*Desalination and Water Treatment*
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6 (2009) 152–159

# Wastewater mineralization using advanced oxidation process

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Received 15 September 2008; accepted 30 April 2009

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## ABSTRACT

Water scarcity and environmental considerations are leading to the search for alternatives for industrial and urban wastewater reclamation. The objective of this research study was to examine the potential of recycling wastewater as an alternative or complementary technique for biological treatment. The degradation of organic matter from strained sewage and secondary treated sewage was studied using the advanced oxidation process (AOP) with hydrogen peroxide as an oxidant and iron oxide-based nanocatalysts. This process may be used when contaminants are resistant or toxic to conventional biological treatments. It also may be used as a complementary technique for polishing treated water.

AOP, which involves the in situ generation of extremely strong oxidants such as hydroxyl radicals in aqueous solution, has recently appeared as a remarkable technique for accelerating the oxidation and degradation of a broad range of organic matter in wastewater. The final products of this process are carbon dioxide, water and inorganic salts. The oxidation of an organic compound by AOP is catalyzed by using transition metal oxides such as iron oxides.

Another alternative for removing organic pollutants from aqueous streams is adsorption on activated carbon. The AOP process may be used on loaded active carbon or other adsorbents for cold regeneration, followed by successive repeated recycling of the adsorbent.

It was shown that organic matter is efficiently destroyed by the Fenton-like reaction using FeOOH in the presence of hydrogen peroxide. The strong effect of nanocatalyst and hydrogen peroxide concentrations on reaction rate is demonstrated. The kinetic reaction was evaluated, and the reaction rate coefficient $k$ was calculated. The optimal pH for destroying the organic matter was found to be around 2.7. Moreover, the results show high efficiency catalytic recovery of used activated carbon after treatment of filtered raw or secondary treated sewage, enabling the inexpensive reuse of the adsorbent.

***Keywords:*** Goethite; Organic pollutants; Fenton-like process; TOC; AOP

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## 1. Literature survey

Over the past few years, a series of new water and wastewater purification methods, called advanced oxidation processes (AOPs), have received considerable attention. Many organic compounds are resistant to conventional chemical and biological treatments. AOPs will probably constitute a good option in the near future. The term ''AOP'' is used to describe an oxidation process that produces hydroxyl radicals ($OH^•$) in a sufficient quantity to enable the oxidation of organic and inorganic water impurities to influence

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water treatment [1]. Hydroxyl radicals are non-selective chemical oxidants that react very rapidly with most organic compounds, they have a high oxidation potential and they are extremely unstable. This is the reason why they must be generated incessantly in situ through chemical reactions.

AOPs offer several distinct advantages over conventional treatment processes since they are very effective in removing resistant organic compounds, are capable of completely mineralizing organic contaminants into carbon dioxide, are less sensitive in the presence of toxic chemicals, and produce less harmful byproducts. The main problem is that at a relatively high load of organic matter, the process may be expensive for water treatment.

Many systems qualify under this broad definition of AOP. These systems use strong oxidants, such as ozone, hydrogen peroxide, Fenton's reagent (transition metal ions), or a combination of strong oxidants with irradiation, such as ultraviolet light (UV), titanium dioxide ($TiO_2$) in combination with light (UV) and oxygen, ultrasound (US), or electron beam [2–4].

The advantages of these systems are their high rates of pollutant oxidation, flexibility concerning water quality demand, and the small dimension of the equipment required. The main disadvantage of irradiation systems is their high treatment costs due to the use of high-energy sources (UV lamps, electron beams [5]).

Fenton's reagent is a mixture of $H_2O_2$ and ferrous iron, which generates hydroxyl radicals according to the reaction. The generation of the radicals involves a complex reaction in an aqueous solution. The hydroxyl radicals can oxidize organics (R) by removing protons, and produce organic radicals ($R^\bullet$) that are highly reactive and can be further oxidized according to the reaction. If the concentrations of reactants are not limited, the organics can be completely mineralized by full conversion to $CO_2$ and water.

$H_2O_2$ and $Fe^{2+}$ can act as an $OH^\bullet$ scavenger and an initiator, respectively, according to the reactions [6]. Perhydroxyl radical ($HO_2^\bullet$) does not play an important role in these oxidation processes since it has low reactivity when compared to $OH^\bullet$.

Previous studies have shown that Fenton's reagent is most effective at an acidic pH between 2 and 4, with an optimum pH of approximately [7,8]. Eq. (7) suggests that the presence of $H^+$ is required for the decomposition of $H_2O_2$, indicating the need for an acidic environment to produce the maximum amount of $OH^\bullet$ [9].

The Fenton-like reaction is applied to the reaction of ferric ions with hydrogen peroxide, as is described in the following Eqs. (8)–(12).

$$\begin{array}{r} Fe^{3+} + H_2O_2 \xrightarrow{k_{1a}} FeOOH^{2+} + H^+ \\ + FeOOH^{2+} \xrightarrow{k_{1b}} Fe^{2+} + HO_2^\bullet, \\ \hline Fe^{3+} + H_2O_2 \xrightarrow{k_1} Fe^{2+} + HO_2^\bullet + H^+, \end{array} \tag{1}$$

$$Fe^{2+} + H_2O_2 \xrightarrow{k_2} Fe^{3+} + OH^- + OH^\bullet, \tag{2}$$

$$Fe^{2+} + OH^\bullet \xrightarrow{k_3} Fe^{3+} + OH^-, \tag{3}$$

$$H_2O_2 + OH^\bullet \xrightarrow{k_4} HO_2^\bullet + H_2O, \tag{4}$$

$$R + OH^\bullet \rightarrow H_2O + R^\bullet \rightarrow \text{Further oxidation}, \tag{5}$$

$$R + H_2O_2 \xrightarrow{k_6} R + H_2O + 0.5O_2, \tag{6}$$

$$Fe^{2+} + 0.5H_2O_2 + H^+ \xrightarrow{k_7} Fe^{3+} + H_2O. \tag{7}$$

## 2. Degradation of organic compounds in wastewater and sewage by the Fenton process

The Fenton process is the only transition metal-mediated chemical oxidation that may be used for treating water. Environmental applications of Fenton's process include the use of various hydrogen peroxide concentrations, and the substitution of different catalysts such as ferric iron and naturally occurring iron oxides. The main advantages of Fenton's reagent as a tool for degrading organic compounds over other oxidizing treatment methods are numerous, including high efficiency, simplicity in destroying the contaminants, leaving no residue, stability to treat a wide range of substances, no need for special equipment, etc. [13]. Fenton's oxidation has an advantage over both the oxidation and coagulation processes [14,15]. The basic mechanism of the Fenton treatment process consists of chemical oxidation and chemical coagulation of organic compounds [16]. The Fenton oxidation process is normally comprised of four stages: pH adjustment, oxidation reaction, coagulation and precipitation [17]. Therefore the organic substances are removed at two stages: the first at oxidation and the second, at coagulation. In addition, the completion of oxidation is dependent on the ratio of hydrogen peroxide to organic matter, while the oxidation rate is determined by the initial iron concentration [18].

Adsorption is another solution for removing organic pollutants from aqueous streams. The most commonly used adsorbent is activated carbon, which has been known for a long time as being the one of most versatile adsorbents for removing organic compounds from solutions. Over the past 20 years, awareness about existing organic substances in natural water has increased the need for activated carbon adsorption to remove these compounds from water [19,20]. Granular activated carbon (GAC) is used in water treatment in the form of fixed beds where the water is in contact with the carbon by gravity flow through the bed. The granular material can act both as a filtering medium and an adsorber. When the granular material is saturated, it is either replaced with fresh carbon or removed and reactivated for further reuse. GAC is the best way for removing a broad spectrum of organic contaminants from drinking water supplies.

Saturation of the adsorptive capacity of GAC requires its removal from the organic compound so that it can be reused. GAC regeneration involves removing components that had been adsorbed and at the same time reestablishes the original capacity of the carbon. The most commonly used method is thermal regeneration, where the saturated carbon is heated in an inert atmosphere at a high temperature (800°C) in the presence of oxidizing gases, such as steam, carbon dioxide and oxygen. The disadvantages of the method include some loss of GAC due to burn-off and mechanical attrition, the very high-energy demand due to the high temperatures necessary, and the necessity for special installations.

Others method are available to regenerate GAC but they are less common and less efficient, including:

1. *Biological treatment*: has numerous limitations in terms of the non-biodegradability and toxicity of some contaminants to microorganisms [21].
2. *Solvent extraction*: the common solvent prohibits the use of this method due to its high cost, possible toxicity, and the need for further treatment to eliminate the extracted contaminations [22].
3. *Electrochemical treatment*: the regeneration of GAC is carried out in an electrochemical batch reactor that consists of two platinum electrodes, an anode and a cathode. The main disadvantage is the problematic scale-up of this method [23,24].

The economical application of activated carbon as an adsorbent depends on an efficient means of regenerating and recycling after its adsorptive capacity has been reached.

A novel approach for improving municipal wastewater recycling by removing or degrading organic matter using an AOP with the iron oxide-based nanocatalyst (FeOOH) was proposed. In our past research [25], we studied the adsorption of organic water pollutants onto activated carbon and the recovery of loaded activated carbon from model organic contaminants, such as ethylene glycol and phenol.

In this research, we introduce a novel AOP for organic pollutants removal. The study focused on two ways of achieving this purpose. The first method was direct, namely, in situ elimination of the organic matter from the solutions. This process involved using AOP in the presence of an iron oxide-based nanocatalyst and oxidant. The second method was indirect, involving two processes. First the organic compounds were adsorbed on activated carbon and then they were decomposed from the adsorber using the same process as the first method. The pollutant chosen for this study was dissolved organic matter from raw sewage following precipitation and 5-μm filtration.

## 3. Experimental

### 3.1. Materials

Iron chloride hexa-hydrate, $FeCl_3 \cdot 6H_2O$ (analytical grade; Merck KGaA, Germany), 30% hydrogen peroxide (analytical grade; PA, Panreac Quimica SA).

### 3.2. Analysis and equipment

The multi N/C 2100/2100S analyzer was used to determine the total organic carbon (TOC) for the filtered sewage solution. Concentration presented as TOC was chosen to represent the data. This is important since the target is to remove all organic compounds, since byproducts may be even more harmful than the original matter.

A morphology study was performed using Cryogenic Transmission Electron Microscopy (cryo-TEM), a Philips CM120 TEM optimized for cryo-TEM work equipped with an Oxford Instruments CT-3500 cooling holder system. The pH was determined using the Consort C-931 electrochemical analyzer. Iron concentration was determined in a data logging Hach DR/2010 spectrophotometer using the FerroVer method.

### 3.3. Preparation of catalysts

The initial material used for preparing the colloidal metal nanoparticle was iron(III) chloride hexa-hydrate. Forced hydrolysis was used to prepare a 7% sol for $FeCl_3 \cdot 6H_2O$. For all of the different metals, the initial acidity was $pH = 0.9$. A series of different catalyst concentrations was then prepared by diluting the initial solution. cryo-TEM was used for characterizing the prepared iron nanoparticle material. Fig. 1 shows an example of a cryo-TEM image of iron nanoparticles (FeOOH) with a concentration of 200 ppm.

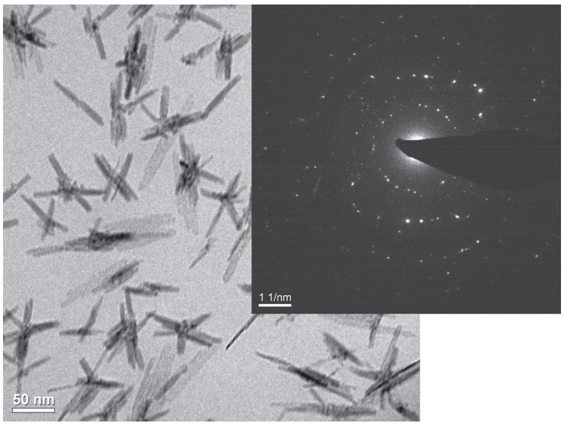

Fig. 1. TEM capture of iron oxides-based nanocatalyst (FeOOH) at a concentration of 200 ppm, and the corresponding electron diffraction pattern.

### *3.4. Experimental setup*

Filtered raw and secondary treated sewage solutions allowed to pass over a small laboratory column containing GAC. Fresh solutions were added until complete adsorbance was achieved. The GAC recovery process was performed in a mixed beaker for 30 min, in the presence of iron nanocatalyst and peroxide. The composition of the solutions is shown in Table 1.

All the experiments carried out at room temperature, with visible light. The pH values during the adsorption on GAC ranged from 6.5 to 7.5. Hydroxyl chloride was added to each sample taken prior the analysis to decrease the pH to below 1, where reaction is stopped.

## 4. Results and discussion

### *4.1. Investigation of the FeOOH nanocatalyst*

The degradation of organic matter was investigated by changing three parameters: the first two were the iron oxide-based nanocatalyst and hydrogen peroxide concentrations, and the third was the pH value. In all of the experiments, the initial TOC concentration of filtered sewage water was 105–115 ppm. The experiments were carried out at room temperature without UV radiation at visible room light. Generally, the results show that the Fenton-like reaction efficiently destroys organic matter from sewage with the iron oxide nanocatalyst (FeOOH) in the presence of hydrogen peroxide without UV or visible radiation sources.

Table 1
Composition of filtered raw and secondary treated sewage

| Component | Filtered raw sewage concentration, ppm | Secondary treated concentration, ppm |
|---|---|---|
| $NO_3^+$ | 1–2 | 5–15 |
| $NH_4^+$ | 40 | 0 |
| $PO_4^{3-}$ | 30–40 as $PO_4^{3-}$ | 30–40 as $PO_4^{3-}$ |
| $SO_4^{2-}$ | 50–60 as $SO_4^{2-}$ | 90 as $SO_4^{2-}$ |
| $Cl^-$ | 300–400 | 300 |
| $K^+$ | 20 | 20 |

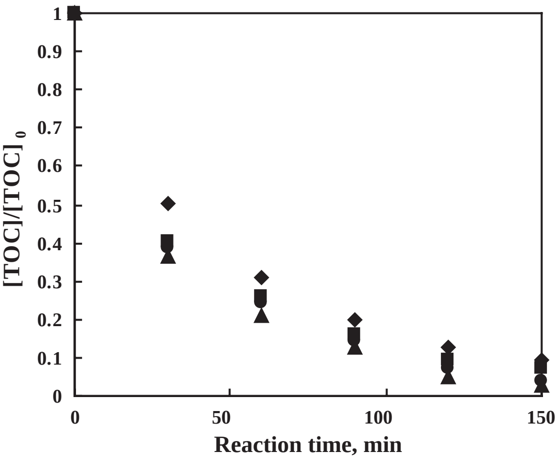

Fig. 2. Strained sewage degradation by AOP technique using different concentrations of iron oxide-based nanocatalyst (FeOOH) and a constant concentration of oxidant. ◆, 1000 ppm; ■, 1500 ppm; ▲, 3000 ppm; ●, 4000 ppm.

Fig. 1 shows the cryo-TEM images and electron diffraction pattern of the as-synthesized iron oxide-based nanocatalyst. From the cryo-TEM image, a rod-like morphology with an average diameter of 70 ± 10 nm was observed. The electron diffraction pattern was revealed with good agreement that the nonoparticles are nanorods of α-FeOOH (Goethite).

Figs. 2 and 3 show the influence of iron oxide-based nanocatalyst concentration on the process. Nanocatalyst concentrations were 0, 1000, 1500, 3000 and 4000 ppm. The hydrogen peroxide concentration was constant at 2650 ppm, and the solution pH value was 2.8. Concentration presented as TOC was chosen to represent the dissolved organic content. The results are normalized based on initial concentration. In general, the figures show that TOC concentration decreases with increased nanocatalyst concentration. The effect of nanocatalyst concentration on the rate of TOC degradation, where other parameters are kept constant, was studied. The results shown in Fig. 3 indicate that the effect of nanocatalyst concentration was significant. The rate of TOC degradation increased with increased nanocatalyst concentration. The reaction rate more than doubled when the concentration was increased from 1000 to 4000 ppm, increasing from 0.006 to 0.014 L/min.

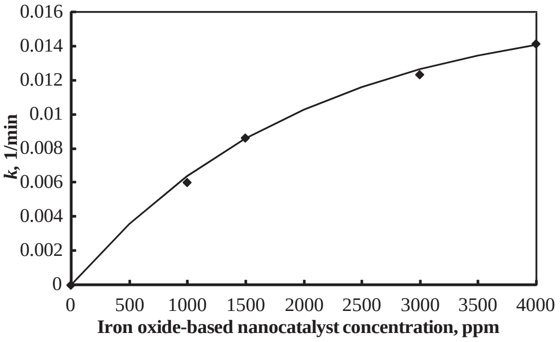

Fig. 3. Reaction rate as a function of iron oxide-based nanocatalyst concentration. ◆, Experimental data, solid line represents the theoretical model.

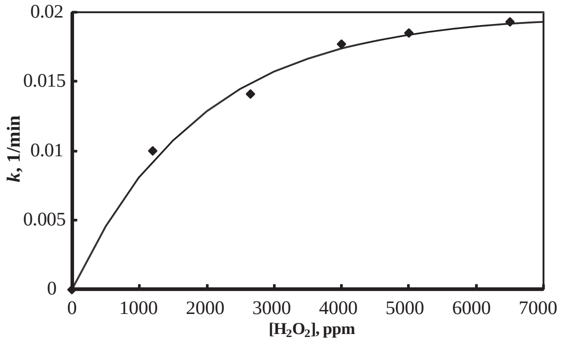

Fig. 5. Reaction rate as a function of oxidant concentration. ◆, experimental data, solid line represents the theoretical model.

The effect of TOC degradation was also investigated by changing the hydrogen peroxide concentration. Figs. 4 and 5 show that hydrogen peroxide had a significant influence on filtered sewage organic degradation rate. The results demonstrate a decrease in TOC concentration and an increase in reaction rate with increasing hydrogen peroxide concentrations. The latter was investigated at 0, 2650, 4000, 5000 and 6500 ppm. The iron oxide-based nanocatalyst concentration was constant at 2650 ppm and the pH value was 2.8. Fig. 5 indicates that after increasing the concentration of hydrogen peroxide to 4000 ppm, the reaction rate reached a constant value.

### 4.2. Theoretical model

The chemical oxidation of the proposed process can be represented by $n$th-order reaction kinetics [11]:

$$\frac{dC}{dt} = -kC^n, \tag{8}$$

with the initial condition as:

$$t = 0; C = C_0, \tag{9}$$

where $C$ is the organic solute concentration represented as TOC, ppm; $C_0$ is the initial TOC concentration; $n$ the order of reaction; $k$ the reaction rate coefficient, 1/min; and $t$ time. The choice of basing the dissolved matter on TOC measurements is important since the target is to remove all organic compounds, since byproducts may be even more harmful than the original matter. For a first-order reaction ($n = 1$), Eq. (8) may be rewritten as:

$$\frac{dC}{C} = -k dt. \tag{10}$$

The solution of Eq. (10) using initial condition (9) can be written in the form:

$$C = C_0 \exp(-kt). \tag{11}$$

The experimental data presented in Figs. 2 and 3 describe a series of experiments that demonstrate the decomposition of strained sewage by AOP using different iron oxide-based nanocatalyst concentrations and constant hydrogen peroxide concentration. Figs. 4 and 5 present the contrary; the oxidant concentration is changed and the iron oxide-based nanocatalyst concentration remains constant.

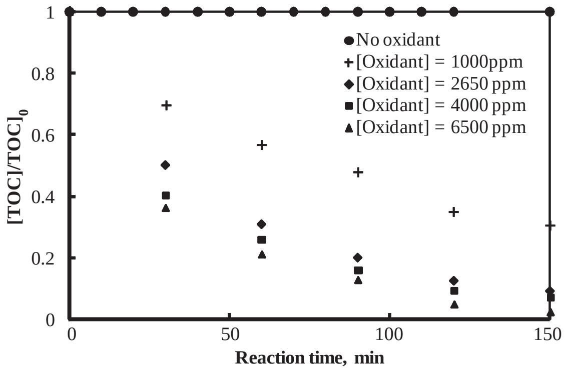

Fig. 4. Degradation of strained sewage by AOP technique using iron oxide-based nanocatalyst at a constant concentration and different concentrations of oxidant. ◆, 2650 ppm; ■, 4000 ppm; ●, 5000 ppm; ▲, 6500 ppm.

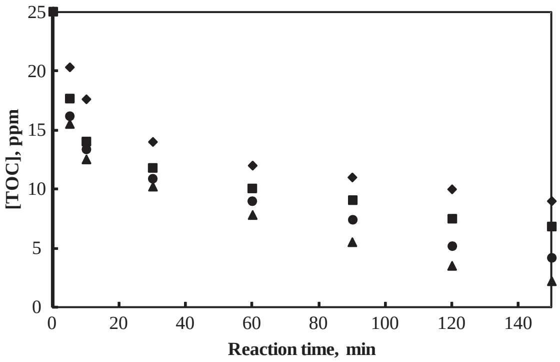

Fig. 6. Degradation of strained and treated sewage by AOP technique using different concentrations of iron oxide-based nanocatalyst and constant concentration of oxidant. ◆, 1000 ppm; ■, 1500 ppm; ●, 3000 ppm; ▲, 4000 ppm.

The experimental data presented in Figs. 2 and 4 enable to define an expression for calculating the reaction rate coefficient, $\kappa$:

$$k = \alpha * \left(1 - \exp^{\beta C}\right), \quad (12)$$

$\alpha$ and $\beta$ are constants. $C$ represents the concentration of the nanocatalyst for Fig. 2 and the concentration of the oxidant for Fig. 4. The best theoretical correlation with the experimental data is achieved with $\alpha = 0.0198$ for hydrogen peroxide concentration and $\alpha = 0.0163$ for iron oxide-based nanocatalyst concentration. $\beta$ is identical for both cases and equals 0.0005.

The reaction rate increases when $\alpha$ or $\beta$ increase either together or separately. It was shown above that the parameter $\alpha$ for hydrogen peroxide is higher than the iron oxide-based nanocatalyst. Therefore, it may be deduced from the theoretical model that the reaction rate of TOC degradation in the strained sewage solution is influenced more by increasing the oxidant concentration than by increasing the iron oxide-based nanocatalyst concentration.

To examine the efficiency of the process, two kinds of treated sewage were investigated. The first solution was raw sewage following precipitation and 5-μm filtration. The second solution was from the same source, yet following biological treatment. The concentrations of the solutions were 115 and 25 ppm, respectively.

Fig. 6 presents the influence of iron oxide-based nanocatalyst on the process, as in Fig. 2 for treated sewage solution. The difference between the two figures is the quality and concentration of the dissolved organic matter. As before, the TOC concentration decreased with an increased iron oxide-based nanocatalyst concentration, degrading to nearly 2 ppm.

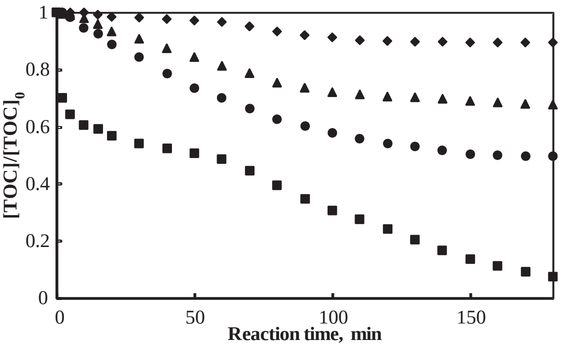

Fig. 7. The influence of pH on the degradation of strained sewage by AOP technique at constant concentrations of iron oxide-based nanocatalyst and oxidant. ◆, pH = 1; ■, pH = 2.75; ●, pH = 3.5; ▲, pH = 4.5.

The catalytic behavior of the nanocatalyst was also investigated by changing the pH values of the catalytic process. The concentrations of the dissolved organic matter, the iron oxide-based nanocatalyst and the hydrogen peroxide remained constant and were 115, 4000 and 6500 ppm, respectively. The pH values in these experiments ranged from 1 to 4.5.

The direct effect of pH on organic content destruction of sewage is shown in Fig. 7. As follows from these data, a change in pH has a strong effect on the kinetics of sewage oxidation and its final concentration. For pH values of 1 and 4, the sewage destruction efficiency was only 10% and 30%, respectively. Increasing the pH value to 2.75 caused an increase in destruction efficiency to 95%. A further increase in pH value to 3.5 led to a reduction in sewage destruction efficiency to 50%. This optimal pH value of sewage destruction with the iron oxide-based nanocatalyst corresponds with the data for the classical Fenton process reported in the literature [2].

### 4.3. Low temperature activated carbon regeneration

Loading organic matter from strained and treated sewage solutions using a mixed beaker containing active carbon is shown in Fig. 8. The figure presents the changes in water concentration with time as the adsorption process continues.

Fig. 8 shows the capability of the activated carbon to remove organic matter from this source, and shows a normalized TOC concentration with time for circulating the solution over 120 min. Both solutions were adsorbed almost completely into the activated carbon and reached a final concentration less than 1 ppm.

The initial strained sewage water concentration was 105–115 ppm. After six adsorption steps, as shown on

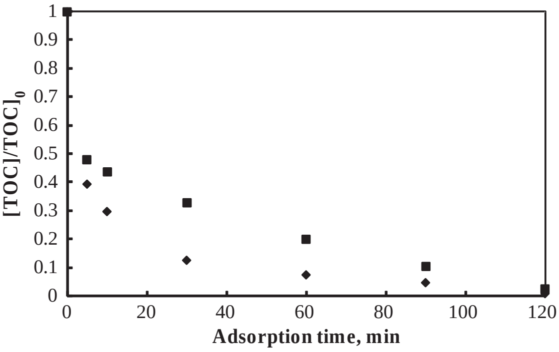

Fig. 8. Sewage adsorption on activated carbon. ■, strained and treated sewage at 25 ppm; ◆, strained sewage at 115 ppm.

the different curves in Fig. 9, the activated carbon was saturated with organic matter.

After achieving significant purification of the dissolved organic matter from the strained sewage solutions, it was necessary to regenerate the activated carbon for reuse. Fig. 9 presents a series of experiments performed to investigate the adsorption–regeneration properties of activated carbon. The experiments were carried out at room temperature without UV radiation.

The adsorption–regeneration technique involved the following steps. The first step was to adsorb sewage on AC. It can be seen from the figure that after one step, the normalized TOC concentration was 0.58, for the second step it increased to 0.63, and after six steps the activated carbon was loaded. Activated carbon loading data are based on mass balance in water solutions. The spent AC was then regenerated and the cycles were repeated. The figure presents four similar cycles.

After the last adsorption stage, the AC was regenerated by the iron oxide-based nanocatalyst and hydrogen peroxide as an oxidant. This adsorption–regeneration process was considered a cycle. Each adsorption step was based on passing 0.5 kg of water containing 105–115 ppm of partly treated sewage through 1 gr of AC. Each cycle represents four such steps, namely 3 kg of water per 1 gr of AC. It is important to note that the ability of the AC to treat an amount of water depends on the initial concentration of adsorbable organic content. As can be seen from the repeated steps, the cold regeneration of loaded active carbon is possible and the AC is ready for a new adsorption step. Using AC as a moderator enables operation under the right pH condition in a small volume of circulating treatment solution. The contents of both the catalysts and the oxidant may be increased to the right level to allow proper and safe operation in a relatively short time compared to the AC loading time.

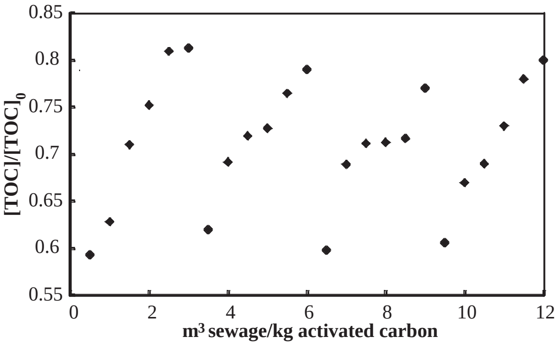

Fig. 9. Adsorption–regeneration cycles of strained sewage on activated carbon.

## 5. Conclusions

The objective of this study was to develop a novel AOP for organic pollutants removal. The study focused on two ways of achieving this purpose. The first method was direct, namely, the in situ elimination of the organic matter from the solutions. This process involved using AOP in the presence of an iron oxide-based nanocatalyst and oxidant. The second method was indirect and involved two processes. First the organic compounds were adsorbed on activated carbon and then they were decomposed from the adsorber in the same process as the first.

The main conclusions of the research study are as follows:

- Organic matter from partly treated sewage is efficiently destroyed by AOP in the presence of an iron oxide-based nanocatalyst and hydrogen peroxide without UV or any radiation source.
- A strong effect of iron oxide-based nanocatalyst and oxidant concentrations on the reaction rate coefficient was shown.
- The theoretical model enables an understanding of the greater influence of oxidant and catalyst concentrations.
- The optimal pH value for removing organic matter is 2.75.
- The removal of organic pollutants was studied using GAC; complete removal was obtained.
- Loaded activated carbon is efficiently recovered by the AOP reaction with the iron oxide-based nanocatalyst in the presence of hydrogen peroxide without UV or visible radiation light sources at room temperature.
- The techniques shown may be utilized in the cold in situ recovery of active carbon loaded with organic matter.

- No significant differences in adsorption properties of organic pollutants from sewage are presented in the regenerate activated carbon. Four adsorption–recovery cycles were carried out without a reduction in the adsorptive properties of the virgin activated carbon.

## Acknowledgements

The authors wish to acknowledge with thanks the partial support of this research project by the Ministry of Science, the Peres Foundation for Peace, and the Hurovitz Foundation.

## Notations

| | |
|---|---|
| AOP | advanced oxidation process |
| $C_0$ | initial concentration of organic pollutant (ethylene glycol) in solution, ppm as TOC |
| $C_1$ | residual concentration of the solution at the end of the catalytic process, ppm as TOC |
| $k$ | reaction rate coefficient $k$, 1/min |
| TOC | total organic carbon, ppm |
| UV | ultraviolet light |
| AC | activated carbon |
| GAC | granular activated carbon |

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