

Effect of solution pH on the kinetics of phenolics uptake on granular activated carbon

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Abstract

The impact of solution pH on the kinetics of adsorption and adsorption-reaction combination of phenol and o-cresol on Granular Activated Carbon (GAC) was evaluated at room temperature (21°C). Batch experiments were performed under oxic and anoxic conditions at pH values of 3, 7, and 11. The results showed that the equilibration time for physical adsorption increased with the increase in pH and occurred in the time range of (7.5–11) days for the adsorption-reaction combination (oxic cases). The polymerization reactions lagged by about 10 h under all of the pH values. Diffusivity coefficients in the oxic cases increased inversely with pH while the highest difference between oxic and anoxic diffusivities was observed at neutral pH. The homogeneous surface diffusion model (HSDM) predicted accurately the anoxic batches and deviated from the oxic data under all pH conditions. Under controlled dissolved oxygen and pH conditions, the isotherm and batch equilibrium capacities matched with maximum deviation of 4%. The effect of solution pH on the rate of the DO-induced enhancement was found to follow a simplified form of self retardant reaction model. The aforementioned model showed strong predictive capability for the formation of polymers with time.

Keywords: Activated carbon; Kinetics; pH; Phenolic; Dissolved oxygen; Polymer; Modeling

1. Introduction

The phenomenon of dissolved oxygen-induced enhancement in the adsorption of aromatics in general and phenolics in particular on activated carbon (AC) is very well

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established [1–8]. The aforementioned phenomenon was attributed to the formation of phenolic polymers on GAC surface in the presence of DO [3,6]. Abuzaid et al. [8] identified two dimers of phenol namely, 2-dihydroxy-1,1-biphenyl and 4-phenoxyphenol as products of the aforementioned reactions.

Solution pH is an important factor affecting AC adsorption. In general, AC adsorption capacity for typical organic pollutants from water increases with the decrease in pH [9]. Wu [10] reported that the highest AC adsorptive capacity for flouride solution was attained at pH 5.0. Alhert and Gorgol [11] investigated the adsorption of the supernatant of two land-fill leachates on GAC. The supernatant exhibited a weak pH effect on the adsorption capacity of GAC for total organic carbon (TOC) with the adsorptive capacity at pH 7 greater than that at pH 12.

The effect of solution pH on the DO-induced polymerization reactions of phenolics on GAC was first studied by Grant and King [1]. They found that those reactions were favored by higher pH conditions. However, in their experimental scheme, pH and temperatures effects were not separated from the effect of DO. Extreme pH values of 12 and 1.8 at a solution temperature of 80°C were studied. However, those conditions are unrealistic in environmental engineering applications.

Nakhla et al. [6] investigated the impact of solution pH on the enhancement in sorption capacity attributed to adsorbate polymerization. They conducted isotherm studies on phenol and o-cresol at room temperature (21°C) and pH values of 3, 7, and 11 in oxic and anoxic conditions. Their results showed that physical adsorption, measured by the anoxic capacity, was favored at low pH while pH 11 promoted polymerization, and the optimum pH for the adsorption of phenolics under oxic conditions was pH 7.

The aforementioned literature review was related to adsorption equilibrium studies. However, Koh and Chung [12] studied the effect of pH on the kinetics of ortho-phosphates adsorption on AC. They found that the adsorption at pH 4 was faster than that at pH 8 and 12. The effect of DO on the adsorption kinetics of phenolics was investigated by Vidic and Suidan [3]. They found that DO affects the kinetics of o-cresol adsorption on GAC in batch experiments resulting in two different uptake curves and diffusivity coefficients. Abuzaid and Nakhla [7] studied the kinetics of phenol adsorption on GAC under four different DO levels. Equilibrium was attained only after 48 h in the anoxic batch while taking about 14 days in the oxic batches. They also, reported a decrease in the apparent surface diffusivity coefficient with the increase in DO level of the sorbate solution.

The homogeneous surface diffusion model HSDM has been used for predicting kinetics in batches and columns. The mathematical formulation of the HSDM is readily available in the literature [13] and is not repeated here. Discrepancy between isotherm capacities and those attained in the kinetics experiments has been reported [14–17] and attributed to adsorption irreversibility and to a continuous decrease in the adsorbate concentration during an isotherm experiment [14].

As a result of the paucity of information in the literature, the main objective of this research was to study the effects of pH on the kinetics of phenol and o-cresol uptake, under oxic and anoxic conditions. Batch kinetic experiments were performed at room temperature and pH values of 3, 7, and 11. The predictive capability of the HSDM for the kinetics of physical adsorption and polymerization reactions was examined. The

effect of pH on the equilibrium capacities attained in isotherm and batch experiments under controlled environment was investigated, as well. Finally, a model which incorporates the effect of pH on the polymerization reactions was developed.

2. Experimental

The adsorbent used in this study was F-400 GAC supplied by Fisher Scientific, USA. The carbon was sieved to the 10×16 US mesh size, with a geometric mean diameter of 0.156 cm. Carbon samples were washed several times with deionized water to remove all fines, subsequently dried at 110°C for one day, and stored in a desiccator.

The experimental procedures for the study of the effects of solution pH on the adsorption isotherms were reported by the authors [6] and, therefore, are not repeated here. The rate experiments were conducted in five-liter completely mixed finite-bath reactors of the type shown in Fig. 1 [7] with a liquid volume of 4.5 l. GAC particles were trapped in a basket inside the reactor to increase external mass transfer by maximizing the fluid velocity relative to that of GAC. One anoxic (zero level of DO) and one oxic (DO around 30 mg l^{-1}) batch were simultaneously run at room temperature (21°C) at each of the pH values of 3, 7, and 11 at identical mixing conditions, initial sorbate and GAC concentrations. The various solution pH values were maintained following the procedure performed in the isotherm experiments [6].

The sorbate uptake was monitored with time until equilibrium was attained. After being filtered, samples were analyzed using Spectronic 21 spectrophotometer (Bausch and Lomb Model UV-D) at a wave length of 270 nm for phenol and o-cresol under all pH conditions with the exception of the pH 11 phenol solution which was measured at a

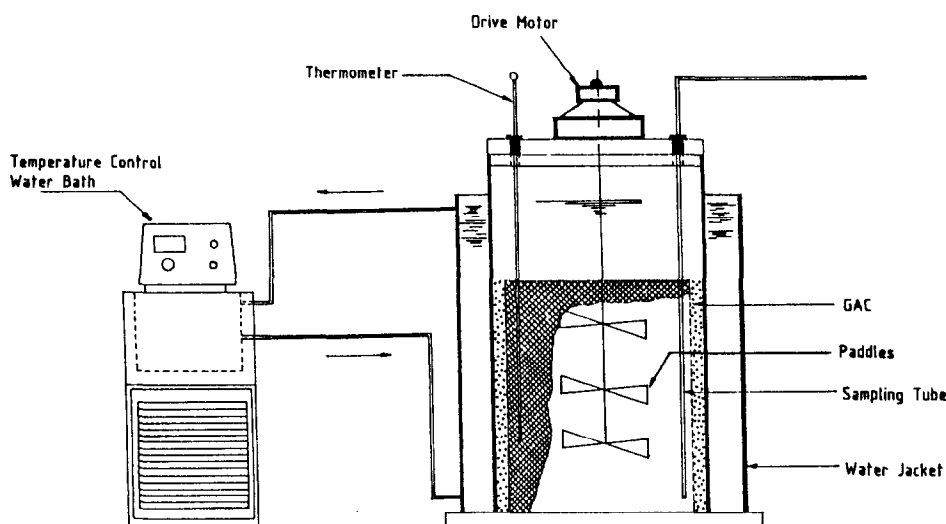


Fig. 1. Schematic of batch reactor.

wave length of 280 nm. The computer search for the values of k_f (the external mass transfer coefficient) and D_s (the surface diffusivity), that fit the HSDM model to the experimental data best, accounted for the mass of adsorbate removed by sampling.

3. Results and discussion

The authors [6] thoroughly investigated the effect of solution pH on the adsorption equilibria of phenol and o-cresol on GAC. Therefore, the isotherm results are not going to be discussed here. However, the isotherm parameters are presented in this article to facilitate comparison between isotherm capacities and those derived from kinetic studies. The parameters (k and $1/n$) of the Freundlich isotherm ($q_e = kc_e^{1/n}$) for different pH and DO conditions of phenol and o-cresol are presented in Table 1.

The influence of solution pH on the kinetics of adsorption and adsorption-reaction combination was evaluated at room temperature (21°C) by, simultaneously, running six batches for each adsorbate, one anoxic batch and one oxic (30 mg l⁻¹ DO) at pH values of 3, 7, and 11. Such a high initial DO level was selected, to amplify any observed differences and allow delineation of the pH role in this complex phenomenon although it is unlikely to prevail in a GAC adsorber.

Fig. 2(a–c) and Fig. 3(a–c) illustrate phenol and o-cresol adsorption kinetic data along with their HSDM lines of best fit at pH values of 3, 7, and 11, respectively. The fractional uptakes (U) defined by;

$$U = \frac{C_0 - C_\infty}{C_0} \quad (1)$$

are also shown, where C_0 and C_∞ are the initial and final concentrations in the liquid phase (mg l⁻¹). From the aforementioned figures, it is clear that pH variations affect the

Table 1
Freundlich constants for phenol and o-cresol isotherms [6]

| Adsorbate | DO designation | pH | k (mg g ⁻¹) (L mg ⁻¹) ^{1/n} | 95% Confidence interval (k) | 1/n | 95% Confidence interval (1/n) | R ² |
|-----------|----------------|----|---|-----------------------------|------|-------------------------------|----------------|
| Phenol | anoxic | 3 | 36.1 | 34.7–37.5 | 0.24 | 0.225–0.255 | 0.96 |
| | oxic | 3 | 61.4 | 60.2–62.6 | 0.19 | 0.163–0.217 | 0.95 |
| | anoxic | 7 | 31.7 | 30.4–33.0 | 0.24 | 0.236–0.244 | 0.99 |
| | oxic | 7 | 83.5 | 80.6–84.8 | 0.18 | 0.167–0.193 | 0.97 |
| | anoxic | 11 | 12.5 | 10.4–14.6 | 0.37 | 0.348–0.392 | 0.95 |
| | oxic | 11 | 32.8 | 29.3–36.3 | 0.31 | 0.279–0.341 | 0.96 |
| o-Cresol | anoxic | 3 | 109.6 | 107.1–112.1 | 0.17 | 0.152–0.188 | 0.97 |
| | oxic | 3 | 134.3 | 131.8–136.4 | 0.14 | 0.137–0.143 | 0.94 |
| | anoxic | 7 | 88.6 | 86.9–90.3 | 0.19 | 0.182–0.198 | 0.96 |
| | oxic | 7 | 190.4 | 186.2–194.6 | 0.13 | 0.114–0.146 | 0.99 |
| | anoxic | 11 | 29.4 | 28.7–30.1 | 0.19 | 0.174–0.206 | 0.96 |
| | oxic | 11 | 65.4 | 63.3–67.5 | 0.20 | 0.181–0.219 | 0.97 |

R² is the coefficient of determination.

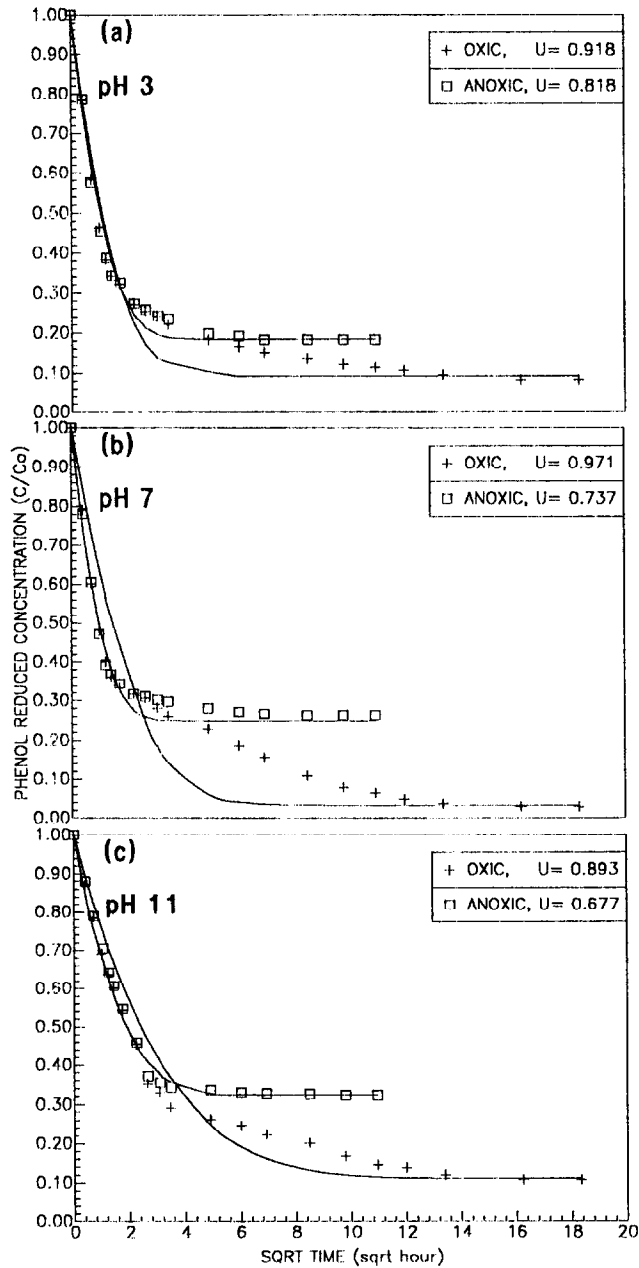


Fig. 2. Closed batch kinetic data with HSDM Fit for phenol at room temperature and (a) pH 3; (b) pH 7; (c) pH 11.

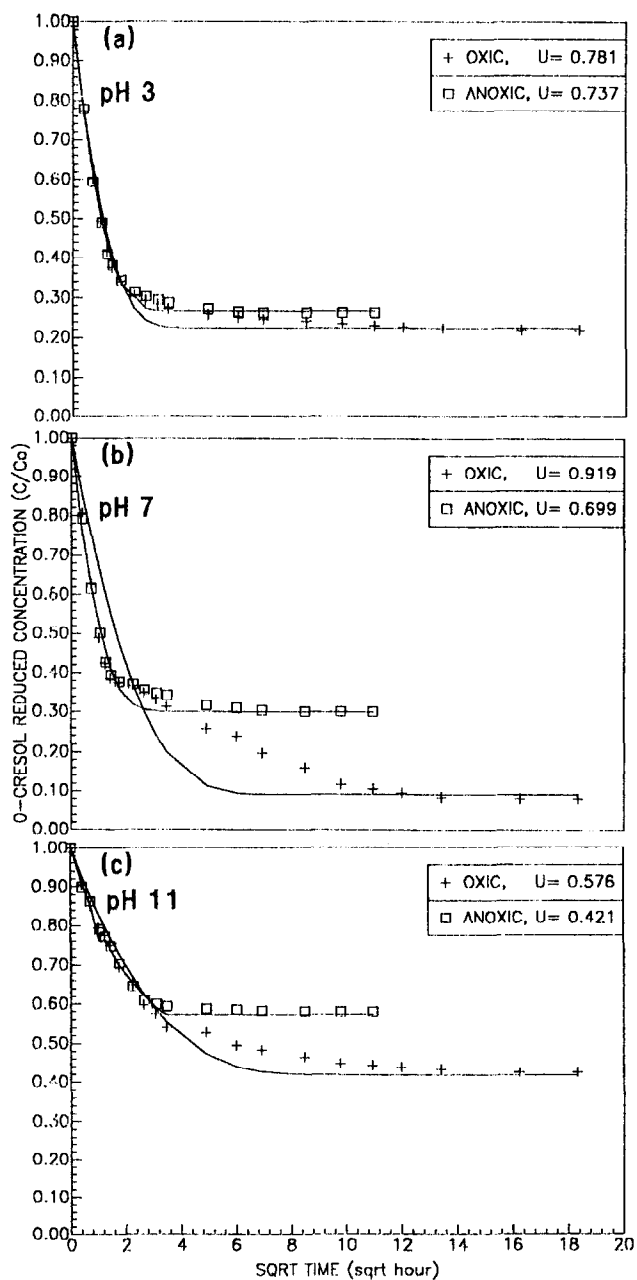


Fig. 3. Closed batch kinetic data with HSDM Fit for o-cresol at room temperature and (a) pH 3; (b) pH 7; (c) pH 11.

Table 2
Apparent HSDM surface diffusivities of phenol and o-cresol

| Adsorbate | DO designation | pH | D_s ($\text{cm}^2 \text{s}^{-1}$) |
|-----------|----------------|----|---------------------------------------|
| Phenol | anoxic | 3 | 4.2×10^{-8} |
| | oxic | 3 | 1.2×10^{-8} |
| | anoxic | 7 | 6.3×10^{-8} |
| | oxic | 7 | 7.6×10^{-9} |
| | anoxic | 11 | 2.4×10^{-8} |
| | oxic | 11 | 3.5×10^{-9} |
| o-Cresol | anoxic | 3 | 7.8×10^{-8} |
| | oxic | 3 | 5.9×10^{-8} |
| | anoxic | 7 | 8.3×10^{-8} |
| | oxic | 7 | 1.4×10^{-8} |
| | anoxic | 11 | 3.3×10^{-8} |
| | oxic | 11 | 1.1×10^{-8} |

kinetics of adsorption presented by the anoxic case as well as the kinetics of adsorption-reaction combination presented by the oxic one. The lag time needed for the reaction to start, which was observed by the authors [7] is clear here. This lag time, which is about 10 h, is not affected by the pH variation which gives rise to the postulation that this time is needed for dissolved oxygen and phenol to diffuse and fill the AC pores before any reaction can proceed.

The data show that the equilibration time for physical adsorption increases with the increase in pH, while for the oxic case in which a polymerization reaction is taking place, the equilibration time is not affected by pH variations. However, while all the pH-varied cases were at equilibrium on the eleventh day of the experiment, the measurements before this time were after 7.5 days from the start of the experiment. So, one can only conclude that equilibrium was attained in the period of (7.5–11) days from the start of the experiment.

Fig. 2 and Fig. 3 depict the good predictivity of the HSDM for physical adsorption (anoxic curves) regardless of pH, while this was not always the case for the oxic curves. This is attributed to the assumptions inherent to the HSDM that make its applicability limited solely to physical adsorption data. Similar findings were observed for o-cresol kinetic adsorption data by Vidic and Suidan [3]. The poor fit of the oxic data to the HSDM model can be attributed to surface polymerization. The variation of the apparent surface diffusivity, estimated from the HSDM fit with pH, is presented in Table 2.

To analyze the effect of pH on the oxic and anoxic uptakes, D_s values were plotted versus pH for phenol and o-cresol in Fig. 4. From the figure it is depicted that for the anoxic case (physical adsorption), the highest surface diffusivities were attained at pH 7. The order of D_s values was at pH 7 > pH 3 > pH 11 which conflicts with the findings of Koh and Chung [12] who observed that the kinetics were increasing with the decrease in pH. For the oxic condition, however, D_s values were decreasing with the increase in pH which agrees with the findings in the literature [9,12]. The reason for this is because standard experiments, oxic conditions are maintained, since, there is no DO removal step. D_s values in the oxic conditions were always lower than those in the anoxic case

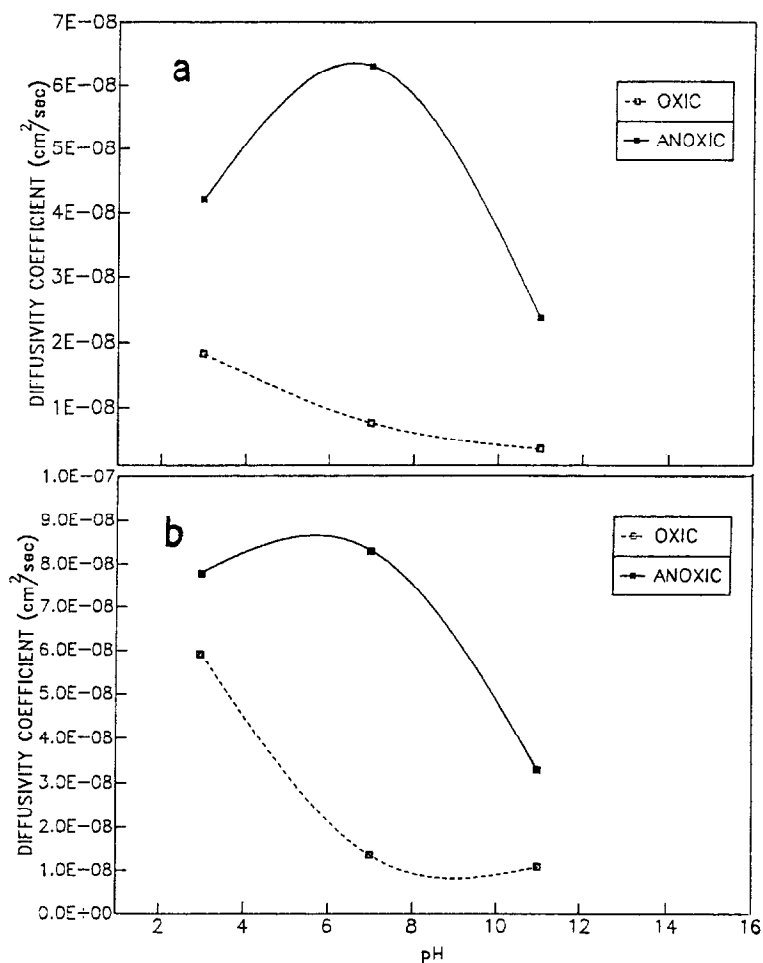


Fig. 4. Relationship between HSDM apparent diffusivities and pH for (a) phenol and (b) o-cresol.

which is attributed to the delay in the equilibration time resulting from the polymerization reactions on the carbon surface. However, the difference between D_s values in the oxic and anoxic batches was highest at pH 7 which means that the rate of the aforementioned reaction is highest at pH 7 compared to pH 3 and pH 11.

From Fig. 2, it is apparent that pH 11 oxic data are relatively better described by the HSDM than the pH 3 data. Sorbate uptake resulting from the surface reaction is influenced by pH in two ways. Adsorption is favored by acidic conditions [9] and since the surface reaction depends on the availability of sorbate on the GAC surface, its rate is likely to be enhanced by pH depression. Also, the degree of sorbate ionization has a significant bearing on its surface reactivity. Data from Grant and King [1] has demonstrated that the phenolate ion is more reactive than phenol and, therefore, surface polymerization is accelerated to the extent that it closely approaches the sorbate

Table 3
Equilibrium isotherm and batch capacities under different pH and DO conditions for phenol and o-cresol

| Adsorbate | DO designation | pH | Iso. cap. (mg g ⁻¹) | Batch cap. (mg g ⁻¹) |
|-----------|----------------|----|---------------------------------|----------------------------------|
| Phenol | anoxic | 3 | 125.7 | 127.9 |
| | oxic | 3 | 141.7 | 143.8 |
| | anoxic | 7 | 120.6 | 116.8 |
| | oxic | 7 | 153.2 | 152.9 |
| | anoxic | 11 | 108.7 | 105.6 |
| | oxic | 11 | 139.4 | 139.8 |
| o-Cresol | anoxic | 3 | 282.6 | 276.4 |
| | oxic | 3 | 285.6 | 289.1 |
| | anoxic | 7 | 262.0 | 262.2 |
| | oxic | 7 | 337.1 | 344.6 |
| | anoxic | 11 | 98.4 | 94.73 |
| | oxic | 11 | 219.3 | 216.0 |

adsorption rate resulting in a relatively good fit of the HSDM to the latter part of the kinetic data. Further, Chrotowski et al. [18] have established that the rate of liquid phase oxidative coupling of phenolics is more rapid in a basic medium than in an acidic environment. The kinetic data for o-cresol (Fig. 3) highlights the composite effect of pH on surface polymerization. For o-cresol, in contrast to phenol, the HSDM model fits pH 3 kinetic data best. The fundamental difference in behavior between phenol and o-cresol in terms of conformity of oxic data to the HSDM lies in the pKa. o-Cresol has a pKa of 10.2 compared with 9.2 for phenol and, therefore, at pH 11 more phenol is ionized and surface reactivity rate is more enhanced. For o-cresol, enhanced physical adsorption in acidic media and the concomitant acceleration of surface reactions to approach diffusion rates has resulted in a better fit of the HSDM.

The isotherm capacities and those attained in the kinetic batches were calculated at equilibrium for the different pH and DO conditions and presented in Table 3. The isotherm capacities were calculated using the Freundlich model incorporating parameters pertinent to the environmental conditions (DO, pH) which were presented in Table 1.

From Table 3, it is clear that at a controlled room temperature (21°C) and at each of the pH and DO conditions, the isotherm and batch capacities are similar with a maximum difference of 4%.

Based on the fact that the DO-induced enhancement phenomenon in the adsorption capacity of phenolics on GAC is caused by the formation of polymers of the sorbate on the carbon surface [3,6–8], it can be postulated that such conversion would allow more solute to migrate to the adsorbent. Therefore, at any time, the formation of such polymers is related to the difference between the oxic and anoxic uptake. In order to investigate the effect of pH variation on those polymerization reactions, the differences between the oxic and anoxic uptakes (P) were calculated for the curves of Fig. 2 and Fig. 3 and presented in Fig. 5 for phenol and o-cresol.

Since those polymerization reactions are controlled by the limited and nonrenewable

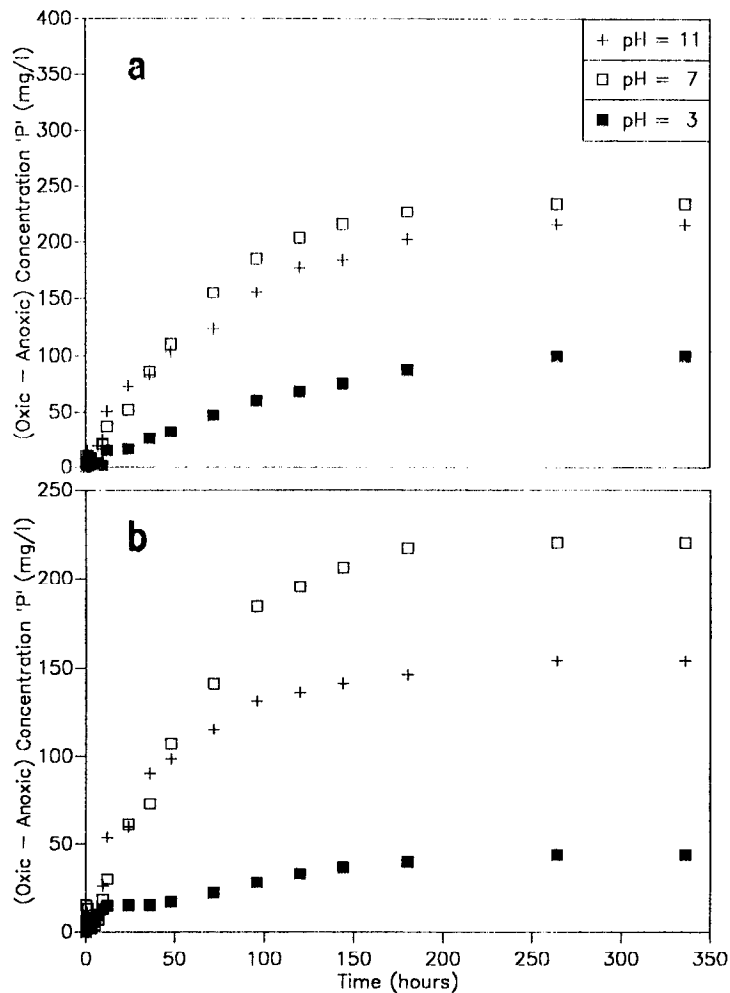


Fig. 5. Relationship between polymerization reactions product "P" and time at different pH values for (a) phenol and (b) o-cresol.

amounts of DO in the adsorption batches and by the limited GAC surface, a simplified zero order retardant reaction model [19] is proposed;

$$\frac{dp}{dt} = \frac{K}{t} \quad (2)$$

which can be solved as;

$$p = K \times \log t + c \quad (3)$$

where, P is the amount of polymers produced determined as the difference between the oxic and anoxic uptakes, t is time, greater than 10 h (lag time), and K and C are constants. Accordingly, P was plotted against $\log t$ and presented in Fig. 6 for the data

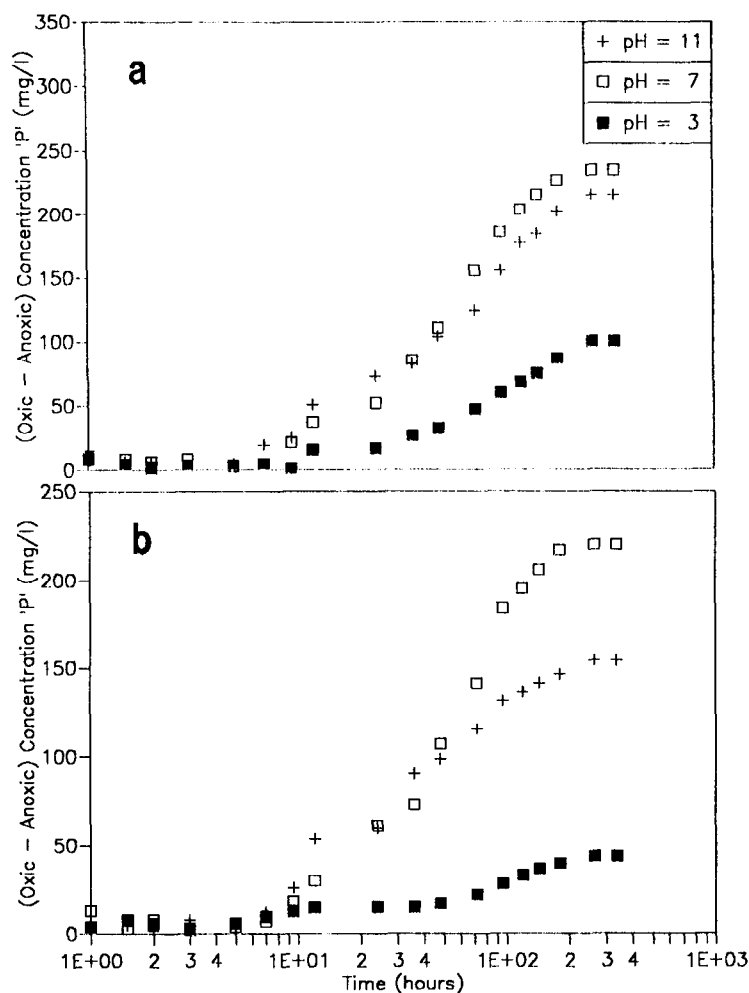


Fig. 6. Relationship between polymerization reactions product "P" and time at different pH values for (a) phenol and (b) o-cresol. (linearization of Eq. (3)).

shown in Fig. 2 and Fig. 3. From Fig. 6, the reaction lag time (about 10 h) which was discussed earlier is obvious. After the lag time, the reaction started and the curves have demonstrated mostly linear relation between P and $\log t$. The slopes and intercepts of the lines were calculated for the different pH levels for phenol and o-cresol and presented in Table 4.

The goodness of the fit of the experimental data to the proposed model attested by high R^2 values is also apparent from Fig. 7. Fig. 7 depicts the good predictability the proposed rate model has for the data.

Efforts were made to develop a relationship between the slope (K) and the intercept (C) in Eq. (3) and pH using the data of Table 4. The nonlinear regression analysis

Table 4
Calculated values of the constants in Eq. (3) for phenol and o-cresol

| Adsorbate | pH | K | C | R ² |
|-----------|----|-------|--------|----------------|
| Phenol | 3 | 69.0 | -74.0 | 0.93 |
| | 7 | 173.0 | -169.0 | 0.96 |
| | 11 | 135.0 | -113.0 | 0.96 |
| o-Cresol | 3 | 25.0 | -19.4 | 0.93 |
| | 7 | 166.0 | -162.9 | 0.96 |
| | 11 | 84.0 | -42.4 | 0.97 |

R² is the coefficient of determination.

program available in the SAS package at KFUPM [20] was used. After substituting for the constants, Eq. (3) takes the form;

$$P = \left[k_1 + k(\text{pH} - 7)^2 + m(\text{pH}) \right] \log t - \left[1.2k_1 + 1.1k(\text{pH} - 7)^2 + 0.5m(\text{pH}) \right] \quad (4)$$

were k_1 equals to 115.2 and 114.3 for phenol and o-cresol, respectively, k equals to 4.43 and 6.98 for phenol and o-cresol, respectively, and m equals to 8.25 and 7.4 for phenol and o-cresol, respectively.

Eq. (4) can be used to evaluate the extent of polymers formation (or additional capacity) with time at different pH values. This is very important from a practical stand point. Since economy is the main factor affecting design and operation of such treatment systems and the initial GAC cost is, relatively, high, a trade off between pH adjustment and the other operational variables can be performed to come up with optimum and cost effective designs.

There are several practical applications of the findings of this study in industrial waste treatment as well as remediation of hazardous waste sites, of which few will be discussed below. Aromatic-bearing wastewater emanating from various industrial operations including oil and gas distillation, petroleum refining and pharmaceuticals are generally amenable to treatment by carbon adsorption. Such wastewaters are typically low in dissolved oxygen. The results of the anoxic experiments suggest that both the rate and the adsorptive capacity are maximum at neutral pH and therefore neutralization of industrial aromatic laden wastewaters prior to GAC adsorption is advantageous. Cecen [21] reported that wastewaters from an industry producing heavy-duty household detergents were highly alkaline and simultaneously heavily laden with organic and oil and grease. Such wastewaters although amenable to treatment by adsorption require pre-neutralization according to the findings reported herein.

Further, many hazardous non biodegradable insoluble contaminants such as PCBs, pesticides and herbicides are amenable to recovery from contaminated media by surfactant and or solvent supplemental technologies such as soil washing/flushing. Surfactant and/or solvent recovery often entails treatment by activated carbon. Therefore, neutralization prior to adsorption resulting in a much sharper breakthrough and more efficient utilization of activated carbon.

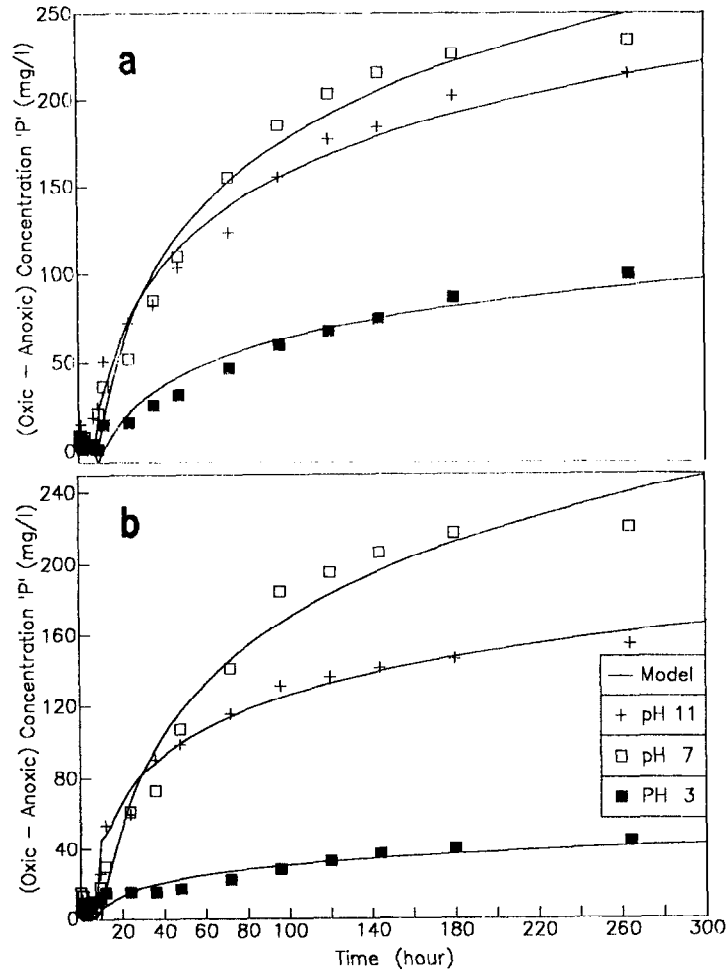


Fig. 7. Closed batch kinetic data for (a) phenol and (b) o-cresol along with the prediction lines of Eq. (3).

The findings of this study also corroborate the importance of neutralization and/or aeration prior to adsorption in pump-and-treat schemes for remediation of organic-laden ground waters which vary substantially in pH depending on the subsurface geochemistry [22].

4. Conclusions

The influence of solution pH on the kinetics of adsorption and adsorption-reaction combination of phenol and o-cresol on GAC was evaluated at room temperature (21°C) by, simultaneously, running six batches for each adsorbate, one anoxic batch and one oxic (30 mg l^{-1} DO) at pH values of 3, 7, and 11.

Based upon the findings of this work, the following conclusions can be drawn:

- Equilibration time for physical adsorption increases with the increase in pH, however, for the oxic conditions, in which polymerization reactions take place, the equilibration time occurs in the time range of (7.5–11) days.
- Diffusivity coefficients in the oxic cases increase inversely with pH while the highest difference between oxic and anoxic diffusivities was at pH 7.
- Anoxic uptakes were predicted accurately by HSDM under all of the pH values while this was not the case for the oxic data.
- Solution pH was found to have a mixed effect on the kinetics of adsorption-reaction systems with largest discrepancies between HSDM fit and data at neutral pH.
- The polymerization reactions lagged by about 10 h under all of the pH values.
- The effect of solution pH on the rate of the DO-induced enhancement was found to follow a simplified form of self retardant reaction model. The aforementioned model demonstrated strong predictive capability for the temporal formation of polymers.

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