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Interaction of Hydrogen Peroxide with Nanoporous Material Prepared by Alkaline Activation of the Brown Coal

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The work analyzes applications of carbon adsorbents in catalytic wet peroxide oxidation (CWPO) being a variant of Advanced Oxidation Processes (AOPs). Under CWPO condition (concentration $[H_2O_2] \leq 30\%$, 20 ± 2 °C) we have studied the activity of nanoporous adsorbent AC-K prepared by KOH-activation (800 °C, 1 h) of brown coal. We have compared AC-K with solid product of thermolysis (SPT) of brown coal formed under the same conditions without KOH. AC-K, which has a high adsorbtion activity, catalyzes decomposition of H_2O_2 to form OH-radicals. This allows to combine two environmentally important processes: concentration of organic pollutants on the surface of adsorbent and their further decomposition by OH-radicals.

Decomposition of H_2O_2 in presence of AC-K or SPT is described by kinetic first-order equation and runs 20-30 times faster in contact with AC-K. Rate constants vary within the range of $0.053-0.28 \text{ min}^{-1}$ (AC-K) and $0.002-0.012 \text{ min}^{-1}$ (SPT) and grow under $[H_2O_2]$ increasing. Oxidative modification of AC-K and SPT surfaces under CWPO conditions has been studied. The dependence between content of OH groups in modified AC-K (24 h) samples and $[H_2O_2]$ is described as a curve with a maximum at $[H_2O_2] = 10\%$, where the maximum modifying effect and the highest increase in OH-groups content (from 1.00 to 1.55 mmole/g) are observed. Modification level is negligible; only 1 % of oxidant reacts to form functional groups.

Keywords: nanoporous carbon, hydrogen peroxide, decomposition kinetics, surface modification.

Research of Advanced Oxidation Processes (AOPs) is a relatively new and rapidly progressing fields [1]. The beginning of AOPs was the discovery of radical oxidation of organic substances by hydrogen peroxide in the presence of ferrum ions (Fenton's reaction) [2]. Such processes are applied to

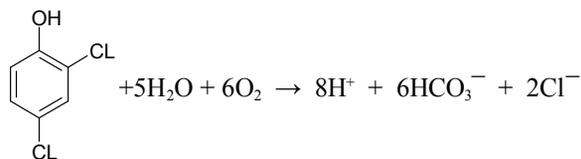
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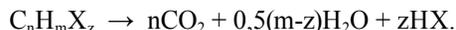
remove organic pollutants (OP) from air and water. Their intensive development was driven by strict regulations set forth for recycle water quality in many countries.

AOPs apply four main oxidants: oxygen, ozon, air and hydrogen peroxide as a reactant of catalytic wet peroxide oxidation (CWPO) [1]. There exist lots of oxidative methods, including those applying ultrasound [3] and UV-irradiation [4], catalytic agent [5-9], supercritical water [10] and many other techniques [11, 12]. These methods are especially efficient to decompose toxic substances or biodegradation resistant pollutants in aqueous media, as well as substances which are hardly decomposed, e.g. aromatic compounds [8, 13, 14], phenol and its derivatives [15-20], oil components [1, 4], pesticides and herbicides [3, 4, 9, 10, 21, 22], dyes [23]. The biggest number of works is focused on destruction of such compounds as: 1) nitrophenols, which are quite resistant to biological decomposition as they are toxic to microorganisms, especially if highly concentrated; 2) chlorophenol, in particular pentachlorophenol – highly toxic antiseptic with anti-fungus and bactericidal effect; 3) dyes of different structure, pesticides and herbicides.

Oxydestruction during AOPs runs with participation of OH-radicals, which decompose OP to low-molecular compounds. For instance, 2,4- dichlorophenol is oxidized to low-molecular non-toxic compounds as shown in equation below [1]



This process is also called mineralization of organic compounds, because they are transformed into simple non-organic substances [1]



Carbon in organic compounds is converted into C-atoms of molecules and ions CO_2 , H_2CO_3 , HCO_3^- , CO_3^{2-} , while X-atoms become part of mineral acids, where $\text{HX}=\text{HCl}$, HBr , HNO_3 , HNO_2 , H_2SO_4 etc. Using appropriate AOPs even OP molecules with cyanide groups can be oxidized to essentially less toxic compounds.

The basic mechanism of oxidative reactions, which basically imitates natural photochemical processes in the Earth atmosphere, includes, in particular, formation of highly reactive short-living oxygen-containing intermediates, namely, OH-radicals. Hydroxyl radical is a powerful highly reactive nonselective oxidant with electrophilic properties. Its reactions have high rate constants and are often controlled by a diffusion [13].

AOPs group also includes processes of OP oxydestruction in the presence of activated carbon (AC), for instance, air oxidation of phenol [18] or trinitrophenol [19], ozonation of aromatic S-containing compounds [8], OP decomposition by hydrogen peroxide in AC presence (CWPO–process) [6,7,9,12,15,20-24]. CWPO–process generates OH-radicals during hydrogen peroxide decomposition, which is promoted (or catalyzed) by activated carbon. This process is demonstrated by the equation below



which is formally similar to Fenton's reaction [2].

Another process reveals in AC-H₂O₂-H₂O systems. Oxidant can modify AC surface by forming different oxygen-containing functional groups (OFG), though as hydrogen peroxide decomposes fast its modification efficiency is low, i.e. this causes a minor increase in surface groups concentration [22, 25-31].

On the other hand, OP molecules get sorbed on AC surface. When adsorbed they are decomposed by OH-radicals slower. According to studies [6, 15], H₂O₂ is decomposed by activated carbon much more slowly in the presence of 4-chlorophenol, which was explained by the adsorbate shielding a number of surface active sites catalytically active in the decomposition of H₂O₂. Nonetheless, the research has registered quite a high conversion rate of 4-chlorophenol: 25 % for 26 min when a solution with a 1 g/dm³ concentration flows through the column with AC [6]. Oxidation of methyl-tret-butyl-ether, trichloroethylene and 2,4,5- trichlorophenol by hydrogen peroxide in the presence of AC shows [7] that adsorbed adsorbate molecules are low-reactive, i.e. they are protected from attacks by OH-radicals. OP adsorption causes an inverse effect – adsorbed molecules are more protected to oxidation by radicals, though OH[•] molecules are placed on AC surface near by OP.

AOPs are hard to apply to weak aqueous solutions, where OP concentrations make 1-100 mg/m³. To resolve the issue, we find it reasonable to combine two processes: 1) OP adsorption on AC for them to be concentrated in small space; 2) OP decomposition by hydroxyl radicals generated from decomposition of hydrogen peroxide catalyzed by AC. The main obstacle here – adsorbed OP decomposes slower. This might bring to nothing technological advantage obtained through preconcentration or might cause a need to add another stage to desorb OP from adsorbent surface, e.g. through ultrasound irradiation [16].

Earlier, we obtained brown coal-derived nanoporous material with highly-developed surface, substantial portion (≤70 %) of micro pores and high adsorption activity towards organic substances in aqueous media, in particular, towards phenol and methylene blue [32-35]. We deemed it reasonable to test this material in AOPs with hydrogen peroxide.

The first stage of the present work focuses on H₂O₂ decomposition kinetics in the presence of AC-K and SPT, as well as seeks to assess oxidative modification of their surface as it strongly affects AC catalytic activity and adsorption power [22, 24].

Experimental

To conduct this work we have prepared two carbonaceous materials from the brown coal of Alexandria coal deposit with properties as described below [33].

1. Solid product of thermolysis (SPT) of the brown coal in argon at 800°C for 1 h (yield ~45 %) [32]. SPT has a specific surface area $S_{\text{BET}}=200$ cm²/g, total pores volume $V_{\Sigma}=0.17$ cm³/g, adsorptive capacities in iodine $A_{\text{I}}=560$ mg/g and methylene blue $A_{\text{MB}}=50$ mg/g. OH-acid groups content is [-OH]=0.14 mmole/g [36].

2. Activated coal (AC-K) is a solid product of alkaline activation, which includes brown coal impregnation by potassium hydroxide, thermolysis (800°C, 1 h, argon), cooling, washing off alkaline and drying (yield ~30 %) [33, 36]. AC-K product has the following properties: $S_{\text{BET}}=1100$ cm²/g, $V_{\Sigma}=0.66$ cm³/g, $A_{\text{I}}=1000$ mg/g, $A_{\text{MB}}=200$ mg/g, [-OH]=1.00 mmole/g.

Reaction of hydrogen peroxide with SPT or AC-K is carried out as follows. A sample (2.0g) dried at 105°C for 2 h was brought in contact with H₂O₂ aqueous solution of preset concentration ([H₂O₂]=5-

30 %) and stirred at room temperature. Solution volume was selected in such a way to ensure the preset mole ratio $\text{H}_2\text{O}_2/\text{coal carbon}$ ($R = 0.5$ or 1.0). Residual concentration of H_2O_2 was measured at times τ . For this purpose, 0.2 cm^3 of aqueous phase was put into a flask with 10 cm^3 of sulphuric acid solution (5N), and titrated with potassium permanganate solution ($0,1\text{N}$). After that, the remaining reaction mixture was mixed with 200 cm^3 of water, stirred, filtered out solid product. This solid was dried at 105°C for 2 h.

In order to determine the content of OH-acid groups ($[-\text{OH}]$, mmole/g), barium hydroxide was used by technique described below [37]. A sample (0.5g) was stirred with 20 cm^3 of $\text{Ba}(\text{OH})_2$ water solution (0.05 N) for 24 h, then the aliquote (5 cm^3) was titrated with 0.01 N HCl . Experimentally measured error for $[-\text{OH}]$ value was 4 %.

Results and discussion

Kinetics. In contact with SPT and AC-K the content of hydrogen peroxide decreases (Fig.1) and reagent fully decomposes for 24 h. As for AC-K, the process of decomposition is much faster. With lower ratio $R=0.5$, $[\text{H}_2\text{O}_2]$ concentration decreases faster, especially during the first 30 minutes of the process. A similar picture is observed for both products and H_2O_2 solutions of any concentration within $[\text{H}_2\text{O}_2] \leq 30\%$ range. Hydrogen peroxide solutions are stable (Fig.1, line 1): within measured errors, $[\text{H}_2\text{O}_2]$ concentration remains unchanged during 24 h.

Kinetics of H_2O_2 decomposition in the presence of AC-K or SPT is adequately described by the first order equation (Fig.2) and is shown as follows: $R = 0.988 \exp(-0.053\tau)$ (for AC-K product at $[\text{H}_2\text{O}_2]=10\%$); $R = 0.913 \exp(-0.0022\tau)$ (for STP with $[\text{H}_2\text{O}_2]=10\%$); $R = 0,897\exp(-0.0048\tau)$ (STP, $[\text{H}_2\text{O}_2]=20\%$); $R = 0.977 \exp(-0,0076\tau)$ (STP, $[\text{H}_2\text{O}_2]=30\%$). For all equations correlation coefficients range from 0.96 to 0.99

With equal initial mole ration $\text{H}_2\text{O}_2/\text{carbon coal}$ ($R=1.0$), the rate of hydrogen peroxide decomposition depends on its initial concentration (Fig. 2) and is drastically different for SPT and AC-K. In case of AC-K, H_2O_2 decomposes much faster: at $[\text{H}_2\text{O}_2] = 30\%$ the reagent decomposes violently with a strong exothermic effect. Effective rate constants k of H_2O_2 decomposition in STP presence range from 0.002 to 0.012 min^{-1} , and their values demonstrate a liner growth as the concentration of reagent raises (Fig. 3). In case of AC-K, rate constants also grow with a raise in oxidizer concentration and range from $k = 0.053$ to 0.28 min^{-1} .

Modification. While contacting with H_2O_2 , weight of SPT remains unchanged or tends to decrease (Fig.4). The OH-groups content also remains practically unchanged and ranges $[\text{OH}]=0.12\text{-}0.16 \text{ mmole/g}$. This value is close to content of phenol groups $[\text{OH}]=0.14 \text{ mmole/g}$ determined for solid thermolysis product of the brown coal at 800°C [36].

In contact with hydrogen peroxide, the changes in composition of the AC-K surface functional groups are more visible, which is apparently down to substantially bigger number (as compared to SPT) of active centers, the concentration of which is directly proportional to the specific surface area.

In longer contact of concentrated H_2O_2 (30 %) with AC-K, the content of OH-groups remains unchanged (Fig.4, line б) and makes $1.01 \pm 0.04 \text{ mmole/g}$ for 24 h. If low concentrated (10 %) solutions are used, the content of acid groups grows monotonously (Fig.4, line б) up to $1.55 \pm 0.04 \text{ mmole/g}$ at 24 h contact.

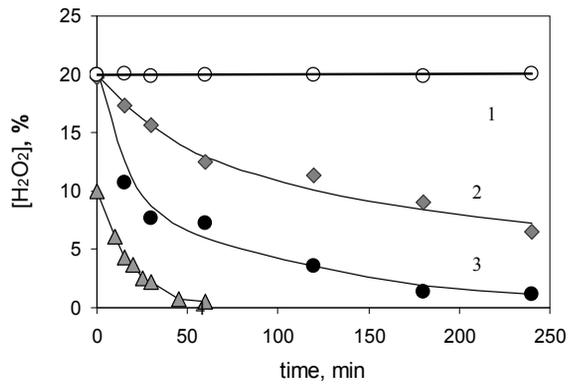


Fig.1 Variation in hydrogen peroxide concentration in contact with SPT and AC-K: 1 – H₂O₂; 2 – SPT, R = 0.5; 3 – SPT, R = 1,0, 4 – AC-K, R = 1.0

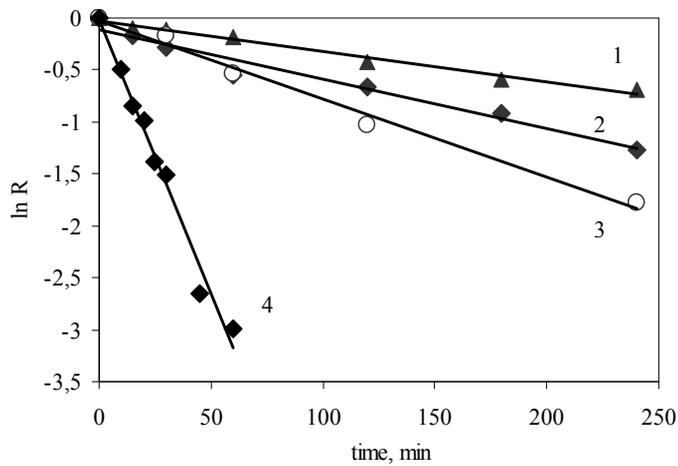


Fig.2 ln R parameter vs time of contact between H₂O₂ and carbon material SPT (1-3) and AC-K (4): 1- [H₂O₂]=10%; 2- [H₂O₂]=20%; 3- [H₂O₂]=30%; 4 – [H₂O₂]=10%

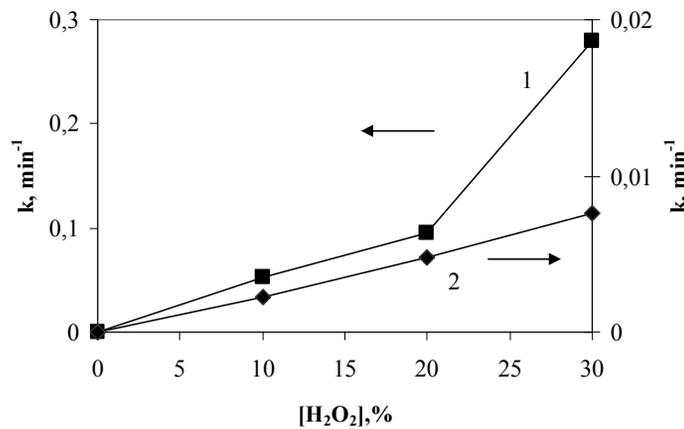


Fig.3. The hydrogen peroxide decomposition rate constants vs concentration: 1- AC-K; 2 -SPT

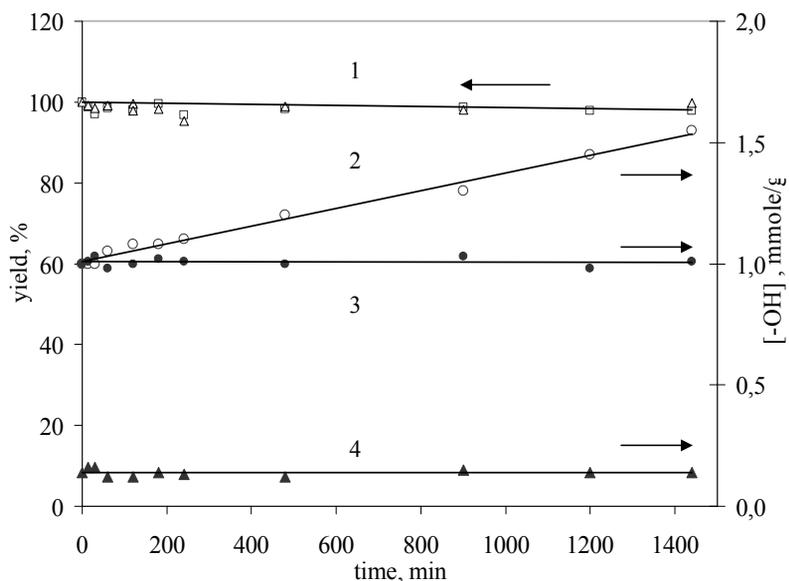


Fig.4 Variation of yield and OH-acid groups content of SPT and AC-K contacting with H_2O_2 : 1- SPT yield if treated with hydrogen peroxide with concentration of 10 %(\square), 20 %(Δ), 30 %(\circ); 2- OH-groups content in AC-K at $[H_2O_2]=10\%$; 3- OH-groups content in AC-K at $[H_2O_2]=30\%$; 4- OH-groups content in SPT at $[H_2O_2]=30\%$

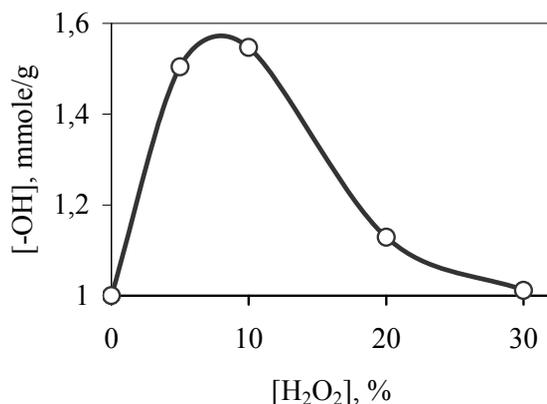


Fig.5 OH-groups content in AC-K products modified with hydrogen peroxide solution of different concentration ($\tau=24h$)

Dependence of OH-groups content in modified AC-K samples (at 24 h contact) on hydrogen peroxide concentration is a curve with a maximum at $[H_2O_2] = 10\%$ (Fig.5). Solution with such concentration displays the biggest modification effect, if we consider the growth in content of OH-acid groups. In this case, H_2O_2 is used to maximum efficiency, though the portion of oxidant used to form phenol groups is small: just 0.7 moles H_2O_2 of 100 moles reagent are used to form hydroxyl groups. H_2O_2 solutions of higher concentration are less efficient. A possible reason may be high rate of hydrogen peroxide decomposition in concentrated solutions, which essentially exceeds rate of modification reaction.

Thus, the first stage of our research showed, that H_2O_2 intensively decomposes in contact with brown coal thermolysis products obtained both in the presence of potassium hydroxide (AC-K product) and without it (SPT). Carbon material C_n acts as electron donor, which reduces OH-radicals according the reaction [23]



By analogy with radical reactions in H_2O_2 -Fe(II)- H_2O systems, we can assume the following interaction of hydroxyl radical to form a less active HO_2^\bullet -radical and its reaction with coal surface



In accepted mild conditions, modifying capacity of hydrogen peroxide is quite low. If treated with SPT, it does not form any functional groups or forms just a few of them (below sensitivity threshold of the method) (Fig.4). Also, reactions to form and further transform OH-acid groups are likely to have similar rates and stationary concentration of OH-groups remains unchanged. In this case, decomposition of hydrogen peroxide is a dominating process.

If AC-K is used, H_2O_2 decomposes faster, but modification is more visible and is demonstrated by increased content of OH-acid groups (Fig.5), which can be formed during reactions between coal arene fragments with hydroxyl radicals. Also, peroxide functional groups of active carbon can be formed through attachment of HO_2^\bullet -radical to cation-radical $\text{C}_n^{+\bullet}$ generated in reaction (2). When low concentration solutions are used, hydrogen peroxide decomposes slower and the contribution of modification reactions grows (Fig.5).

The second stage of this work will focus on an influence of organic adsorbates on AC-K behavior in CWPO. Changes in H_2O_2 decomposition kinetics in the presence of AC-K following adsorption of phenol and chlorophenols will be the subject of our further researches.

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Взаимодействие пероксида водорода с нанопористым материалом, полученным щелочной активацией бурого угля

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Рассмотрены применения углеродных адсорбентов в catalytic wet peroxide oxidation (CWPO) как варианте Advanced Oxidation Processes (AOPs). В условиях CWPO (концентрация $[H_2O_2] \leq 30\%$, 20 ± 2 °C) изучено поведение нанопористого адсорбента АУ-К, полученного КОН-активацией (800 °C, 1 ч) бурого угля. Проведено сравнение АУ-К с твердым продуктом термоллиза (ТПТ) бурого угля, полученного в тех же условиях без КОН. АУ-К, обладающий высокой адсорбционной активностью, является катализатором разложения H_2O_2 с образованием ОН-радикалов, что даёт возможность объединить два экологически значимых процесса: концентрирование органических экотоксикантов на поверхности адсорбента и их последующее расщепление ОН-радикалами.

Разложение H_2O_2 в присутствии АУ-К и ТПТ описывается уравнением кинетики I-го порядка и в контакте с АУ-К протекает в 20-30 раз быстрее. Константы скорости варьируются в интервалах $0,053-0,28 \text{ мин}^{-1}$ (АУ-К) и $0,002-0,012 \text{ мин}^{-1}$ (ТПТ) и с увеличением $[H_2O_2]$ возрастают. В условиях CWPO изучена окислительная модификация поверхности АУ-К и ТПТ. Зависимость содержания ОН-кислотных групп модифицированных образцов АУ-К (24 ч) от $[H_2O_2]$ передается кривой с максимумом при $[H_2O_2] = 10\%$, где наблюдается максимальный модифицирующий эффект и наибольший прирост содержания ОН-групп (с 1,00 до 1,55 ммоль/г). Уровень модификации мал; не более 1 % окислителя идет на образование функциональных групп.

Ключевые слова: нанопористый углерод; перекись водорода; кинетика разложения; модификация поверхности.
