The role of activated carbon as a catalyst in GAC/iron oxide/H$_2$O$_2$ oxidation process

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ARTICLE INFO

Article history:
Received 31 January 2010
Received in revised form 6 April 2010
Accepted 8 April 2010
Available online xxxx

Keywords:
Granular activated carbon
Fenton process
Catalysis
Hydrogen peroxide

ABSTRACT

The catalytic properties of granular activated carbon (GAC) in GAC/iron oxide/hydrogen peroxide (H$_2$O$_2$) system was investigated in this research. Batch experiments were carried out in de-ionized water at the desired concentrations of ethylene glycol and phenol. Rate constants for the degradation of hydrogen peroxide and the formation rate of iron species were determined and correlated with mineralization of ethylene glycol at various GAC concentrations. The observed first order degradation rate of hydrogen peroxide in the absence of iron oxide and organic matter increases linearity with the increasing of the GAC concentration. The decomposition rate of hydrogen peroxide was suppressed significantly as the solution pH became acidic or by reducing the surface area of the GAC. The reduction of the surface area was obtained by loading an organic compound (such as phenol) on the GAC or by using the oxidizing agent (H$_2$O$_2$). The addition of both chemicals, phenol and H$_2$O$_2$, affects mainly the surface area of the small pores, resulting in reducing the catalytic activity inside the micropores.

The catalytic properties of the GAC were used to accelerate the formation rate of the ferrous ions, which is known in the literature to be the limiting rate reaction in the classic Fenton like reagent. It was shown that the ethylene glycol mineralization rate was increased by more than 50%.

Finally, optimization of the GAC consumption leading to the fastest mineralization of the ethylene glycol, resulting in decreasing of the decomposition rate of H$_2$O$_2$ while enhancing the generation rate of ferrous ions.

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1. Introduction

Activated carbon (AC) has been long known as one of the most versatile adsorbents to be used for removal of organic compounds from solutions. The main influential aspect in the adsorption process is the heterogeneous surface chemistry of the AC. The creation of heterogeneity surface is a result of geometrical structure, that include the difference between the size and shape of pores, and their chemical structure, which comprise numerous heteroatom content (oxygen, sulphate and nitrogen) [1], that are bounded and concentrated on the structure, which comprise numerous heteroatom content (oxygen, sulphate and nitrogen) [1], that are bounded and concentrated on the edges of the carbon layers. At the edge of the carbon plane, next to the molecular bond there are unsaturated carbon atoms. These sites are associated with high concentration of unpaired electrons which results in a larger propensity for oxygen chemisorptions. At high enough temperature the chemisorptions of oxygen increase and the molecules dissociate into atoms that react chemically with the carbon atoms to form oxygen surface compounds [2]. These oxygen surface groups are the most important in influencing the surface properties of activated carbons, because they determine the surface charge in the activated carbons, hydrophobicity and the electronic density of the graphite-type layers [1]. This heteroatom can be formed during the activation process or can be introduced by different oxidizing treatments [3].

The properties and the formation of acid (L-type) or base (H-type) groups on the surface of the activated carbon depend on the precursor and the scheme of preparation. The scheme of preparation depends on the temperature degree of the exposed precursor to the oxygen, resulting in different oxygen complexes inside the pores. H-type or the basic type raw carbons, such as coconut shell and coal dust, are first heated to a high temperature (1200 °C) in a vacuum atmosphere and then exposed to air at room temperature. These carbons are characterized by adsorbed hydrogen ions at the beginning of the activation. Chromene and pyrone are examples of the oxygen functional group existing in the L-type carbon [4,5]. The L-type or acidic carbon types are low temperature oxidized carbons which are characterized by adsorbed hydroxyl ion. The L-type raw carbons, such as woodbased, are generated at low activation temperature, at about 200–400 °C in the air. The main oxygen functional groups which exist in the L-type carbon are: carbonyl, phenolic hydroxyl, carbonyl, carboxylic acid, anhydrides, lactone, and cyclic peroxide [6–8].

Surface charge depends on the medium pH and the carbon surface characteristics. Negative surface charge is caused by the dissociation of the surface groups of an acidic nature. The positive surface charge formed by basic groups or by the presence of surface zones having a strong presence of p electrons which act as Lewis bases [9].

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Please cite this article as: A. Bach, R. Semiat, The role of activated carbon as a catalyst in GAC/iron oxide/H$_2$O$_2$ oxidation process, Desalination (2010), doi:10.1016/j.desal.2010.04.020
Carbon materials such as granular activated carbon (GAC) have been used for a while now in heterogeneous catalysis, due to the fact that they are able to act as direct catalysts or as a catalyst support for specific needs [10,11]. Granular activated carbon (GAC) form is preferred over powder activated carbon (PAC) type because it is easier to handle. The GAC is a more versatile adsorbent than PAC because it can be used as column filler for gas or liquid applications and it can be regenerated after use.

The reason for the catalytic activity of the GAC is assumed to be their graphic structure and their functional groups on their surface [12].

The advantage of GAC in the catalytic process is that it contains a granular structure with high surface area, so that fixed bed reactors can be used.

GAC has shown a catalytic activity regarding hydrogen peroxide \((\text{H}_2\text{O}_2)\) degradation. The hydrogen peroxide concentration, the solution temperature, carbon porosity, chemical properties of the surface, surface area and the medium pH are part of numerous factors which influences the decomposition of the hydrogen peroxide [13]. The medium pH is a major factor that influences the hydrogen peroxide decomposition. The nature of the activated carbon surface, whether it is acid or basic, affects the extent and rate of the degradation of hydrogen peroxide. It was shown in some works summarized by Khalil et al. [5] that the decomposition was increased to above a pH of 8. It was suggested that at a pH higher than 8 the hydrogen peroxide dissociates into hydroxyl ion and hydroxyl radical by accepting an electron from the activated carbon. This radical decomposes more hydrogen peroxide to water and peroxide radical. The dissociation of peroxide radical can be written as follows:

\[
\text{OOH}^{-} \rightarrow \text{H}^{+} + \text{O}_2
\]

(1)

The superoxide ions can decompose another hydrogen peroxide as follow [14,15]:

\[
\text{H}_2\text{O}_2 + \text{O}_2^{-} \rightarrow \text{OH}^{-} + \text{OH}^{+} + \text{O}_2
\]

(2)

The scheme of GAC preparation can control the decomposition rate of \(\text{H}_2\text{O}_2\). If the activation process of the GAC proceeds at high temperature, it causes the acid sites of the GAC to decompose and meanwhile increases the basic sites' numbers, which accelerates the hydrogen peroxide decomposition.

Advanced oxidation processes (AOPs), have received considerable attention as wastewater treatment processes, due to their ability to degrade, and in many cases mineralize, various organic compounds that are otherwise resistant to conventional biological and chemical treatments [16]. AOP is an oxidation process by which hydroxyl radicals \((\text{OH}^{+})\) are generated in a large quantity and oxidizes various organic pollutants [17]. AOPs are based on strong oxidants, such as, hydrogen peroxide \((\text{H}_2\text{O}_2)\), and/or a combination of strong oxidants with catalyst including Fenton reagent, which based on transition metal ions (ferrous ions).

The oxidation properties of \(\text{H}_2\text{O}_2\) and hydroxyl radicals depend on the pH of the solution. At a solution pH of 0 the redox potentials for \(\text{H}_2\text{O}_2\) and hydroxyl radicals are 1.77 V and 2 V respectively. At a solution pH of 14 the redox potentials for \(\text{H}_2\text{O}_2\) and hydroxyl radicals are 0.84 V and 2.8 V respectively. As results of this fact, acidic conditions are applied for oxidative treatment of wastewaters with \(\text{H}_2\text{O}_2\) [12].

Active carbon acts as an absorber for different dissolved materials, yet on the same time it interacts as a catalyst that can be used to degrade adsorbed or dissolved organic matter. Both properties may serve to remove contaminants from different types of waters, however, there is not sufficient understanding of the two different, yet sometime complementary properties of different types of GAC. The present study is focused on the catalytic behavior of GAC instead of its ability to serve as an absorber. Although carbon materials are actually used in some industrial catalytic processes, their full potential has not been exploited yet. The main use of carbon materials in catalysis which is reported in the literature seems to be as catalyst support, with less number of applications being envisaged as a proper catalyst. In view of this problem, this study will be concentrated on the use of GAC as a catalyst in the GAC/iron oxide/\(\text{H}_2\text{O}_2\) oxidation process. GAC performed as an electron donor to reduce the ferric ions in order to accelerate the formation rate of ferrous ions, which is known to be the rate-limiting constituent in hydroxyl radical production in Fenton like reagent.

Rate constants for the degradation of hydrogen peroxide and the mineralization of ethylene glycol were determined by altering the GAC concentration, and correlated with the generation of iron species. Finally, optimization of the GAC as a catalyst is reviewed in the GAC/iron oxide/\(\text{H}_2\text{O}_2\) oxidation process for ethylene glycol mineralization.

2. Experimental

2.1. Materials

Iron (3)-chloride hexa-hydrate, \(\text{FeCl}_3\cdot 6\text{H}_2\text{O}\) and hydrogen peroxide, 30%, were purchased from Merck, Germany; phenol, analytical grade (Fluka) and chemically pure ethylene glycol (BIO LAB Ltd, Israel). All chemicals were of analytical grade and were used as received.

The GAC was charcoal activated granulated pure and was purchased from Riedel-de Haen, the particle size of the GAC was 0.84–2.4 mm, 20–60[mesh], the internal surface area was nearly 1000 m\(^2\)/g. The purchased GAC was made in a high temperature scheme and in the pH range of \(-9–11\).

2.2. Experimental setup

Batch experiments were carried out in 250 mL beaker, stirred by a magnetic stirrer, with 200 mL of ethylene glycol solution in de-ionized (DI) water, at the desired concentration, and room temperature. The GAC was well washed with de-ionized water and oven dried at 50 °C.

Hydrogen peroxide, iron oxide and/or GAC were added simultaneously at the beginning of each experiment. The pH was adjusted by using \(\text{HCl} (1 \text{~N})\) or \(\text{NaOH} (5 \text{~N})\). At pre-determined time intervals samples were withdrawn from the beaker for analysis. Saturated or partly loaded GAC was obtained by adsorption of phenol on the GAC under batch experiments.

2.3. Analysis

Multi N/C 2100/2100 analyzer (Analytik Jena, Germany) was used to determine the total organic carbon (TOC). Total iron concentration was measured by the HACH DR2010 Portable Data logging spectrophotometer, using method 8008 with FerroVer iron Reagent Powder Pillows. Ferrous ions concentration was measured using the 1,10 Phenanthroline method (HACH method 8146), with ferrous iron reagent powder concentrations.

Hydrogen peroxide concentration was determined by \(\text{KI}/\text{S}_2\text{O}_3^-\) according to Kolthoff and Sandell [18]. The pH of the solution was determined by using Consort C931 pH meter.

Specific surface areas and pore size distribution were determined by the single point Brunauer, Emmet, and Teller (BET) method via nitrogen adsorption at 77 K with a Micromeritics, ASAP 2010.

The preparation and characterization of the FeOOH, have been described in details elsewhere [19].

3. Results and discussion

3.1. Decomposition kinetics of hydrogen peroxide in GAC/\(\text{H}_2\text{O}_2\) system

The decomposition of hydrogen peroxide with GAC in the absence of TOC (Total Organic Carbon) is shown in Fig. 1a. The \(\text{H}_2\text{O}_2\)
peroxide, decomposition of the hydrogen peroxide. catalytic sites available in the examined solution, resulting in greater GAC (basic functional groups) have a major effect upon the catalytic initial GAC concentration. \([\text{H}_2\text{O}_2]_0 = 6500 \text{ mg/L}, [\text{TOC}] = 0 \text{ mg/L}.\)

The degradation rate in Fig. 1b was determined for 95% decay of hydrogen peroxide. The solution contained no organic matter and the pH was approximately 7 without adjusting the pH by buffer.

As shown from Fig. 1b (another, larger set of experiments), the GAC concentration affects the degradation rate of hydrogen peroxide. The reaction rate increased with the increase of the GAC concentration. It was reported [12] that GAC degraded hydrogen peroxide to water and oxygen and not to hydroxyl radicals. The decomposition is followed by exchanging hydroxyl group with a hydrogen peroxide anion. The formed surface peroxide is regarded as having an increased oxidation potential, which enables the decomposition of another H$_2$O$_2$ molecule with release of O$_2$ and regeneration of the carbon surface, as shown in the following equations:

\[
\text{AC} - \text{OH} + \text{H}^+ \text{OOH}^- \rightarrow \text{AC} - \text{OOH} + \text{H}_2\text{O} \\
\text{AC} - \text{OOH} + \text{H}_2\text{O}_2 \rightarrow \text{AC} - \text{OH} + \text{H}_2\text{O} + \text{O}_2
\]

It is assumed that high GAC concentration leads to increase the catalytic sites available in the examined solution, resulting in greater decomposition of the hydrogen peroxide. The observed first order degradation rate constant of the hydrogen peroxide, \(k_{H_2O_2}\), increases linearly with increasing the GAC concentration. A second order rate expression for \(r_{H_2O_2}\), the rate reaction of hydrogen peroxide decomposition can be derived for the hydrogen peroxide decomposition in the presence of GAC with a mass normalized rate coefficient, \(k_{n}\), as:

\[
r_{H_2O_2} = -\frac{d[\text{H}_2\text{O}_2]}{dt} = k_n[\text{GAC}][\text{H}_2\text{O}_2] = k_{H_2O_2}[\text{H}_2\text{O}_2]
\]

The medium pH level and the chemical nature of the examined GAC (basic functional groups) have a major effect upon the catalytic activity of the GAC for hydrogen peroxide rate decomposition (Fig. 2). It is shown that increasing the pH level resulted in raising the decomposition rate coefficient of the H$_2$O$_2$. Between pH 3 to 8.5 the degradation rate coefficient is increased slowly, but from pH 8.5 to 13.5 the degradation rate coefficient is increased faster. Control experiments were performed without GAC in the solution and it was found that there is no spontaneous degradation of hydrogen peroxide within 3 h, under the studied pH range. Therefore any degradation shown in Fig. 2, resulted from the interaction with the GAC in the solution.

The rate of the decomposition of hydrogen peroxide is a first order with respect to the H$_2$O$_2$ concentration for all the range of the examined pH. The results show that the reaction rate for H$_2$O$_2$ decomposition is almost six times higher at basic pH than acidic pH. However, since the acid/base properties of the GAC also influence the pH of the reaction suspension, one cannot easily distinguish between the two effects, i.e. the change in the nature of the GAC surface and in the pH of the reaction medium.

It was reported [5] that the basic functional groups that include chromene and pyrone, were found to initiate a chain of reaction. In acidic pH these groups are oxidized to carboxonium ions and the activated carbon becomes less effective, regarding its catalytic ability upon hydrogen peroxide degradation.

Since the catalytic decomposition of the hydrogen peroxide inside the GAC is a surface reaction [20], the available surface area of the GAC is expected to have a crucial impact.

Fig. 3 demonstrates the effect of saturated GAC and partly loaded GAC samples with phenol on the decomposition rate coefficient of hydrogen peroxide. The uptake capacity \((q, \text{mg/g})\) was measured as follow:

\[
q = \frac{|C_0 - C_t|}{M}
\]

Where \(C_0 \text{ (mg/L)}\) is the initial phenol concentration in the solution and \(C_t \text{ (mg/L)}\) is the phenol concentration at reaction time \(t\). \(V \text{ (L)}\) and \(M \text{ (g)}\) are the solution volume and the GAC mass respectively.

Hydrogen peroxide degradation was not observed in phenol/ hydrogen peroxide system (data not shown), indicating that phenol by itself is not reacting with hydrogen peroxide during the reaction time applied in this system. As shown in Fig. 3, hydrogen peroxide concentration is plotted on a log scale as a function of the reaction time for different initial concentrations of GAC, ranging from 5 to 60 g/L. The fit of the data to a set of straight lines indicates that the decomposition of H$_2$O$_2$, in the presence of GAC, follows a first order kinetic rate expression with respect to H$_2$O$_2$ concentration. A second order rate expression for \(k_{H_2O_2}\) follows by exchanging hydroxyl group with a hydrogen peroxide anion. The formed surface peroxide is regarded as having an increased oxidation potential, which enables the decomposition of another H$_2$O$_2$ molecule with release of O$_2$ and regeneration of the carbon surface, as shown in the following equations:

\[
\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2
\]

Please cite this article as: A. Bach, R. Semiat, The role of activated carbon as a catalyst in GAC/iron oxide/H$_2$O$_2$ oxidation process, Desalination (2010), doi:10.1016/j.desal.2010.04.020

**Fig. 1.** a: change of H$_2$O$_2$ concentration at various concentrations of GAC. \([\text{H}_2\text{O}_2]_0 = 8250 \text{ mg/L}, [\text{TOC}] = 0 \text{ mg/L}.\) b: degradation rate coefficient of hydrogen peroxide as a function of the initial GAC concentration. \([\text{H}_2\text{O}_2]_0 = 6000 \text{ mg/L}, [\text{TOC}] = 0 \text{ mg/L}.\)

**Fig. 2.** Decomposition rate coefficient of hydrogen peroxide catalyzed by GAC as a function of the solution pH. \([\text{GAC}] = 12.5 \text{ g/L}, [\text{H}_2\text{O}_2]_0 = 8250 \text{ mg/L}, \text{reaction time 60 min.}\)
decomposition with GAC could be explained by first order reaction either in the absence or in the presence of adsorbed phenol into the GAC. The results indicate that the catalytic activity of the GAC has been affected by the absorbance of the phenol on the GAC. It is observed that while the quantity of adsorbed phenol increased, the reaction rate of H$_2$O$_2$ decreases. For example, virgin GAC decomposed hydrogen peroxide twice faster than saturated GAC. The presence of the adsorbed phenol is apparently blocking the catalytic sites availability for reacting with the hydrogen peroxide.

The surface area distribution was investigated for virgin and saturated GAC with phenol (Table 1). It is shown that the major part of the GAC that was affected by the phenol adsorption is the surface area of the micropores. The small pores’ surface area of the GAC loaded with phenol declined by 80%, compared to virgin GAC. Therefore, it was implied from the results obtained from Table 1 and Fig. 3 that the catalytic sites for the hydrogen peroxide decomposition are presented mainly inside the micropores of the GAC. Increasing the available micropores area enhances the hydrogen peroxide decomposition.

GAC oxidation by hydrogen peroxide induces physical changes in the carbon, such as altering the surface area, pore volume, and pore volume distribution [1].

The virgin GAC presented in Table 1 was oxidized by hydrogen peroxide (1.5 M) for 8 h. The changing of pores’ distribution in the activated carbon was observed after the oxidation process. While the total surface area remained almost unchanged, the surface area of the micropores declined from 489 m$^2$/g to 374 m$^2$/g. These results are suitable with a previous study [21], which reported that oxidation of activated carbons with aqueous solutions of hydrogen peroxide produces not only carboxyl, ketone and ether groups, but also textural changes in the surface of activated carbons. Obviously, the reaction with the peroxide changes the structure of the GAC all over the range of the pore size.

The catalytic activity of oxidized GAC (by hydrogen peroxide) as reflected by H$_2$O$_2$ degradation was studied. The decomposition rate of H$_2$O$_2$ with the repeating oxidation of GAC is shown in Fig. 4. Each repetition was performed during 2 h with a hydrogen peroxide concentration of 0.25 M. It was observed that the catalytic activity of the GAC has been affected by the H$_2$O$_2$ repeating oxidation, shown as a decrease in the degradation rate of hydrogen peroxide. This result is comparable with the result in Table 1, which means that with every oxidizing repetition the GAC structure was changed, mainly due to the surface area of the micropores, which finally lead to a decrease in the catalytic activity of the GAC. These results agree with earlier research [1], which reported that acidic oxygen surface complexes, such as carboxylic group are introduced mostly onto GAC when they are treated by strong oxidation treatment, such as hydrogen peroxide, resulting in a decrease in the hydrogen peroxide degradation rate by preventing its dissociation.

### 3.2. GAC as an electron transfer in the GAC/iron oxide/H$_2$O$_2$ system

The iron oxide in the GAC/iron oxide/H$_2$O$_2$ system was prepared by dissolution of ferric chloride in de-ionized water. Some soluble iron ions exist in aqueous solution as pH changes from 0 to 5 due to the dissolution of iron oxide [22]. Hydrated ferric ion, Fe(OH)$_2$$^{3+}$, is formed with hydroxylated complexes such as, FeOH(OH)$_2$$^5$ Fe(OH)$_2$$^{+2}$(OH)$_2$$^{4+}$ as seen in the following equations [23]:

$$[FeCl_3\cdot6(H_2O)]\rightarrow[Fe(H_2O)_6]^{3+} + 3Cl^- \quad (7)$$

$$[Fe(H_2O)_6]^{3+} + H_2O\rightarrow[Fe(H_2O)_5(OH)]^{2+} + H_3O^+ \quad (8)$$

$$[Fe(H_2O)_3(OH)]^{2+} + H_2O\rightarrow[Fe(H_2O)_4(OH)_2]^{+1} + H_3O^+ \quad (9)$$

Under these conditions hydroxylated complexes of ferrous iron do not exist [24]. Dissolution of iron oxide, such as FeOOH, occurs via protonation [25]. The general reaction between the iron oxide and the protons is presented by Eq. (10):

$$FeOOH + 3H^+\rightarrow Fe^{3+} + 2H_2O \quad (10)$$

All these complexes along with the ferric/ferrous ions participate in the Fenton like reaction. The formation rate of ferrous ions in the GAC/iron oxide process was marked, and normalized with the total iron concentration (Fig. 6a).

The formation rate of ferrous ions followed first order kinetics. The k$_{Fe^{2+}}$ is the first order formation rate of ferrous ions determined experimentally by plotting ln[Fe$^{3+}$]/[Fe$^{3+}$]$^{eq}$ against the reaction time (Fig. 5). [Fe$^{3+}$]$^{eq}$ represents the concentration of ferrous ions in equilibrium in GAC/iron oxide system.

The generation rates of ferrous ions increases with the increase of the weight ratio of the GAC to the total iron. The observed first order formation rate of bivalent iron increases linearity with increasing the GAC concentration. It is proposed that high GAC concentration leads to a larger number of catalytic sites available in the examined carbon, resulting in higher formation of Fe$^{3+}$.

Competitive reactions occur when hydrogen peroxide is introduced into the process.

### Table 1

<table>
<thead>
<tr>
<th>Pore size distribution of various conditioned GAC.</th>
<th>BET (m$^2$/g)</th>
<th>Micropore area (m$^2$/g)</th>
<th>External surface area m$^2$/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin GAC</td>
<td>1198</td>
<td>489</td>
<td>709</td>
</tr>
<tr>
<td>Saturated GAC with phenol q = 450 mg/g</td>
<td>661</td>
<td>98</td>
<td>563</td>
</tr>
<tr>
<td>GAC after oxidation of H$_2$O$_2$ H$_2$O$_2$ 1.5 M</td>
<td>1177</td>
<td>374</td>
<td>803</td>
</tr>
</tbody>
</table>

Fig. 3. Hydrogen peroxide decomposition catalyzed by GAC pre adsorbed with phenol, as function of adsorbance levels. [H$_2$O$_2$]$_0$ = 8250 mg/L.

Fig. 4. Hydrogen peroxide decomposition rate coefficient catalyzed by GAC for numbers cycles, [H$_2$O$_2$]$_e$/[GAC]$_e$ = 660 mg/g.

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The following reaction mechanisms are suggested in order to account for the results obtained in the GAC/iron oxide/H₂O₂ process.

\[ \text{AC} + \text{Fe}^{3+} \rightarrow \text{AC}^{+} + \text{Fe}^{2+} \]  \hspace{1cm} (11)

\[ \text{Fe}^{+3} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{+2} + \text{HO}_2^- + \text{H}^+ \]  \hspace{1cm} (12)

\[ \text{AC}^{+} + \text{H}_2\text{O}_2 \rightarrow \text{AC} + \text{HO}_2^- + \text{H}^+ \]  \hspace{1cm} (13)

\[ \text{Fe}^{+2} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{+3} + \text{OH}^- + \text{OH}^- \]  \hspace{1cm} (14)

\[ \text{Fe}^{+2} + \text{OH}^- \rightarrow \text{Fe}^{+3} + \text{OH}^- \]  \hspace{1cm} (15)

\[ \text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \]  \hspace{1cm} (16)

\[ \text{HO}_2^- + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{O}_2 \]  \hspace{1cm} (17)

In many Fenton systems, the rate-limiting constituent in hydroxyl radical production is ferrous ions production (Eq. (12)). The formation of ferrous ions in the GAC/iron oxide/H₂O₂ system may be explained by the fact that activated carbon (AC) is considered to function as an electron transfer catalyst with AC and AC⁺ as the reduced and oxidized catalyst states. AC performs as an electron donor in order to reduce the ferric ions to ferrous ions (Eq. (11)). The formation of ferrous ions in the GAC/iron oxide/H₂O₂ process is presented in Fig. 6b, and normalized with the total iron concentration.

The formation rate of the ferrous ions is increased with raising the GAC concentration until maxima is reached (GAC = 75 g/l), then the formation rate is declined. The difference between the results obtained in Fig. 6a and b is due to the competing reaction existing between the formation of ferrous ions by Eqs. (11) and (12), and their consumption by Eqs. (14) and (15). The competition between the decomposition of hydrogen peroxide and the formation of ferrous ions by increasing the GAC concentrations (Figs. 1 and 6a) is the main key for understanding the mechanism. At a GAC concentration higher than 75 g/l, the formation rate of ferrous ions declines due to the very high decomposition rate of hydrogen peroxide.

Ferrous ions concentration can be measured as long as their formation rate (Eqs. (11) and (12)) is higher than their consumption rate (Eqs. (14) and (15)). The “lag time” (Fig. 6b) refers to the period of time in which no ferrous ions concentration could be detected in the measurement instrument, i.e. in this period of time the rate of formation and consumption was equal. After few minutes of reaction, the hydrogen peroxide concentration approached zero, hence the consumption mechanism is stopped and only Eq. (11) continues (formation mechanism). The results demonstrate that the minimum lag time was obtained at the maximum formation rate, [GAC] = 75 g/l.

The hydrogen peroxide decomposition was measured in the GAC/iron oxide/H₂O₂ process (Fig. 7). The decomposition was determined for the first 8 min’s reaction by increasing the weight ratios between hydrogen peroxide and total iron. The GAC concentration was constant for all experiments (12.5 g/l) and the pH was nearly 3. As shown in Fig. 7 the weight ratio between hydrogen peroxide and the total iron affect the extent degradation of hydrogen peroxide. The extent of decomposition decreased following the decrease in the weight ratio. The consumption of hydrogen peroxide is due to competing reaction of GAC, hydroxyl radicals and ferrous/ferric ions (Eqs. (12)–(14), (16)) upon hydrogen peroxide degradation. The smallest decomposition for the first 8 min was obtained in the...
absence of iron oxide (20%), thus any further degradation in the same time interval is due to the presence of the iron oxide.

3.3. Ethylene glycol mineralization

The catalytic activity of the activated carbon for ethylene glycol mineralization was studied and shown in Fig. 8. Ethylene glycol, expressed as total organic carbon (TOC), was picked as the model solution, since it is not adsorbed on the examined GAC. The GAC in the GAC/iron oxide/H$_2$O$_2$ oxidation process was performing as an additional catalyst to the iron oxide in order to accelerate the formation rate of ferrous ions, which is known to be the rate-limiting constituent in hydroxyl radical production in Fenton like reagent.

The ethylene glycol rate of mineralization followed first order kinetics in the GAC/iron oxide/H$_2$O$_2$ process, according to Eq. (18):

$$r_{\text{TOC}} = \frac{d\text{TOC}}{dt} = -k_{\text{TOC}}[\text{TOC}]$$

Here $r_{\text{TOC}}$ is the rate of ethylene glycol mineralization. $k_{\text{TOC}}$ was determined for mineralization of 98% of TOC (the initial TOC was 200 mg/L) at the various GAC concentrations and constant weight ratio between hydrogen peroxide to total iron (Eq. (16)).

As shown from Fig. 8, addition of GAC into the model solution, promotes the mineralization rate of ethylene glycol. The mineralization rates initially increased upon increasing the GAC concentration up to an optimal rate obtained at a concentration between 20–35 mg/L, after which the mineralization rate decreased. The results illustrate that without GAC in Fenton like reaction, the mineralization rate was determined at less than 0.12 min$^{-1}$ and by increasing the GAC concentration to the optimal range that mentioned before, the mineralization rate was nearly 50% raised to 0.19 min$^{-1}$. In addition, the figure shows that increasing the GAC concentration above 60 g/L caused the mineralization rate to be lower than classic Fenton like reaction, in the absence of GAC. Ethylene glycol mineralization was not observed in the absence of iron oxide (data not shown), indicating that GAC with hydrogen peroxide system cannot oxidize ethylene glycol within the reaction time applied. The meaning of the last result is that the examined GAC does not decompose H$_2$O$_2$ into hydroxyl radicals so no oxidation of the organic matters in Fenton system occurs. This result is comparable with previous study [12], suggested that hydrogen peroxide is decomposed to water and oxygen in the presence of GAC.

Several competing effects may contribute to an optimal range of the rate of mineralization as a function of the GAC concentration. The maximum reaction rate shown in Fig. 8 is different than the maximum rate of Fe$^{2+}$ obtained with GAC concentration in Fig. 6b. Apparently, the two systems are different and the existence of EG changes the reaction rate dependence on the Fe$^{2+}$ concentration.

In Fenton like process, the rate-limiting reaction is the reaction between ferric ions with hydrogen peroxide in order to form ferrous ions (Eq. (12)). Introducing activated carbon into the model solution results in increasing the rate of the limiting reaction by raising the formation rate of ferrous ions. It was shown earlier that the formation rate of ferrous ions increased with increasing the GAC concentration (Fig. 6a). On the other hand, increasing the GAC concentration increases the hydrogen peroxide decomposition (Fig. 1). The reaction between GAC and H$_2$O$_2$ is undesired due to the fact that hydroxyl radicals were not produced and due to the reduction in the catalytic reaction efficiency. Therefore, optimal range of mineralization rate of ethylene glycol is obtained by optimization of the GAC concentration resulting in increasing the formation rate of ferrous and decreasing the decomposition rate of hydrogen peroxide.

4. Conclusions

The study reported in this paper presented GAC as a catalyst of dissolved peroxide for mineralization of organic matter in the GAC/iron oxide/H$_2$O$_2$ oxidation process.

The degradation rate of hydrogen peroxide in the GAC/H$_2$O$_2$ system, which followed first order kinetics, increased linearity with increasing of the GAC concentration. The decomposition of hydrogen peroxide by GAC was found to be undesired due to the fact that hydroxyl radicals were not produced and due to the reduction in TOC degradation efficiency.

Solution acidity plays a major role in this catalytic oxidation system, by decreasing the catalytic activity toward H$_2$O$_2$.

A change in the surface property of the GAC (mainly surface area of the micropores) was obtained by using the oxidizing agent (H$_2$O$_2$) or by the existence of the adsorbed phenol on the surface GAC. This change was found to affect the catalytic activity of the GAC toward H$_2$O$_2$ decomposition rate.

GAC concentration was found to play a major role in the ethylene glycol catalytic oxidation. Our results clearly show that the GAC in the GAC/iron oxide/H$_2$O$_2$ system accelerates the formation rate of ferrous ions (which is known to be the rate-limiting constituent in hydroxyl radical production) compared to iron oxide/H$_2$O$_2$ system in the classic Fenton like process. Optimization of GAC concentration would decrease the catalytic activity toward H$_2$O$_2$ and increase the generation rate of ferrous ions, resulting in increase of the ethylene glycol mineralization rate.

References

Please cite this article as: A. Bach, R. Semiat, The role of activated carbon as a catalyst in GAC/iron oxide/H₂O₂ oxidation process, Desalination (2010), doi:10.1016/j.desal.2010.04.020