

Activated carbon (AC) containing transition metal oxides (MeO_x) in phenol adsorption and catalytic oxidation of adsorbed phenol by hydrogen peroxide

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Abstract—An adsorbent-catalyst (AD-CAT) material was prepared from activated carbon containing several percentages of transition metal oxides (MeO_x). This material possesses a high adsorption capacity towards phenol and simultaneously can catalytically oxidize phenol molecules adsorbed on activated carbon surface by hydrogen peroxide solution. Due to the catalytic promoting properties of MeO_x aggregates, the oxidation of adsorbed phenol can be performed under the rather mild condition with high selectivity towards CO₂ and H₂O. The experimental obtained results demonstrate that phenol adsorption over AD-CAT material follows the Freundlich isotherm, the catalytic oxidation reaction rate of adsorbed phenol follows the kinetic equation of zero order to phenol and hydrogen peroxide, and the surface oxidation reaction pathway evolves through Langmuir-Hinshelwood mechanism.

Keywords: Adsorbent-catalyst material. Activated carbon. Transition metal oxide. Phenol. Hydrogen peroxide.

I. INTRODUCTION

It is well known that phenol and its derivatives (phenols) are the most common organic pollutants in wastewaters discharged from petrochemical, chemical and pharmaceutical industries.

Up to now, there has been much research effort to eliminate or abate phenol in wastewaters [1-4]. The principal techniques used for the treatment of phenols are commonly including:

1/ adsorption using activated carbon [5,6],

2/ wet air catalytic oxidation (WACO) or wet hydrogen peroxide catalytic oxidation (WHPCO) [7-10],

3/ aerobic or anaerobic biodegradation [11].

Activated carbon (AC) is well considered as an excellent adsorbent for adsorption of phenol, xylene, toluene, ... which have their molecular dimension of about 7 Å. The phenols adsorption capacity of AC can generally reach to 15-20 wt% [12]. However, the use of AC for the phenols abatement in water or in wastewaters always meets the two principal drawbacks:

(i) the cost of AC preparation is relatively high and (ii) the regeneration of exhausted AC is so far not significantly successful to approach a lifetime enough long of AC used in the environmental technology. These drawbacks limited the application of AC for the phenol removal in wastewaters.

On the other hand, from the environmental view-point, the regeneration of exhausted AC by steaming or/and heating could deliver phenols from AC, and hence give a secondary pollution. In WACO process, although in the presence of catalysts the reaction condition was still relatively hard: temperature and pressure of the reaction system were usually higher than those ambient. For example, A. Fortuny et al. carried out WACO for phenol conversion at 140°C and 4.7 MPa [9]. Moreover, in WACO catalysts were usually deactivated rapidly and the phenol oxidation were usually incomplete [10].

In WHPCO, the reaction was carried out under rather mild condition (ambient temperature and atmospheric pressure). With this technique, phenol mineralization was not high, thus by products were formed during reaction process and mainly were undesired organic pollutants [4,8,13].

In this work, transition metal oxides were dispersed on AC forming a bifunctional adsorbent-catalyst (AD-CAT) material which acts as an adsorbent for phenol accumulation, and then simultaneously oxidizes phenol adsorbed on AC surface with the participate of hydrogen peroxide.

It is particularly noted that over AD-CAT material the adsorption and oxidation occurred following two distinguished steps: phenol adsorption in the first step, and the catalytic oxidation of adsorbed phenol was continuously performed in the second one. As results, adsorption character and surface reaction pathway over AD-CAT material may be distinguished from parent AC.

This paper presents the studied results on phenol adsorption, kinetics and reaction pathway of adsorbed phenol oxidation over AD-CAT solid.

II. EXPERIMENTAL

A. Materials

Activated carbon selected for the present work was Tra Bac activated carbon (TB-AC) which was manufactured from coconut shell in Tra Vinh province of Vietnam. TB-AC powder has a dimension of 50-100 μm. Some principal characteristics of TB-AC are as follows:

Specific surface area (m ² /g)	: 1020.00
Average pore diameter (Å)	: 20.00
Pore volume (cc/g)	: 0.557

B. Chemicals:

Phenol, hydrogen peroxide and transition metal salts (in nitrate form) were of analytical grade and used without further purification

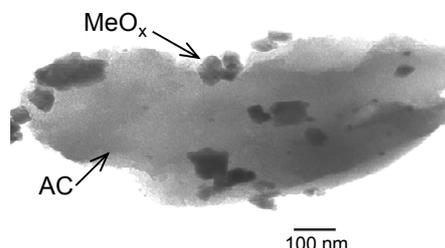


Figure 1. TEM image of 0.5wt% (MeO_x) AD-CAT samples (MeO_x: transition metal oxides)

C. Adsorbent-catalyst (AD-CAT) materials.

AD-CAT samples were prepared from TB-AC impregnated with transition metal salt solutions having desired concentration in order to obtain the loadings of metal (Me) ranging from 0.5 to 10 wt%. Procedure of AD-CAT material preparation was described in the Vietnamese patent, N^o.1-2009.00580.

Results by IR, TPR-H₂, TPD-O₂ (data not shown here), and TEM techniques confirmed that the synthesized AD-CAT samples contain oxide aggregates with dimension of 50-100nm, which dispersed mostly on external surface of AC (Fig.1)

D. Adsorption equilibrium experiments

The phenol adsorption experiments were conducted in a batch mode. Firstly, the different amounts of AD-CAT samples were put into several 0.25L flasks, which contained 0.1L of phenol solution (5000mg/L). Then, the flasks were kept in a rotary shaker (200rpm) at 40°C for 72 hours to give enough time to achieve the equilibrium state. Prior to UV measurement, all of samples were filtered for the separation of AD-CAT solid present in phenol solution. The concentration of the filtrate was determined by an UV spectrometer (Shimadzu UV-160A, Japan) at 264.5nm. The adsorption capacity of AD-CAT sample at the equilibrium state was calculated as follows:

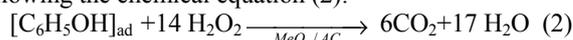
$$q_e = (C_o - C_e) \frac{V}{W}$$

Where: q_e is the phenol adsorbed amount (mg/g),
 C_o is the initial concentration of phenol (mg/L),
 C_e - the equilibrium concentration (mg/L),
 V and W are the volume of solution (L) and mass of the AD-CAT sample used (g), respectively.

E. Regeneration of the AD-CAT sample saturated with phenol by hydrogen peroxide (H₂O₂) in aqueous medium

After saturated adsorption with phenol, (AD-CAT)_{sat} sample was washed with distilled water and dried at 70°C for 1 hour in a vacuumed dryer. Then 2g (AD-CAT)_{sat} powder sample (100-500µm) was put into a 0.25L Pyrex round-

bottom flask containing 0.1L distilled water. The flask with that suspension was carefully closed and maintained at a constant temperature of 25°C by a thermostat and agitated with a stirrer magnetic. After that, a necessary amount of H₂O₂ was loaded into the flask with the suspension. The moment at which H₂O₂ was put into the suspension was considered as starting of the oxidation reaction between H₂O₂ and phenol adsorbed on AC surface [C₆H₅OH]_{ad} following the chemical equation (2):



Where, MeO_x/AC is (AD-CAT) material, in which MeO_x as catalytic phase. During reaction, at regular time intervals a volume of 2.10⁻³L of the suspension was withdrawn, filtered and analyzed using a HPLC (class VP Shimadzu, Japan) equipped with C-18 column using mobile phase (acetone- nitride : methanol : water = 1:1:8) and a UV detector operating at 210 nm. The identification of products was performed by using corresponding standard chemicals.

The amount of H₂O₂ was used corresponding to 1.5-fold amounts calculated stoichiometrically from equation (2).

III. RESULTS AND DISCUSSION

A. Adsorption equilibrium

Fig. 2 shows the adsorption of phenol onto the TB-AC, 0.5wt% MeO_x/TB-AC and 7.0wt% MeO_x/TB-AC samples. It can be noted that the adsorption of phenol onto all three solids respects fairly the Freundlich isotherm $q_e = q_F \cdot C_e^{\frac{1}{n}}$, where, q_F and n are Freundlich characteristic factors of every certain "adsorbate-adsorbent" system. $n > 1$: the adsorption is favorable, and vice versa.

The Freundlich isotherms of the equilibrium data were determined as follows:

$$\begin{cases} q_{e,1} = 66 \cdot C_e^{0.168} & n=6.0 & R^2=0.990 & \text{for TB-AC sample} \\ q_{e,2} = 42 \cdot C_e^{0.218} & n=4.6 & R^2=0.984 & \text{for 0.5wt\% MeO}_x/\text{TB-AC sample} \\ q_{e,3} = 25 \cdot C_e^{0.226} & n=3.8 & R^2=0.989 & \text{for 7wt\% MeO}_x/\text{TB-AC sample} \end{cases} \quad (4)$$

In all the cases, the correlation coefficients (R^2) from the plot of $\log q_e$ versus $\log C_e$ were found to be 0.99 exhibiting a highly reliable level of obtained equations. From equations (4) it may be realized that Freundlich isotherm describes well the adsorption of phenol onto AC and MeO_x containing AC.

The adsorption occurs on a heterogeneous surface through a multilayer adsorption mechanism [6], and the adsorption capacity of these solids has the following order:

$q_e(\text{TB-AC}) > q_e(0.5\text{wt\% MeO}_x/\text{TB-AC}) > q_e(7.0\text{wt\% MeO}_x/\text{TB-AC})$. Thus, the presence of transition metal oxide which aggregates on the activated carbon will result in a decrease in the adsorption uptake of AC. However, this decrease did not

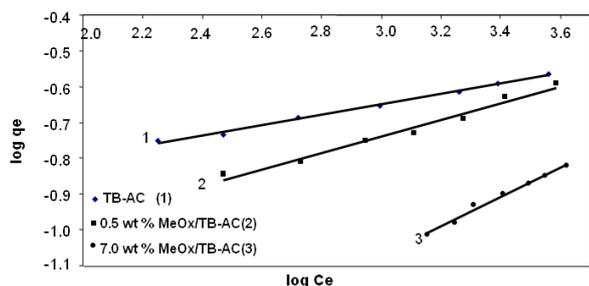


Figure 2. Freundlich isotherm of phenol adsorption on TB-AC (1), 0.5wt% MeO_x/TB-AC (2) and 7.0wt% MeO_x/TB-AC (3) solids.

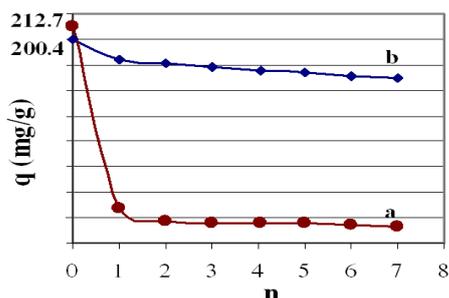


Figure 3. Adsorption capacity of samples as a function of the numbers of regenerated cycles(n): TB-AC sample (a), 0.5wt% MeO_x/TB-AC sample (b).

follow a linear relation with the loading of oxides. Therefore, one must to take into account that the amount of MeO_x in adsorbent-catalyst material play a vital role in achieving optimally both adsorptive and catalytic functions of AD-CAT sample for the phenol abatement. The higher the loading of MeO_x is, the more the decrease in q_F and n does. In the present work, the loading of 0.5wt% MeO_x was selected for the study on kinetics and reaction pathway.

B. Regeneration of AC and [AD-CAT] sample

Figure 3 demonstrates the evolution of phenol adsorption capacities, which were obtained after consecutive regeneration cycle of saturated phenol adsorbed samples by hydrogen peroxide solution for 5h.

From Fig.3 it can be seen that whereas hydrogen peroxide cannot restore the adsorption capacity of TB-AC sample, initial adsorption capacity of 0.5wt% MeO_x/TB-AC sample was decreased in only several percentages (5.78%). Compensatively, phenol adsorption capacity of this sample was negligibly decreased after many regenerated cycles. The obtained result was rather similar to that published in the paper [14]. This means that the transition metal oxide plays an important role in catalytic oxidation of phenol molecules adsorbed on AC surface.

C. Reaction pathway and kinetics of regenerated oxidation reaction of [AD-CAT]_{sat} material

For this purpose four different experiments were carried out to collect information.

(i) Fig. 4 shows the variation of phenol concentration in liquid phase when 2g of 0.5wt% MeO_x/TB-AC sample

which has been saturated by adsorbed phenol was introduced into 0.1L of distilled water, at 40°C under well stirring condition.

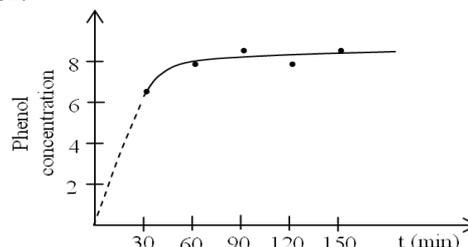


Figure 4. Phenol concentration as a function of time in the soaked process of phenol saturated 0.5wt% MeO_x/TB-AC powder in distilled water.

From Fig. 4 one can be observed that a small amount of adsorbed phenol within [AD-CAT] sample was delivered from solid surface into the liquid phase. By 60 min, the phenol concentration reached the equilibrium level ($7.8 \cdot 10^{-3}$ mol/L). Thus, the equilibrium amount of phenol in solution is equal:

$$m_{e, \text{phenol}} = 7.8 \cdot 10^{-3} \text{ mol/L} \times 0.1 \text{ L} \times 94 \cdot 10^{-3} \text{ mg/mol} = 73.32 \text{ mg phenol.}$$

It is known that, the adsorption capacity of phenol over 0.5wt% MeO_x/TB-AC solid is equal to 200.40 mg phenol/g (see Fig.3). So, the amount of adsorbed phenol from 2g solid is: $m_{ad, \text{phenol}} = 200.40 \text{ mg/g} \times 2 \text{ g} = 400.80 \text{ mg}$

Like that, during the contact time between phenol saturated 0.5wt% MeO_x/TB-AC sample and distilled water, by 60 minutes, the fraction of the phenol desorbed from the solid surface should be:

$$\alpha (\%) = \frac{73.32 \text{ mg}}{400.80 \text{ mg}} \cdot 100 (\%) = 18.29 \%$$

Thus, it was suggested that a certain phenol amount adsorbed on activated carbon surface was delivered from solid into liquid phase.

(ii) 0.1L phenol solution of 1,000 mg/L and a certain amount of H₂O₂ were introduced into a flask. The experimental conditions were kept similar to (i). The concentration of phenol and H₂O₂ were registered following the time intervals as indicated in Table 1.

TABLE I. H₂O₂ AND PHENOL CONCENTRATION AS A FUNCTION OF REACTION TIME.

Time (min)	Phenol (mol/L)	H ₂ O ₂ (mol/L)
0	10.6×10^{-3}	0.135
30	10.49×10^{-3}	0.136
150	10.51×10^{-3}	0.134

Table 1 shows that without catalyst, H₂O₂ practically does not chemically react with phenol in liquid phase.

(iii) 2g of TB-AC sample saturated adsorbed phenol, denoted as [TB-AC]_{sat}, was introduced into 0,1L of distilled water under following conditions: at 40°C, in the stirring state and with an amount of H₂O₂ being 1.5-fold stoichiometric one (Table. 2).

TABLE II. H₂O₂ AND PHENOL CONCENTRATION IN LIQUID PHASE AS A FUNCTION OF EXPERIMENTAL TIME

Time (min)	Phenol (mol/L)	H ₂ O ₂ (mol/L)
30	8.9892×10 ⁻³	0.1226
150	10.2900×10 ⁻³	0.1224

Table 2 indicates that [TB-AC]_{sat} sample released a few amount of phenol from its surface. This phenomenon is similar to the case of [AD-CAT]_{sat} sample as seen above (i) part). However, H₂O₂ concentration was mostly constant during the experimental process which once again indicated without catalyst the reaction between H₂O₂ and phenol in liquid phase does not occur.

(iv) 2g of [AC-CAT]_{sat} sample which is the 0.5wt% MeO_x/TB-AC saturated by adsorbed phenol was tested in

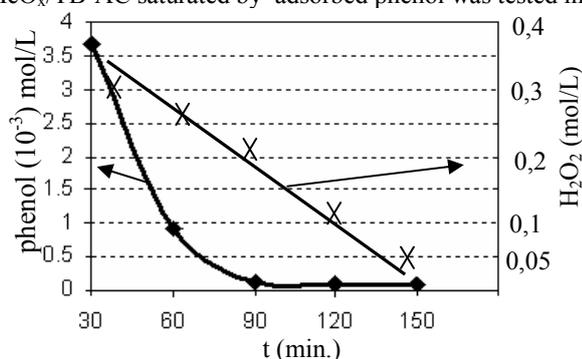


Figure 5. The evolution of phenol (♦) and H₂O₂ (x) concentrations in liquid phase during regeneration oxidation reaction over [0.5wt% MeO_x/TB-AC]_{sat} sample.

the contact with H₂O₂ under the same conditions used above. The obtained results of this experiment were demonstrated in Figure 5.

From Fig.5, it is observed that H₂O₂ concentration decreases following a linear relation with reaction time. In the meantime, phenol concentration decreases rapidly from 3.8.10⁻³ M to ~ 0 in the interval of 90 min. This phenomenon is obviously not due to the chemical interaction between H₂O₂ and phenol in solution (as shown above).

The explication for observed decrease in phenol concentration is that H₂O₂ molecules from the solution comes to react with phenol molecules adsorbed on carbon surface creating free active sites. These sites can again re-adsorb phenol from liquid phase.

In fact, after 90min, phenol concentration in solution was practically equal approximately to zero, whereas H₂O₂ concentration was still relatively high (~2.10⁻³ M). During the period from 90 to 150 min, H₂O₂ concentration continuously reduced. This means that H₂O₂ molecules continuously diffused into AC to oxidize phenol molecules on carbon surface and complete the regenerated oxidation cycle of spent AC.

It is interestingly noted that in all HPLC patterns of analyzed liquid samples there were only 2 peaks characteristic of H₂O₂ and phenol. This indicates that the oxidation of adsorbed phenol leading essentially to CO₂ and

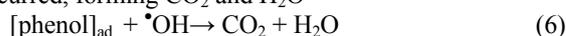
H₂O, not forming intermediates such as hydroquinone, catechol, acids ..., as frequently seen in WHPCO of phenol [5,13].

Based on the results obtained above, it is suggested that the regeneration of exhausted AC by H₂O₂ can be conducted as follows:

- H₂O₂ from solution penetrated into the AC and subsequently was decomposed at MeO_x site forming essentially •OH radicals [15]



- Then, •OH radicals spill over to the adsorptive sites occupied by phenol. At these sites the surface reaction between •OH radicals and adsorbed phenol molecules occurred, forming CO₂ and H₂O



D. Experimental kinetic equation of oxidation reaction of adsorbed phenol by H₂O₂.

From Fig.5 it can be noted that the change of H₂O₂ concentration in liquid phase from the beginning to the completing time (0-150 min.) of regenerated reaction was practically decreased as a linear function of time. Consequently, the rate of reaction (2) can be expressed as follows:

$$r_{\text{H}_2\text{O}_2} = -\frac{dC_{\text{H}_2\text{O}_2}}{dt} = -\frac{d}{dt}(-k_{\text{H}_2\text{O}_2} t) \quad \text{and} \quad r_{\text{H}_2\text{O}_2} = k_{\text{H}_2\text{O}_2} \quad (7)$$

Where: $r_{\text{H}_2\text{O}_2}$ is the reaction rate. It is determined based on the H₂O₂ concentration evolution; $C_{\text{H}_2\text{O}_2}$ is the H₂O₂ concentration in solution; $k_{\text{H}_2\text{O}_2}$ is the reaction rate constant regard to H₂O₂.

If the rate calculated based on phenol, we have the following expression:

$$r_{\text{phenol}} = -\frac{dC_{\text{phenol}}}{dt} = -\frac{1}{14} \frac{dC_{\text{H}_2\text{O}_2}}{dt} = \frac{1}{14} k_{\text{H}_2\text{O}_2} \quad (8)$$

From $dC_{\text{H}_2\text{O}_2} = -k_{\text{H}_2\text{O}_2} dt$ one can get $C_{\text{H}_2\text{O}_2} = -k_{\text{H}_2\text{O}_2} \cdot t + C_{\text{H}_2\text{O}_2}^0$

Based on experimental data of Fig.5, $k_{\text{H}_2\text{O}_2}$ was calculated as follows:

$$k_{\text{H}_2\text{O}_2} = \frac{C_{\text{H}_2\text{O}_2}^0 - C_{\text{H}_2\text{O}_2}}{t} = \frac{(3,67 - 0,07) \cdot 10^{-3} \text{ mol/L} \times 0,1\text{L}}{(150 - 60) \text{ min} \times 2\text{g}} = 0,002 \text{ mmol/g} \cdot \text{min}$$

$$\text{or } k_{\text{phenol}} = \frac{1}{14} k_{\text{H}_2\text{O}_2} = 0,8 \text{ mg phenol/g} \cdot \text{h}$$

In summary, regeneration oxidation of phenol adsorbed on activated carbon containing MeO_x in H₂O₂ solution was really a surface reaction. In this case mostly phenol molecules were attached to the surface of adsorbent. Thus, the phenol population on surface, of course was more than that in the cases of WACO and WHPCO. This was well favorable for the chemical interaction between phenol and H₂O₂. •OH radicals formed from H₂O₂ decomposition over MeO_x catalytic centers within AC can easily move to phenol molecules to carry out chemical reaction. Experimentally, the reaction rate equation of zero order with respect to both

phenol and hydrogen peroxide was obtained, revealing the abundance of hydroxyl radicals and phenol active species on AC surface.

E. Proposed reaction pathway of regeneration oxidation of phenol adsorbed on AC

As demonstrated above, in the suspension system consisting of H₂O₂ aqueous solution and solid powder of a 0.5wt%MeO_x/TB-AC catalytic adsorbent, H₂O₂ and phenol did not chemically interact each other in liquid phase. In contrast, H₂O₂ molecules entered into porous AC and were adsorbed on MeO_x aggregates to generate •OH radicals. These radicals then migrated to phenol molecules linked on adsorptive centers of AC and reacted (6). Being a surface reaction, the reaction rate can be expressed:

$$r = k \times \theta_{\text{phenol}} \times \theta_{\text{H}_2\text{O}_2} \quad (9)$$

To react, phenol molecules have to at least be chemically adsorbed on AC in monolayer surface phase. The surface coverage of phenol was expressed by Langmuir isotherm:

$$\theta_{\text{phenol}} = \frac{K_{\text{phenol}} \times C_{\text{phenol}}}{1 + K_{\text{phenol}} \times C_{\text{phenol}}} \quad (10)$$

Where

θ_{phenol} : the surface coverage of phenol adsorbed on AC sites.

K_{phenol} : adsorptive equilibrium constant of phenol on AC sites.

C_{phenol} : equilibrium concentration of phenol in solution in adsorption step.

In this investigation, it was experimentally shown that H₂O₂ molecules were not adsorbed on AC and practically did not generate •OH radicals on AC, but H₂O₂ released •OH radicals only on MeO_x sites (without MeO_x on AC, oxidation of phenol does not occur). Supposing that to create •OH radicals, H₂O₂ is first adsorbed in MeO_x sites following the Langmuir equation

$$\theta_{\text{H}_2\text{O}_2} = \frac{K_{\text{H}_2\text{O}_2} \cdot C_{\text{H}_2\text{O}_2}}{1 + K_{\text{H}_2\text{O}_2} \cdot C_{\text{H}_2\text{O}_2}} \quad (11)$$

Where $\theta_{\text{H}_2\text{O}_2}$: the surface coverage of H₂O₂

$C_{\text{H}_2\text{O}_2}$: H₂O₂ concentration in solution in oxidation step

$K_{\text{H}_2\text{O}_2}$: adsorptive equilibrium constant

Consequently,
$$r = k \cdot \frac{K_{\text{phenol}} \cdot C_{\text{phenol}}}{1 + K_{\text{phenol}} \cdot C_{\text{phenol}}} \cdot \frac{K_{\text{H}_2\text{O}_2} \cdot C_{\text{H}_2\text{O}_2}}{1 + K_{\text{H}_2\text{O}_2} \cdot C_{\text{H}_2\text{O}_2}}$$

In this work, C_{phenol} and $C_{\text{H}_2\text{O}_2}$ were rather large, so

$$K_{\text{phenol}} \cdot C_{\text{phenol}} \gg 1 \text{ and } K_{\text{H}_2\text{O}_2} \cdot C_{\text{H}_2\text{O}_2} \gg 1$$

$$\text{Therefore } r = k = \text{const} \quad (12)$$

The expression (12) is fairly in conformity with expressions (7) and (8).

Like that, the reaction between adsorbed phenol on AC surface and hydrogen peroxide can be considered as a typically heterogeneous reaction that proceeds following the Langmuir-Hinshelwood mechanism. It should bear in mind that phenol and H₂O₂ were adsorbed on two different sites:

phenol on AC and H₂O₂ on MeO_x sites. Because MeO_x aggregates were dispersed essentially on the external surface of AC (see fig. 1), whereas phenol molecules were adsorbed on the inside surface in micro- and mesopores, so •OH radicals must migrate from MeO_x sites to AC sites to attack phenol molecules.

Perhaps, it can still be noted that in this case phenol was adsorbed with a suitable state in which the bonds of aromatic ring of phenol molecule become weaker than C-OH and C-H bonds. Therefore phenol ring was broken by •OH radicals easily, prior to the oxidation action can occur to give essentially CO₂ and H₂O products, consequently under this condition hydroquinone, catechol...cannot be formed.

IV. CONCLUSION

The obtained results of this investigation deduced the following conclusions:

(i) Activated carbon containing a few amounts of transition metal oxides (MeO_x) can be a good material for abatement of phenol contamination in water and wastewater in terms of adsorption capacity and regenerated cycle (lifetime).

(ii) Reaction between phenol adsorbed on activated carbon and hydrogen peroxide solution is truly a heterogeneous surface reaction. Kinetics of this reaction respects the zero order equation towards both phenol and hydrogen peroxide. Reaction pathway follows the Langmuir – Hinshelwood mechanism, but reaction reagents adsorbed chemically on distinguished adsorptive site groups.

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