved 90% color and 60% TOC (total organic carbon) removal at 150 g/L pellet catalyst dosage, 2 g/L $H_2O_2$ and 25 °C. The heterogeneous Fenton with the same catalyst caused improvement in the biodegradability of anaerobic effluent from 0.07 to 0.55. The catalyst was also applied to pre-treat the raw MDW and increased it's biodegradability by 4%. The color of the resultant anaerobic effluent was also reduced. The kinetics of total TOC removal was found to depend on operation temperature. It was best described by simultaneous first and second order kinetics model for the initial reaction and second order model for the rest of the reaction.

## 1. Introduction

Many industrial processes generate a lot of wastewater which cannot be disposed off into natural bodies without causing pollution even after biological treatment due to high concentration of recalcitrants. This necessitates appropriate secondary treatment after the primary digestion. The molasses distillery wastewater (MDW) is among the effluents which require post-treatment after biological digestion. This is because of its high recalcitrant COD (chemical oxygen demand) ( > 1.5 g/L). This COD is caused by melanoidins and related compounds. Melanoidins are the dark colored recalcitrants formed by the reaction between sugars and amino acids at medium temperature ( > 50 °C) and in basic pH medium [1]. These conditions are prevalent in sugar production process where by-products of molasses are generated. The MDW is produced in large quantities as the effluent of ethanol distilleries which use molasses as their substrates [1]. For example a firm producing bioethanol from molasses distillery wastewaters will release ten liters of effluent called molasses distillery wastewater (MDW) for every liter of bioethanol produced. The volume can be further increased by another tenfold if dilution with fresh water is done before MDW is anaerobically digested [2]. This high water requirement in such processes can be offset by reusing the treated effluent. However, the possible reuse of anaerobically digested MDW as dilution water is only tenable if the recalcitrants are first removed or their biodegradability increased.

One of the methods commonly applied to increase the biodegradability of the recalcitrants in wastewater is by the use of Advanced Oxidation Processes (AOPs): Ozone [3], UV/$H_2O_2$ [4], ultrasonic [5], Fenton [6], electrochemical [7], photocatalysis [8] and ultraviolet oxidation [9]. The use of ozonation as post-treatment has an advantage of low sludge formation but its application is limited by the high installation and operation costs. The problem becomes even more complicated if the process involves high daily volumes of effluents. Another limitation of ozonation process is the low COD removal especially where the influent has reasonably high COD. The UV and photocatalysis processes are also costly because of the high energy requirements. Moreover, the later process is in research stages and its industrial application in complex wastewater is not yet optimized. The

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Fenton process is simple to operate and moderately effective. However, the process operates at very low pH values (2–3) and the oxidation chemicals are costly. The electrochemical process has the challenge of application in complex effluents because there are many types of particles, compounds, cations and anions which interfere with the process. The application ultrasonic oxidation in treatment of complex effluent is limited by the high installation/process costs as well as low COD removal.

Wastewater treatment by the Fenton process involves oxidation of COD by the highly reactive hydroxyl radicals formed by the reaction of ferrous ions and hydrogen peroxide. The enhancement of biodegradability of wastewater after the treatment with Fenton process has been reported before in treatment of chip board effluent where the $BOD_5$/COD ratio was raised from 0.09 to 0.33 [10]. Another study with Fenton pre-treatment process reported some improvements in COD removal from 90% to 99% in poultry manure wastewater after anaerobic digestion with upward anaerobic sludge blanket (UASB) reactor [11]. In addition to improving biodegradability of the effluent, the Fenton process removes the remnant COD, toxicity and the color of the effluent. The Fenton process combined with coagulation was reported to effectively remove the textile color [6]. Another study on Fenton oxidation process with some pharmaceutical wastewater observed 45–65% reduction of COD by the oxidation step; the overall COD removal was 98% when a biological step was added [12]. This demonstrates that the toxic wastewater had clearly become biodegradable after Fenton oxidation. The electro-Fenton pre-treatment has also been applied in olive oil mill wastewater pre-treatment where more than 65% polyphenols were removed; this improved the subsequent anaerobic digestion [13]. Similar reports on enhanced biodegradability of landfill leachate after pre-treatment with Fenton process have also been documented [14]. Fenton oxidation has also been applied in the removal of lignin from cellulosic biomass before anaerobic digestion and thereby increasing its methane yield [15].

The classical Fenton process is the simplest and the oldest form of Fenton processes and has been used in treatment of various wastewaters [9,16]. The process has several limitations which include: high sludge formation, operation at adverse pH values (normally 2–3), high remnant metal ions in the sludge and treated effluent, inactivation of heavy metal ions in the sludge by formation of hydroxide complexes and the need to separate the catalyst after the process. In pursuit of overcoming these limitations, several other processes have been developed from the classic Fenton process. The first process was to couple light energy from ultraviolet source or emissions from the sun in a process called photo-Fenton oxidation [17]. The extra energy helps in dissociation of the hydrogen peroxide molecules for easy reactivity. It also helps to convert ferric ions back to ferrous ions catalyst after the reaction. The process has been instrumental in improving the kinetics and the performance of Fenton process including: decreasing the demand for the catalyst and improving the color removal [18,19]. There are also reports of enhanced performance in COD removal, increase in biodegradability [20] and detoxification of toxic effluents [21,22] after treatment with photo-Fenton oxidation. However, the photo-Fenton process does not address the other limitations especially the low pH operation and the problem of high heavy metal ions in the final effluent. The addition of energy requirement also adds to the process cost.

Another key modification to the classic Fenton process aims at eliminating the limitations of low pH operation and recovery of spent catalyst from the effluent by the use of heterogeneous Fenton processes. It entails embedment of the ferrous catalyst and the acid group on a carrier material. By limiting the catalyst supply in the effluent, the method ensures that minimal sludge is formed by coagulation process. In addition, the amount of heavy metal ions in the sludge and treated effluent is minimized. The catalyst ions are supposed to be slowly released from the embedment where they react with the hydrogen peroxide to form the radicals. The need for extremely low operation pH can also be avoided by immobilising the acid on the carrier material. After the process, the heterogeneous catalysts are easily separated from the effluent and sludge for reuse.

Many groups have reported different materials as possible carrier medium for heterogeneous Fenton oxidation: synthetic zeolite [23], clay [24], activated carbon [25] and modified iron-carbon catalyst [26]. The main limitations of the most suggested material is either low effectiveness or the high costs. Activated carbon and synthetic zeolites adsorbents are the most studied heterogeneous carrier materials because of their high effectiveness. The former is limited by its high costs as well as the production of large amount of sludge. Zeolites are the compounds of aluminosilicates and can be artificially synthesized by reacting sodium aluminate with sodium silicate. The ratio of silica to the alumina determines the type (X or Y) of the synthetic zeolite. The Y type of synthetic zeolite is the most commonly applied type in preparation of heterogeneous Fenton catalysts [23,27,28]. One way of producing heterogeneous Fenton catalyst from synthetic zeolite is by impregnation of ferric ions followed by calcinations [29]. Another process is by the ion exchange for example where the sodium in zeolite containing high sodium content is replaced with ferric ions [28]. The synthetic zeolites have been used as heterogeneous material for Fenton oxidation in wastewater treatment where high effectiveness ( > 80% TOC and 100% color removal) was reported [23]. It was also observed that the catalyst was able to work well at pH 5 and the accumulation of heavy metals in the treated effluent was reduced by 17 fold compared to homogeneous Fenton process [23].

The high cost of the synthetic zeolites is the main limitation in its application especially in the developing countries. Natural zeolites occur on earth surface in many parts of the world. They are used commercially as adsorbents to remove dyes [30] and heavy metals [31]. The natural zeolite materials are cheap due to their abundance and have been tried before as adsorbent for the removal of color in industrial effluent but not with great results [32]. The main limitation of natural zeolite as a catalyst carrier in Fenton process is its low effectiveness especially in the effluents loaded with high organic matter. The current study seek to develop an effective heterogeneous Fenton catalysts which will overcome the limitation of the classic Fenton oxidation by operating at high pH, reducing the sludge formation, minimizing the remnant heavy metal ions in the treated effluent, and being recoverable after use for future reuse. In addition, the catalyst should be cost effective for application in treatment of various effluents. The investigations tested several modifications of natural zeolite as the first steps in attempt to develop a cheap and more effective carrier material for heterogeneous Fenton process. Moreover, the kinetics of the heterogeneous Fenton process and the effect of the temperature and pH were also investigated for the selected methods of zeolite modification.

## 2. Materials and methods

### 2.1. Materials

The Nordzucker AG, Braunschweig, Germany provided the raw MDW which had been pre-concentrated to 600 g/L and packaged in 20 l plastic containers. The natural zeolite purchased from Egezeolit Company, Turkey. Hydrogen peroxide (w/v 35%), sodium hydrogen sulphite (w/v 39%), and hydrochloric acid (w/v 32%) were all purchased from Merck KGaA, Darmstadt, Germany. Other chemicals also purchased from the same company include: Nitric acid, sulphuric acid, sodium hydroxide, trace element compounds and ferrous chloride heptahydrate ($FeSO_4{\cdot}7H_2O$) which were of laboratory grade.

### 2.2. Anaerobic digestion

The pre-concentrated MDW was diluted to COD 10–12 g/L with tap water. The trace nutrients were added, including calcium, nickel, cobalt,