

## Original Research

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

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## ARTICLE INFO

## Keywords:

Fenton  
Heterogeneous  
Wastewater  
Zeolite  
Treatment

## 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<sub>2</sub>O<sub>2</sub> 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 its 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<sub>2</sub>O<sub>2</sub> [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

Peer review under responsibility of Chinese Materials Research Society.

E-mail addresses: [marimi@mu.ac.ke](mailto:marimi@mu.ac.ke), [arimison@yahoo.com](mailto:arimison@yahoo.com).<http://dx.doi.org/10.1016/j.pnsc.2017.02.001>

Received 18 December 2015; Received in revised form 17 February 2017; Accepted 28 February 2017

Available online 28 March 2017

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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<sub>5</sub>/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<sub>4</sub>·7H<sub>2</sub>O) 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,

molybdate, zinc, manganese, copper salts, and pH was adjusted to 7 with sodium hydroxide. The substrate was transferred to a 3-l tank with a Rushton stirrer as an anaerobic bioreactor. The inoculum pellet sludge was obtained from a brewery wastewater treatment plant and was added to 30% of the bioreactor volume. The temperature of the bioreactor was controlled at 35 °C by a water jacket. The reactor was operated in a sequence batch mode with a daily substrate feed of 1.4 l. The anaerobically digested effluent was decanted after settling and stored at 4 °C for further tests. Its main parameters include COD 1000–1300 mg/L, BOD<sub>5</sub> 60–130 mg/L, conductivity 6–8 mS/cm and pH 7–8. The other characteristics of the effluent have been documented [33].

### 2.3. Modification of natural zeolite pellets

Natural zeolite pellets were washed with tap water and rinsed with distilled water before drying overnight in an oven at 105 °C. Various treatments were carried out on the pellets as preparation for embedding ferrous ions on it. For each treatment, 200g zeolite pellets were put in a 500 mL labelled beaker and 100 mL of 2 M of the treating solution (sulphuric acid, nitric acid, hydrochloric acid or sodium chloride) added. The mixtures in the beakers were shaken at 120 rpm for 6 h by a rotor shaker which was placed inside an oven maintained at 60 °C. The excess treating solution was then poured out and the zeolite pellets dried overnight in the oven at 100 °C. After cooling, 100g samples of this zeolite were weighed into separate beakers clearly marked and 100 mL of 0.2 M FeSO<sub>4</sub> solution added into each beaker. For control experiment, no acid/base pre-treatment was done but the catalyst was embedded directly on the pellets as described [27]. The beakers were shaken by a rotor shaker placed in the oven at 60 °C at 120 rpm for 6 h. The excess solution was kept for analysis and the pellets washed ten times with excess tap water to remove unbound ferrous ions. The pellets were rinsed twice with distilled water and dried overnight in oven at 105 °C. They were then cooled and weighed before use. All the water from the washings was added to the unused FeSO<sub>4</sub> solution from the oven. The solution was mixed to homogeneity and a sample was drawn for iron content analysis by the AAS machine.

### 2.4. Heterogeneous Fenton process

The pH of anaerobically digested MDW was adjusted to a set value (1.5, 2, 3, 4, 6 or 7) by use of 10 M HCl. Different amounts of sulphuric acid modified zeolite (3–20g) were placed in the beaker before adding 100 ml of pH adjusted MDW. This was followed by adding 500 mL of 35% H<sub>2</sub>O<sub>2</sub> while shaking at 120 rpm with a rotor shaker. The samples (2 mL each) were taken at different time interval and their pH was increased beyond 10 by adding 2 drops of 10 M NaOH to stop any further reaction and induce coagulation. The experiment was repeated without taking samples and the final treated effluent was coagulated by adjusting its pH to 4–5 using NaOH and HCL. The mixture in the beaker was allowed to clarify by allowing it to sit still for 20 min. The clarified top effluent was pipetted out and used for BOD and remnant iron content analysis. The experiment was repeated using catalyst pellets modified by other modifying solutions.

The best performing modifications in terms of color and TOC removal were H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>; the two were used to perform further investigations. The optimal catalyst dose was determined by carrying out the experiment with various catalyst dosages and optimal H<sub>2</sub>O<sub>2</sub>:COD ratio of 2 [34]. The optimal reactants conditions were used to study the effects on the temperature by operating at different temperatures (20–60 °C) and pH values (2.5–7). All the tests were repeated twice or thrice for duplicity purposes.

The optimal dosage of sulphuric acid modified zeolite catalyst (0.5 g/l) was used to study the biodegradability changes with time. The laboratory beakers; 200 mL capacity were filled with 100 ml MDW which had pH adjusted to 4. Into each beaker, 15 g of the modified

catalyst was added before pouring in 500 ml of 35% H<sub>2</sub>O<sub>2</sub> to start off the reaction. Two beakers were withdrawn from the shaker at set time (5 min, 1 h, 2 h, 4 h and 18 h). The reaction in these beakers was stopped by adding 500 ml of sodium hydrogen sulphite solution. The pH was adjusted to 4–5 using sodium hydroxide solution. It was allowed to sit still for an hour for clarification to occur. The top clear effluent was pipetted out and used for TOC, COD and BOD<sub>5</sub> analysis.

The kinetic tests on TOC removal by heterogeneous Fenton were done with 500 ml beaker filled with 200 ml MDW at pH 3.5. Twenty grams of modified zeolite (sulphuric acid or nitric acid) was added in each beaker before pouring in 1 ml of 35% H<sub>2</sub>O<sub>2</sub> to start off the reaction. Two samples of 1.5 ml each were drawn from each beaker after a set time and placed into eppendorf tubes using a pipette. The reaction in the tubes was immediately stopped by adding into each tube two drops of concentrated NaOH solution. The tubes were shaken and allowed to sit still for twenty minutes for sedimentation to take place. The top clear portion of the effluent was pipetted out and used for TOC analysis.

### 2.5. Pre-treatment of raw MDW by heterogeneous Fenton

The test on enhancement of biodegradability was carried out with 100 mL raw MDW. The effluent with TOC (4–5) g/L and unaltered pH (4.8) were placed in labelled beakers in a shaker and various weights of sulphuric modified zeolite (1–16) g/L added. Various dosages of hydrogen peroxide were finally added to start off the reaction. The beaker contents were shaken at 120 rpm for 24 h. The end samples were taken without allowing the beaker contents to settle and their TOC and biodegradability analyzed.

### 2.6. Analysis

The total organic carbon (TOC) and dissolved organic carbon (DOC) were analyzed by Analytik Jena Multi N/C 3100 while the turbidity was analyzed by Hach 2100 AN turbidometer. The measurement of the pH was done by a WTW microprocessor pH meter. The COD was analyzed using a Hach Lange kit and the color was quantified with a Hach Lange DR 500 spectrophotometer. The remnant iron ions in the treated effluent were analyzed by AAS while the BOD was measured with an OxiTop system, according to the German DIN EN 9408. The iron bound on zeolite was calculated by subtracting the unbound iron from the total iron supplied. The unbound iron was analyzed by AAS machine from the homogenized solution containing unused ferrous solution and all the washing water for the pellets after iron embedment. The difference between the ferrous ions supplied and total amount of unbound iron quantified with AAS was used to calculate the ferrous ions embedded on the modified zeolite pellets.

## 3. Results

### 3.1. Color removal by heterogeneous Fenton system

The preliminary tests on color removal by heterogeneous Fenton with sulphuric acid modified zeolite catalysts produced the highest color removal. At room temperature, the catalyst was able to achieve almost 90% color removal with initial pH of effluent at 4 (Fig. 1a). The modification of natural zeolites by treatment with NaOH produced no improvement in the color removal and so this experiment was not continued. Among the preliminary tests made, the natural zeolite pre-treatment by hydrochloric acid had the lowest color removal at 25 °C and pH 4. For all the zeolite treatment methods tested, the optimal color removal occurred between zeolite concentrations 100–150 g/L (Fig. 1a). The choice of hydrogen peroxide concentration 2 g/L used in this experiment is based on optimal H<sub>2</sub>O<sub>2</sub>/COD ratio of 2 reported elsewhere [34]. When the recovered catalysts pellets were reused

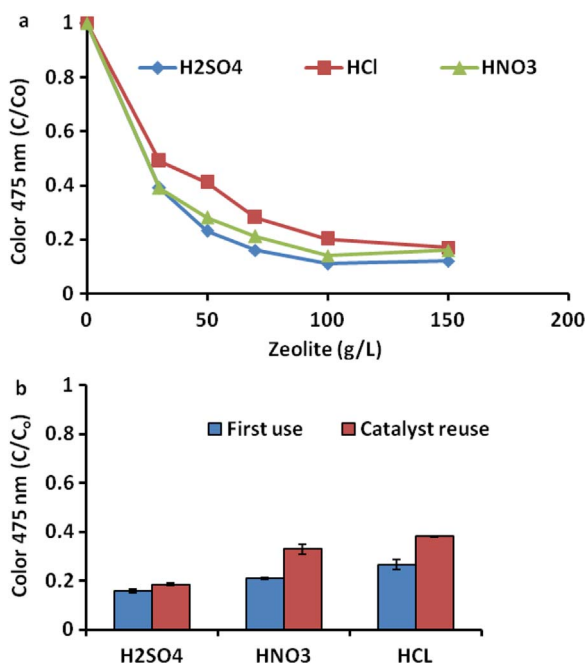


Fig. 1. Heterogeneous Fenton color removal at room temperature with 2 g/L H<sub>2</sub>O<sub>2</sub>, 150 g/L modified catalyst for: different heterogeneous catalyst dosages (a) catalyst reuse experiment, (b).

without re-modification treatment, the process was able to remove more than 80% of the original color (Fig. 1b).

3.2. TOC removal by heterogeneous Fenton process and the pH effects of the process

The recalcitrant TOC after biological digestion of MDW is between 1–2 g/L. The goal of the post-treatment is either to eliminate the TOC or make it more biodegradable especially if the effluent is to undergo some reuse or disposal in productive land. The survey of the modification process indicated that the sulphuric acid/ferrous ion pre-treatment produced the best results in TOC removal with almost 60% removal at pH 3–4 and 298 K (Fig. 2a). The reuse of the same catalyst on the similar process removed more than 40% TOC. Nitric acid modification produced catalysts with had the second best performance. However, this was only 41% TOC removal in the first run (Fig. 2a).

The performance of the modified zeolite catalysts were dependent on the initial pH of the substrate. At pH ≤2, the nitric acid modified zeolite gave the highest performance in terms of TOC removal. However, at pH ≥3, the sulphuric acid modified zeolite catalyst showed the highest TOC removal (Fig. 2b). The ability of sulphuric acid modified zeolite to perform better in TOC removal at slightly higher pH values is possibly due to its ability to adsorb and retain some acid on its surface.

3.3. Heterogeneous Fenton and the temperature effects of the process

The two best modified zeolite catalysts (sulphuric acid and nitric acid) were used to test the effect of the temperature on the MDW color removal (Fig. 3a) and TOC removal (Fig. 3b). For both sulphuric acid and nitric acid pretreated zeolite pellets, the highest temperature tested (333 K), produced the highest color removal which was over 90%. The results indicate that the removal of MDW color by heterogeneous Fenton is dependent on the operation temperature where the increase in temperature increases the color removal.

However, the effect of the temperature on overall TOC removal for sulphuric acid and nitric acid treated zeolite had different pattern, Fig. 3b. The highest TOC removal was at 303 K for the sulphuric acid

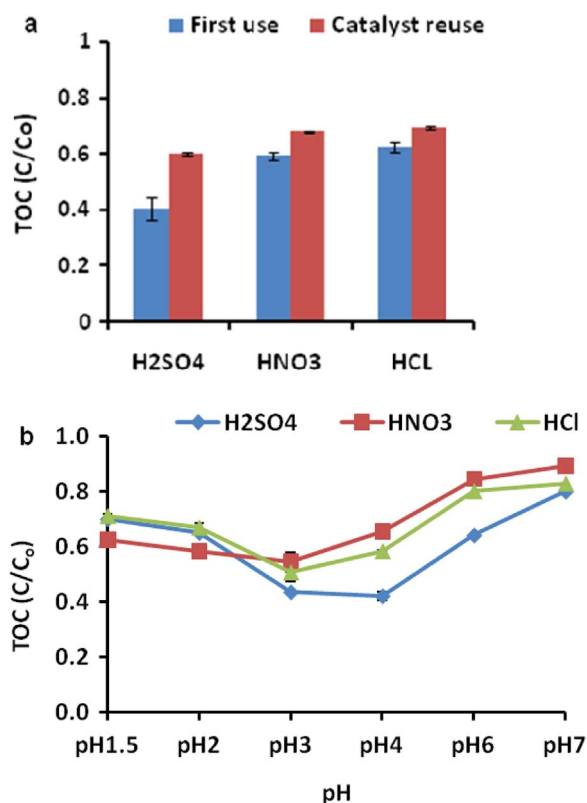


Fig. 2. The TOC removal by heterogeneous Fenton at room temperature, 150 g/L modified catalyst, 2 g/L H<sub>2</sub>O<sub>2</sub> for first use and reuse of catalyst (a) and the pH effects of TOC removal by the process at room temperature, 150 g/L modified catalyst, 2 g/L H<sub>2</sub>O<sub>2</sub> (b).

modified zeolite. For the zeolite pretreated by nitric acid, the increase in temperature from 293 K to 323 K increases the performance. The effect of temperature on TOC removal in heterogeneous Fenton can be

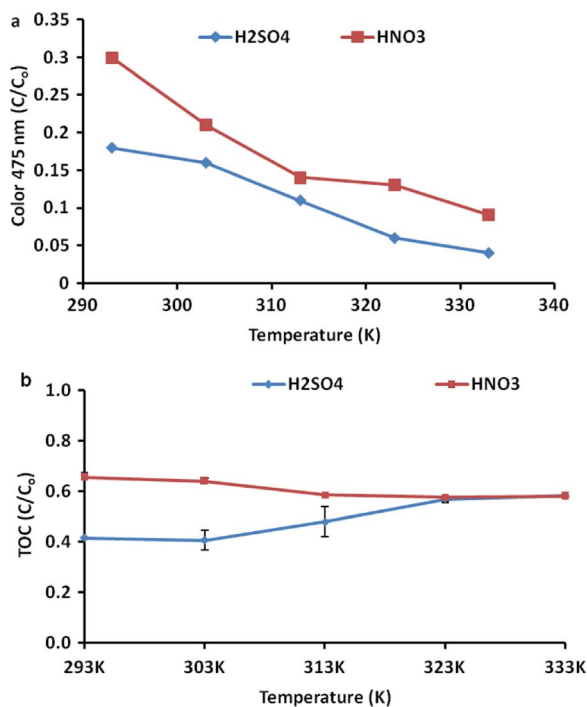


Fig. 3. The temperature effects at optimal pH (3 or 4) of the color (a) and overall TOC (b) removal by the heterogeneous process at room temperature, 150 g/L modified catalyst, 2 g/L H<sub>2</sub>O<sub>2</sub>.

explained by the two main processes involved; oxidation and coagulation. High temperature increases the kinetic energy and collision frequency of particles which favors the rate of oxidation. However, the effect is not the same with coagulation process. The overall TOC removal was highest at medium temperature because of the effect of temperature on coagulation. High temperatures favour the kinetics of dissociation of particles coalescing together which prevents the formation of big particles. The room temperatures are best suited for high TOC removal because bigger particles can be formed by coagulation. Very Low temperatures may not favour the process because of the slow kinetics. The sensitivity of coagulation rate by ferric ions to increased temperatures has been reported elsewhere [35]. This explains the slight decrease in performance of the zeolite treated by sulphuric acid with higher temperatures.

### 3.4. The TOC removal kinetics by heterogeneous Fenton

The determination of Fenton reactions kinetics is usually difficult. This is because these processes are complex in nature which includes the presence of many reacting species and occurrence of simultaneous oxidation and coagulation processes. This determination is even more difficult where the effluent has a complex matrix like in MDW. The overall TOC removal was used to gauge the process kinetics. The results from these studies indicate that the process generally follows second order kinetics (Fig. 4). This is in agreement with previous studies with homogeneous Fenton which reported the same [34].

The kinetics of overall TOC removal was fitted into the first order model Eq. (1).

$$\frac{dc_t}{dt} = -kt \quad (1)$$

The data was fitted into the model by plotting the equation of  $\ln(c_t/c_0)$

against time but the data did not agree with the model. The data was also fitted into the second order kinetics model described by the Eq. (2):

$$\frac{dc_t}{dt} = -kc_t^2 \quad (2)$$

The model was applied by plotting  $1/c_t$  versus time. The data for the time period after ten minutes fitted more accurately into the second order kinetics model for both modified zeolite catalysts. Moreover, the data was also tested with the model equation for the simultaneous first and second order reactions model proposed by Emami et al. 2010 [36], which is described by the following equation with  $C=c_t/c_0$ . It was plotted using Eq. (3).

$$\ln\left(\frac{C}{1-C}\right) = kt \quad (3)$$

The results fitted in the simultaneous first and second order model well for the data from zeolite catalyst modified with nitric acid for the initial time period (less than 10 min) where the  $k$  values were  $0.032 \text{ (min)}^{-1}$ ,  $0.038 \text{ (min)}^{-1}$  and  $0.049 \text{ (min)}^{-1}$ , for the reaction at (293 K), (303 K) and (323 K) respectively. The reaction rate for the rest of the reaction was however reversed with the reaction at highest temperature (323 K) having the smallest  $k$  value,  $0.005 \text{ L/(g-min)}^{-1}$  and (303 K) with the highest value,  $0.007 \text{ L/(g-min)}^{-1}$  from the second order model.

### 3.5. Heterogeneous Fenton and biodegradability

The heterogeneous catalyst optimization at pH 3.5 and after 4 h indicated that 0.45 g/L dosage of embedded ferrous ions was optimal for the COD removal and biodegradation (Fig. 5a). Though an increase in catalyst beyond the optimal value slightly increases the COD removal, the biodegradability is not enhanced because excess ferrous

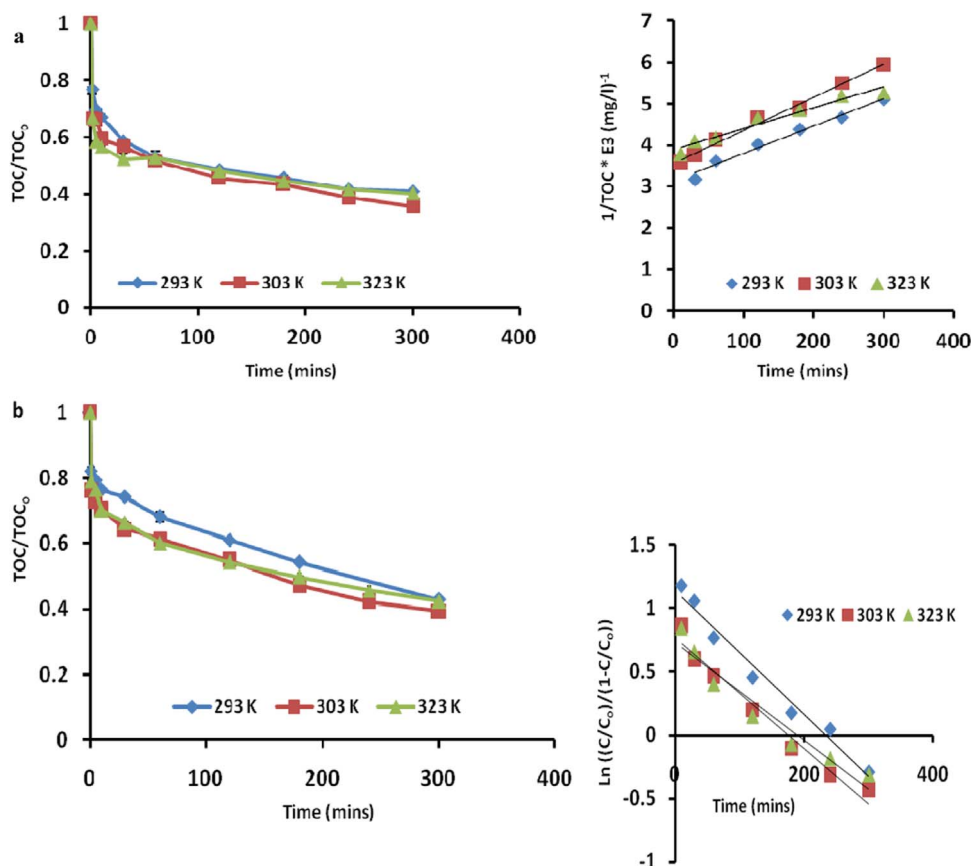


Fig. 4. The kinetics of TOC elimination by heterogeneous Fenton with 2 g/L H<sub>2</sub>O<sub>2</sub> and 150 g/L Zeolite at temperatures (293 K, 303 K and 323 K), pH 3.5 for sulphuric acid modified zeolite with its second order kinetics (a) and nitric acid modified zeolite with simultaneous first and second order kinetics, pH (b).

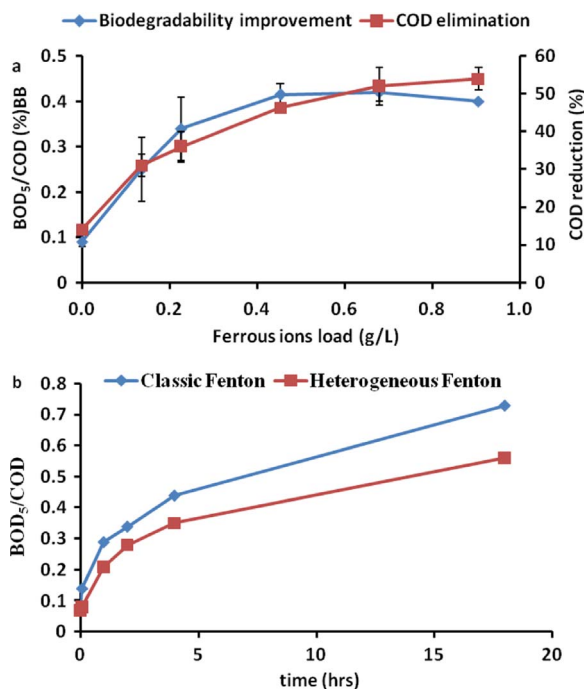


Fig. 5. The COD and biodegradability changes in anaerobically digested MDW after heterogeneous Fenton with sulphuric acid modified zeolite catalyst, 2 g/L H<sub>2</sub>O<sub>2</sub> at pH 2.5 after 5 h (a) and comparison of biodegradability changes with time with 2 g/L H<sub>2</sub>O<sub>2</sub>, pH 2.5, 170 mg/L Fe<sup>2+</sup> for classic Fenton instead of 0.65 Fe<sup>2+</sup> g/L in modified zeolite (b).

ions scavenge on the radicals formed. It also results in formation of ferric ions which may form iron oxyhydroxides and deposit producing unnecessary sludge [14].

The tests performed using modified zeolite catalyst as heterogeneous Fenton agree with those from classic Fenton process that the biodegradability of treated effluent increase with time (Fig. 5b). The results indicate that the classic Fenton had higher biodegradability increase compared to the heterogeneous process for similar duration of reaction time.

### 3.6. Pre-treatment of raw MDW by heterogeneous Fenton process

The pre-treatment of raw MDW was done with controlled reactants in heterogeneous Fenton process with the ratio of hydrogen peroxide to influent COD of 1:36. The process resulted in more than 4% increase in biodegradability which was accompanied by less than 4% loss of COD (Fig. 6). Moreover, the pre-treatment of the raw MDW before anaerobic digestion reduced the color of the effluent after anaerobic digestion by almost 30%. It was also observed that the optimum heterogeneous

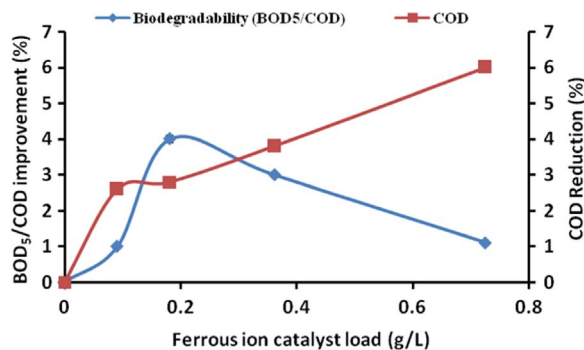


Fig. 6. The variation of the COD and biodegradability of raw MDW after pretreatment with sulphuric acid modified zeolites at room temperature, 20 g/L catalyst pellets, 2 g/L H<sub>2</sub>O<sub>2</sub> and pH 4.8.

Fenton pH with natural zeolite catalyst pretreated by sulphuric acid was 4–5. This implies that the raw MDW before anaerobic digestion which has pH 4.8 can be pretreated using the zeolite modified catalyst in heterogeneous Fenton preoxidation without the need to pre-adjust its pH.

## 4. Discussion

Fenton process is an established advanced oxidation technology and its use in removal of color and organic matter from various wastewaters has been reported [6,11,16,17,19,37]. The main purposes of Fenton oxidation process in post-treatment of wastewater include the removal of COD, color and toxicity before the effluent disposal. Among the limitations of the classic Fenton processes, the requirement of operation at low pH (2–3) is the main problem to most complex effluents. For example, most of the cost involved in treatment of molasses distillery wastewater by the Fenton method goes to adjust the pH prior to the oxidation process and neutralisation of treated effluent [38]. The high remnant metal contents in the effluent treated by classic Fenton process (> 30 g/L) [38] is also very problematic. This is because most environmental authorities worldwide have the limit of iron below 10 g/L for the safe disposal. The development of an effective heterogeneous Fenton catalyst has the potential to solve these limitations. This study was aimed at using an abundantly available material, natural zeolite to develop a heterogeneous Fenton catalyst. The material is cheap and freely available on earth surface in many parts of the world. There is no documentation of a cheap and effective modification of natural zeolite material as heterogeneous Fenton catalyst [27].

The Fenton oxidation is effected by the reaction of hydroxyl radicals which oxidize and/or mineralize the substrate aided by their high reactivity. The process is a chain of reactions which begins by generation of the radicals as shown in Eq. (4);



The reaction of radical is complex because it can attack any ion species in the effluent thereby producing different product for each reaction. In presence of the organic matter at optimal substrate/reactants ratio the following reaction takes place;



The catalyst is regenerated as follows;



In case of excess ferrous catalyst the radicals are scavenged as follows;



It is thus important that in homogeneous Fenton processes, the presence of the optimal ratio of the reactants is maintained. In heterogeneous Fenton, the catalyst is not freely available in the solution but embedded on a carrier material. This makes the process more flexible in terms of optimum reactants' ratio dependence. However, the process may have slower kinetics compared to homogeneous processes. This is because the catalysts ions are embedded on the carrier material which provides less contact area for the oxidants/catalyst compared to the homogeneous processes. This study showed that the reaction would proceed beyond 200 min compared to less 120 min reported for room temperature in homogeneous Fenton process [34]. The heterogeneous Fenton has additional advantage in that the catalyst embedment ensures that there is no excess catalyst in the solution hence no possibility of high sludge formation due to coagulation or deposition of iron oxyhydroxides [14].

The optimal H<sub>2</sub>O<sub>2</sub>:COD ratio used in heterogeneous Fenton with anaerobically digested MDW was 2.12. It was reported earlier for

homogeneous Fenton oxidation [34]. This study also observed that the optimal ratio of the ferrous ions embedded on sulphuric acid modified zeolite pellets to COD was (1:3). The similar ratio of ferrous ions to COD in homogeneous Fenton processes is much higher (1:20) [34]. This is however case dependent and will be determined by how ferrous ions were embedded on the zeolite and the washing done to remove unbound or loosely bound ferrous ions. The heterogeneous process achieved up to 60% COD removal and increased the biodegradability of digested MDW from 0.07% to 0.5% at room temperature conditions.

In addition to TOC and color removal, the heterogeneous Fenton process can be applied to pre-treat the raw wastewater and increase its biodegradability before biological treatment. The improvement of MDW biodegradability is caused by oxidation of recalcitrant to more biodegradable products and their removal through coagulation process. Our previous studies indicated that the improvement of biodegradability after coagulation process was negligible [39]. This implies that the oxidation of recalcitrant contributes more to improving biodegradability than the coagulation process associated with the Fenton process. Another disadvantage of the classic Fenton is the high remnant metal ions. The remnant iron concentration in treated effluent for classic Fenton can go beyond 50 mg/L [38] but with heterogeneous Fenton, the same was less than 10 mg/L. The maximum iron allowed in most European countries is between 3–10 mg/L, which implies that the heterogeneous Fenton has an edge over homogeneous Fenton in this regard.

Previous studies have reported that the increase in temperature improves the TOC removal by conventional Fenton process [34,36]. In this study, the effects of temperature on TOC and color removal were different. The higher temperature favors the color removal for the experiment with catalyst as modified zeolites. However, the TOC removal had completely opposite effects especially with the sulphuric acid-ferrous modified catalyst. This can be explained by the two processes; coagulation and oxidation, which are involved in the elimination of TOC and color in the Fenton processes. Oxidation involves conversion of ferrous ions into ferric ions and the vice versa. The conversion of ferric ions to ferrous ions is slow which makes it the limiting step of the Fenton process. The increase in temperature increases the kinetics of this sub-reaction and so the process is faster. Coagulation on the other hand is affected by the increase in temperature which provides particles with energy to break off from the coagulated mass and flow back into solution. It is thus logical to say that the color removal in Fenton process is affected more by oxidation than coagulation of recalcitrant colorants. The TOC loss is however predominantly caused by the coagulation process.

The increase in biodegradability of digested MDW after treatment with Fenton and heterogeneous Fenton was found to depend on the reaction time for both classic and heterogeneous Fenton processes (Fig. 5b). It was also observed that the biodegradability after 18 h is far much higher than that after 30 min for the both processes. This implies that even though the COD removal is almost instantaneous for classic Fenton, both processes require long operation time (> 5 h) for the enhancement of recalcitrants' biodegradability to values above 0.5. The time requirement for biodegradability enhancement is probably occasioned by the slow oxidation rate of the recalcitrants or their derivatives to more biodegradable compounds. Similar reports of changes in biodegradation depending on time after Fenton treatment have been documented in other compounds [7].

In pre-treatment processes involving bioenergy recovery, the decrease in COD is undesirable because it reduces the process energy potential. A balance on the need to increase biodegradability and the loss in COD by pre-treatment is thus necessary. The Fenton process has been used to pre-treat the lignocellulosic biomass before anaerobic digestion. The pre-treatment served to break down the lignin and thereby helped to increase the methane yield [15]. This study used the heterogeneous Fenton to increase the biodegradability of raw MDW before anaerobic digestion. Of the oxidant dosages tested (0, 0.33, 0.67,

1.0, 1.3) g/L, the minimum COD loss and the maximum biodegradability increase was with 0.33 g/L H<sub>2</sub>O<sub>2</sub> dosage. The experiment resulted in about 4% increase in biodegradability with less than 4% COD loss. However, this occurred at controlled catalyst dose of 0.2 g/L embedded catalyst. An increase in catalyst dose resulted in high COD removal because the excess ferrous ions were converted to ferric ions which caused coagulation. It is important to note that the process was carried out without alteration of raw MDW pH and at room temperature for 24 h. This suggests that the modified catalyst can be used to solve the limitation of convention Fenton process of low pH operation in post-treatment and high sludge formation which causes high COD loss for the pre-treatment process.

## 5. Conclusion

The most effective modification of natural zeolite for heterogeneous Fenton catalyst was sulphuric acid-ferrous treatment which achieved color and TOC removal above 90% and 60% respectively. The second performing catalyst was nitric acid-ferrous modified zeolite. The effectiveness of the modified catalysts was found to depend on the temperature and the pH with the highest temperatures used (333 K) producing the highest color removal. However, the effect of the high temperatures on the removal rate of TOC differed for the two modified catalysts. The optimum temperatures for overall TOC removal are 303 K and 323 K for sulphuric-ferrous modified and nitric acid-ferrous catalysts respectively. Moreover, the optimal pH for sulphuric-ferrous modified catalyst is 4 while that of nitric acid-ferrous catalyst is 3. The biodegradability of the digested MDW treated by heterogeneous Fenton using modified catalysts has been found to depend on reaction time. The value exceeds 0.55 after 18 h.

In addition to posttreatment, the modified zeolite can be used as a heterogeneous Fenton catalyst in the pre-treatment of the raw MDW before anaerobic digestion with the minimal COD loss. The pretreated effluent has the color eliminated by 30% after anaerobic digestion. It is found that the second order kinetic model describe best the overall TOC reaction after ten minutes for the sulphuric acid modified reaction. The TOC removal data from nitric acid modified catalyst fit in both second order model and simultaneous first and second order model. However the latter fits better for the initial reactions kinetics. The modification of natural zeolite by nitric acid and sulphuric acid treatment has the potential for producing heterogeneous Fenton catalysts and should be therefore studied further.

## Acknowledgement

The support and assistance of Ms Christina Senge and Liane Kapitzk of Technical University of Berlin in laboratory analysis is appreciated. The financial support by Deutscher Akademischer Austausch Dienst and National Commission of Science, Technology and Innovation Kenya, reference no. 91548162 is also acknowledged. The analysis equipment from technical environment protection department of Technical University of Berlin provided all the analysis equipments and it is highly appreciated.

## References

- [1] M. Coca, M. Teresa García, G. González, M. Peña, J.A. García, *Food Chem.* 86 (2004) 421–433.
- [2] M.M. Arimi, Y. Zhang, G. Götz, K. Kirihamiti, S.-U. Geißen, *Int. Biodeterior. Biodegrad.* 87 (2014) 34–43.
- [3] A. Battimelli, D. Loisel, D. Garcia-Bernet, H. Carrere, J.P. Delgenes, *J. Chem. Technol. Biotechnol.* 85 (2010) 968–975.
- [4] J. Dwyer, L. Kavanagh, P. Lant, *Chemosphere* 71 (2008) 1745–1753.
- [5] R.J. Emery, M. Papadaki, L.M.F. Dos Santos, D. Mantzavinos, *Environ. Int.* 31 (2005) 207–211.
- [6] S.F. Kang, C.H. Liao, M.C. Chen, *Chemosphere* 46 (2002) 923–928.
- [7] A.L. Estrada, Y.Y. Li, A. Wang, *J. Hazard. Mater.* 227 (2012) 41–48.
- [8] J.X. Kang, L. Lu, W. Zhan, B. Li, D.S. Li, Y.Z. Ren, D.Q. Liu, *J. Hazard. Mater.* 186

- (2011) 849–854.
- [9] I. Oller, S. Malato, J. Sánchez-Pérez, *Sci. Total Environ.* 409 (2011) 4141–4166.
- [10] D.R. de Souza, E.T.F.M. Duarte, G. de Souza, Girardi, V. Velani, A.E. da Hora, Machado, C. Sattler, et al., *J. Photochem. Photobiol. A Chem.* 179 (2006) 269–275.
- [11] K. Yetilmeysoy, S. Sakar, *J. Hazard. Mater.* 151 (2008) 547–558.
- [12] H. Tekin, O. Bilkay, S.S. Ataberk, T.H. Balta, I.H. Ceribasi, F.D. Sanin, et al., *J. Hazard. Mater.* 136 (2006) 258–265.
- [13] S. Khoufi, F. Aloui, S. Sayadi, *Water Res.* 40 (2006) 2007–2016.
- [14] Y. Deng, J.D. Englehardt, *Water Res.* 40 (2006) 3683–3694.
- [15] K. Michalska, K. Miazek, L. Krzystek, S. Ledakowicz, *Bioresour. Technol.* 119 (2012) 72–78.
- [16] R. Molina, I. Pariente, I. Rodríguez, F. Martínez, J.A. Melero, *Chem. Technol. Biotechnol.* 89 (2014) 1189–1196.
- [17] A.M. Senn, Y.M. Russo, M.I. Litter, *Sep. Purif. Technol.* 132 (2014) 552–560.
- [18] M. Tekbaş, H.C. Yatmaz, N. Bektaş, *Microporous Mesoporous Mater.* 115 (2008) 594–602.
- [19] M. Tokumura, H.T. Znad, Y. Kawase, *Water Res.* 42 (2008) 4665–4673.
- [20] C. Sirtori, A. Zapata, I. Oller, W. Gernjak, A. Agüera, S. Malato, *Water Res.* 43 (2009) 661–668.
- [21] O. González, C. Sans, S. Esplugas, *J. Hazard. Mater.* 146 (2007) 459–464.
- [22] I. Oller, S. Malato, J. Sánchez-Pérez, M. Maldonado, R. Gassó, *Catal. Today* 129 (2007) 69–78.
- [23] M. Aleksić, H. Kušić, N. Koprivanac, D. Leszczynska, A.L. Božić, *Desalination* 257 (2010) 22–29.
- [24] E. Garrido-Ramírez, B. Theng, M. Mora, *Appl. Clay Sci.* 47 (2010) 182–192.
- [25] Y. Yao, L. Wang, L. Sun, S. Zhu, Z. Huang, Y. Mao, et al., *Chem. Eng. Sci.* 101 (2013) 424–431.
- [26] C. Zhang, M. Zhou, G. Ren, X. Yu, L. Ma, J. Yang, et al., *Water Res.* 70 (2015) 414–424.
- [27] M. Blanco, A. Martínez, A. Marcaide, E. Aranzabe, A. Aranzabe, *J. Anal. Chem.* 5 (2014) 46718–46719.
- [28] M.L. Rache, A.R. Garcia, H.R. Zea, A.M.T. Silva, L.M. Madeira, J.H. Ramirez, *Appl. Cat. B Environ.* 146 (2014) 192–200.
- [29] M. Noorjah, V.D. Kumari, M. Subrahmanyam, L. Panda, *Appl. Cat. B Environ.* 57 (2005) 291–298.
- [30] S. Wang, Z. Zhu, *J. Hazard. Mater.* 136 (2006) 946–952.
- [31] E. Erdem, N. Karapinar, R. Donat, *J. Colloid Interface Sci.* 280 (2004) 309–314.
- [32] V. Meshko, L. Markovska, M. Mincheva, A. Rodrigues, *Water Res.* 35 (2001) 3357–3366.
- [33] M.M. Arimi, Y. Zhang, S.U. Geißen, *Sep. Purif. Technol.* 150 (2015) 286–291.
- [34] P. Bautista, A. Mohedano, M. Gilarranz, J. Casas, J. Rodriguez, *J. Hazard. Mater.* 143 (2007) 128–134.
- [35] J.R. Domínguez, J. Beltrán de Heredia, T. González, F. Sanchez-Lavado, *Ind. Eng. Chem. Res.* 44 (2005) 6539–6548.
- [36] F. Emami, A.R.T. Bagha, K. Gharanjig, F.M. Menger, *Desalination* 257 (2010) 124–128.
- [37] B. Riaño, M. Coca, M.C. García-González, *Chemosphere* 117 (2014) 193–199.
- [38] M.M. Arimi, Y. Zhang, S.S. Namango, S.U. Geißen, *J. Environ. Manag.* 168 (2016) 10–15.
- [39] M.M. Arimi, Y. Zhang, G. Götz, S.U. Geißen, *Environ. Technol.* 36 (2015) 1–9.