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Predictions of H_2S Breakthrough Capacity of Activated Carbons at Low Concentrations of Hydrogen Sulfide

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Abstract. In this study a combined approach based on known theoretical solution of a dynamic model, where the parameters of the model are determined from the experimental data at high concentration of an adsorbate is used. The breakthrough time for the required conditions is calculated from the extrapolation of the experimental data fitted by the theoretical equation derived from the model. Parameters of the model used, e.i. kinetics coefficient and the capacity of an adsorbent are found by fitting theoretical and experimental breakthrough curves obtained for high concentrations of H_2S. The results are compared to those collected in "real life" long term tests of coconut shell based activated carbons at North River Water Pollution Control Plant in New York City.

Keywords: adsorption, activated carbon, dynamics, hydrogen sulfide

Introduction

Hydrogen sulfide is among the pollutants effectively adsorbed on activated carbons. To remove this odoriferous and toxic species from air, the New York City Department of Environmental Protection (DEP) installed 109 carbon towers in 12 Water Pollution Control Plants (WPCPs). Each tower contains around 11 tons of activated carbon. So far, mainly caustic-impregnated carbons have been used to remove hydrogen sulfide odor. Due to their many disadvantages, the DEP currently carries out long-term tests to replace caustic impregnated carbons with unmodified ones. The later materials have a high capacity for physical adsorption, which is beneficial for removal of volatile organic compounds (VOCs) also present in effluent air. When the capacity of activated carbon to remove H_2S is exhausted, due to deposition of sulfur and other H_2S oxidation products, the spent adsorbent has to be replaced by a fresh material. It raises the question on the estimation and/or prediction of the lifetime of the adsorbents. Due to the low H_2S concentration (usually in the range of 10–300 ppb) in WPCP columns operation time varies between 4 and 6 years.

A commonly used standard method to estimate the performance of carbon as H_2S adsorbent is ASTM D6646-01. This is an accelerated test in which a carbon bed (1″ × 9″) is exposed to wet air with 10,000 ppm of H_2S. Then the breakthrough time at 50 ppm is measured. For carbon considered as good the test time can last from few to tens of hours. Besides the practical point of view and usefulness of the comparison of the

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results obtained at the same conditions, the accelerated test does not reflect the performance of carbon at low concentration of H_2S.

Prediction of the breakthrough time and capacities of adsorbents at very low concentration of H_2S may be done using different approaches. The first involves choosing an appropriate theoretical model and calculating the breakthrough curve and capacity from such model (Ruthven, 1984). This requires knowing "a priori" mass transfer coefficients, diffusivity, and the parameters of adsorption isotherm. The second type of approach is completely empirical and based on performing the experiments in appropriate conditions (low concentration, the same hydrodynamic conditions and geometry of the adsorbent bed) and determining the breakthrough time and capacity directly from the experimental data (Cooney, 1999).

The objective of this research is to develop a combined approach based on the theoretical solution of an adsorption model, where the parameters of the model are determined from the experimental data at high concentration of an adsorbate. Then the breakthrough time for the required conditions is calculated from the extrapolation of the experimental data fitted by the theoretical equation derived from the model.

Materials and Methods

Coconut shell based activated carbon, 208C, from Waterlink, Barnabey and Sutclife Corporation was used in this study in Laboratory (Lab) and Plant (Plant) conditions. According to nitrogen adsorption isotherm this carbon can be characterized as a microporous material with the volume of micropores, $V_{\mathrm{mic}}(\mathrm{DR}) = 0.44\ \mathrm{cm}^3/\mathrm{g}$, the total pore volume, $V_t = 0.46\ \mathrm{cm}^3/\mathrm{g}$ and BET surface area $S_{\mathrm{BET}} = 880\ \mathrm{m}^2/\mathrm{g}$.

The dynamic Lab test was used to evaluate the performance of carbon for H_2S adsorption. Humidified air (relative humidity 80% at 20°C) containing a determined inlet concentration (10000, 5200, 1560, 920 or 450 ppm) of H_2S was passed through a column of carbon (diameter 2.5 cm, bed height about 14 cm), and the outlet concentration of H_2S measured by an electrochemical sensor. Total flow rate was chosen as 1.65 L/min in order to have the same residence time (t_R = 3.3 sec) as for a 6-ports plant column at North River WPCP. To have comparable adsorption conditions of experiment the test was stopped at the ratio of the breakthrough concentration (C_b) to the initial concentration (C_o) equal to 0.01. Then the breakthrough capacity for H_2S adsorption was calculated using the concentration of adsorbate, flow rate, breakthrough time and weight of carbon sample.

The long-term tests of the performance of activated carbon as H_2S adsorbent were done at the commercial adsorber installed in the North River WPCP. The adsorber consists of two carbon beds (top and bottom; 3.66 m in diameter and 0.92 m height) where wet air stream from plant facilities is supplied with an average flow rate of 350 m^3/min. Every half a year the carbon samples were taken from three sampling ports (1, 2 and 3) located at the bed depth of 23, 46 or 69 cm, and then were analyzed in CCNY laboratory. This study covers seven testing periods.

X-Ray Fluorescence analysis was applied to study the sulfur content in carbons. The SPECTRO model 300T Benchtop Analyzer from ASOMA Instruments, Inc equipped with high-resolution detector was used. A company created and calibrated method, which separates signal from sulfur and chlorine was applied. In order to evaluate the reaction products, total adsorption, and water content thermal analysis (TA) was carried out using TA Instruments Thermal Analyzer. The instrument settings were: heating rate of 10 deg/min in nitrogen atmosphere, 100 mL/min flow rate. Using the special calibration experiments with initial and exhausted carbons it was found that water desorbs at temperatures below 150°C, VOCs—at the range of 200 and 500°C and sulfur—at 350–450°C. The composition of VOCs adsorbed at Plant conditions was studied using GC/MS (Shimadzu QP5050) with XTI-5 column. The samples for GC/MS analysis were extracted from carbon samples using *n*-hexane.

Results and Discussion

The mechanism of simultaneous H_2S and VOCs removal from wet air, have likely an adsorption-catalytic nature. It means that reagents, hydrogen sulfide and oxygen, adsorb on the active sites of the solid surface and then catalytically react with formation of elemental sulfur and water, which are then adsorbed in micropores (Adib et al., 2000; Bandosz, 2002). The process is completely irreversible at temperatures lower than melting point of sulfur. The VOCs and water can physically adsorb in micropores, where they compete for available active sites. Due to the high adsorption potential of VOCs and its affinity to the carbon surface, they are adsorbed strongly, and can substitute adsorbed water in micropores. If we assume the isothermal conditions of process, which is correct at low concentration of H_2S and VOCs, and plug flow of reaction gases in a fixed bed reactor, the following mathematical model can be used to describe the dynamics of adsorption (Cooney, 1999). The basic equations of the model are summarized as follows:

Mass balance (continuity) equations for fixed bed adsorber:

$$\partial C_i \,/\, \partial t + U \partial C_i / \partial x + (1-\varepsilon)/\varepsilon \partial q_i \,/\, \partial t = 0 \quad (1)$$

Kinetics of adsorption:

$$\partial q_i / \partial t = k_i C_i (q_{\mathrm{ei}} - q_i) \quad (2)$$

Initial and boundary conditions:

$$t = 0, \quad C_i(x) = 0; \quad q_i(x) = 0 \quad (3)$$

$$x = 0, \quad C_i(t, x) = C_{\mathrm{oi}} \quad (4)$$

Isotherms of adsorption for each component:

$$q_{\mathrm{ei}} = f(C_i, T) \quad (5)$$

The similar model was proposed first by Bohart and Adams (Bohart et al., 1920) for one component adsorption. It is widely used to describe the dynamics of adsorption when chemical reaction takes place. Equation (1) represents the differential mass balance for component "i" in a fixed bed adsorber with corresponding initial and boundary conditions (3–4). At an initial moment of time, $t = 0$, the bed is free from adsorbates and reaction products. Concentrations of adsorbates in a gas phase, C_i, and an adsorbed phase, q_i, are equal to zero at any point of the bed. Inlet concentrations of each gas components are constant and equal to C_{oi}, at any moment of time.

The "quasichemical" rate law (2) is used to describe kinetics of process. Rate of adsorption, $\partial q_i/\partial t$, is proportional to the concentration of the i-component of mixture "C_i" and to the fraction of the capacity of an adsorbent "$(q_{\mathrm{ei}} - q_i)$", which still remains at present moment of time, q_{ei} is the constant value of q_i which corresponds to the equilibrium condition in the presence of others $i - 1$ components, and k_i—is the kinetics coefficient. It is important to notice that "q_i" is the average concentration of adsorbate in the solid phase, expressed in units of an adsorbate mass per unit volume of a solid phase. It is linked to the value of adsorption "a_i", which has dimension of "g of adsorbate per g of adsorbent" in the following expression: $a_i = q_i(1-\varepsilon)/d_c$, where ε—is the porosity of the carbon bed and d_c—is the adsorbent bulk density.

Application of the model and determination of its parameters was done in two steps. First, the model was simplified to a one-component system (H_2S in Lab test) and parameters for H_2S adsorption were determined. Then those parameters were used to model the process of H_2S, VOCs' and H_2O adsorption in real Plant conditions.

However, it was found experimentally that water adsorption facilitates the H_2S removal by activated carbons, when its value exceeds 10–20% wt. the H_2S adsorption practically does not depend on H_2O content. Taking this into account, and also the absence of any VOCs at the Lab conditions, the process of H_2S adsorption can be described by mass balance and kinetics equations for one component (H_2S) with corresponding boundary conditions. In this type of model the rectangular isotherm (6) is commonly used to describe the equilibrium in a reaction system.

$$q_e = \begin{cases} 0, & \text{if } C = 0 \\ q_s, & \text{if } C > 0 \end{cases} \quad (6)$$

For zero axial dispersion, the differential mass balance equation was solved using the rate expression and rectangular isotherm. The solution can be expressed as (Cooney, 1999):

$$C/C_{\mathrm{o}} = \exp(\tau)/(\exp(\tau) + \exp(z) + 1), \quad (7)$$

where $z = kq_{\mathrm{s}} \times / U(1-\varepsilon)/\varepsilon$ and $\tau = kC_{\mathrm{o}}\,(t - x/U)$ are dimensionless variables, U is the average axial velocity of the flowing gas mixture in the interstitial spaces. To calculate the breakthrough curves one needs to be interested only in variation of concentration at the end of the bed, namely at $x = L$. For this case a very simple equation is derived for breakthrough time, t_b, of an adsorbent bed with a bed depth is equal to L:

$$t_{\mathrm{b}} = L/U + (x_{\mathrm{L}} - \mathrm{Ln}(C_o/C_b - 1))/kC_{\mathrm{o}}, \quad (8)$$

where $x_{\mathrm{L}} = kq_{\mathrm{s}}L/U\,(1-\varepsilon)/\varepsilon$, and C_{b} is the H_2S breakthrough concentration.

Parameters of the model e.i. kinetics coefficient, k, and the capacity of an adsorbent, q_{s}, were found by fitting the theoretical and experimental breakthrough curves for $C_{\mathrm{o}} = 10{,}000, 5{,}200, 1{,}560, 920$ and 450 ppm (Fig. 1). The average values of these parameters are equal to: $k = 7000\ \mathrm{cm}^3/(\mathrm{g\ min})$ and $q_{\mathrm{s}} = 0.061\ \mathrm{g/cm}^3$.

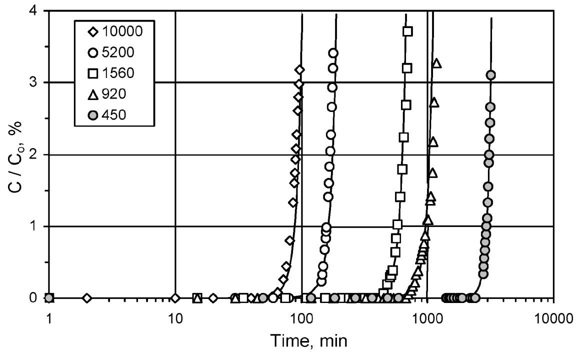

Figure 1. Experimental (points) and calculated (lines) H_2S breakthrough curves at different initial concentrations of hydrogen sulfide.

It was also found that the dynamics of H_2O adsorption can be described by Lodewyckx-Vansant (L-V) model (Lodewyckx et al., 1997).

Analyses of carbon samples taken from the Plant column at different testing periods showed that H_2S, VOCs and H_2O are adsorbed at different rates. The highest rate was found for H_2O and lowest for H_2S. H_2S is mainly oxidized to elemental sulfur, which precipitates in carbon micropores blocking their entrances, VOCs and sulfur can substitute adsorbed H_2O, H_2S is probably adsorbed in pore space available after VOCs adsorption, total adsorption of all component reaches 35–40% wt, VOCs adsorption gradually increases with tendency of saturation at around 30% wt. The average amount of adsorbed sulfur does not exceed 3% wt after 3.5 years of operation.

For proper dynamics modeling it is necessary to estimate the composition and nature of VOCs. GC-MS analysis of exhausted carbon samples shows the presence of more than 11 main components. Decane, dodecane, 1,2,4-trimethylbenzene and xylene and their derivatives are present at the highest concentration (Bagreev et al., 2002). All these species have high boiling temperature (from 140 up to 220°C), density around 0.7–0.9 g/cm^3 and low saturation vapor pressure at ambient conditions. TA analysis showed that VOC desorption from activated carbons occurs at temperature between 200 and 500°C.

In our case a multicomponent model of adsorption can be reduced to three main components: first—H_2S, second—VOC with "average" properties of found species, and third—H_2O. Moreover, H_2O adsorption can be described as quasiequilibrium due to the high concentration of H_2O and the long operation time of the carbon bed. Rectangular type isotherms were used to model the equilibrium of VOC and H_2S. The amount of H_2S adsorbed depends on available space left after VOC adsorption and it can be described by equation:

$$q_{s1} = (V_{\text{mic}} - q_2(1-\varepsilon)/d_c d_2) d_1 p_1 d_c/(1-\varepsilon), \quad (9)$$

where q_2—is the actual amount of VOCs adsorbed, d_1 and d_2 are the densities of sulfur and VOC, and p_1 is the packing factor for adsorbed sulfur.

The model equations were solved using a numerical method with known parameters (q_s and k) of H_2S adsorption corrected for hydrodynamics conditions. The parameters for VOC adsorption and L-V model parameters for H_2O adsorption where found by fitting the experimental and calculated data. The results of these fittings are present on Fig. 2, where numbers in the plot legends represent the port location. The initial concentrations of H_2S and VOC were 0.15 ppm and 1.4 ppm, correspondingly. Comparison of the H_2S breakthrough capacities received from the Lab test and the Plant test shows that the presence of VOC significantly decreases the amount adsorbed from 72 mg/g to 25 mg/g due to competitive character of H_2S and VOC adsorption.

In general, expression (8) may be used to predict the breakthrough time for any inlet concentration if a kinetics coefficient and a capacity of adsorbent are known. We can neglect the first term in Eq. (8) due to its small value in comparison with the second one, and after taking logarithm of both side of Eq. (8) we have:

$$\text{Log}(t_b) = \text{Log}((x_L - \text{Ln}(C_o/C_b - 1))/k) - \text{Log}(C_o) \quad (10)$$

If we "stabilize" value C_o/C_b at some certain level, for example $C_o/C_b = 100$, and take into account that for one component adsorption x_L does not depend on C_o and time, the linear equation can be obtained:

$$\text{Log}(t_b) = K_1 - K_2\text{Log}(C_o), \quad (11)$$

where $K_1 = \text{Log}((x_L - \text{Ln}\,(C_o/C_b - 1))/k)$ and $K_2 = 1$. Plotting the experimental data for breakthrough time versus the initial concentration (Fig. 3) and fitting these data using Eq. (11) one can found coefficients K_1 and K_2. Then the breakthrough time for a low concentration can be easily predicted by extrapolation of experimental data to "ppb" level (Fig. 3) or from a direct calculation of t_b using Eq. (10) for the particular concentration. In the case of multicomponent adsorption x_L value depends on the kinetics of VOCs adsorption.

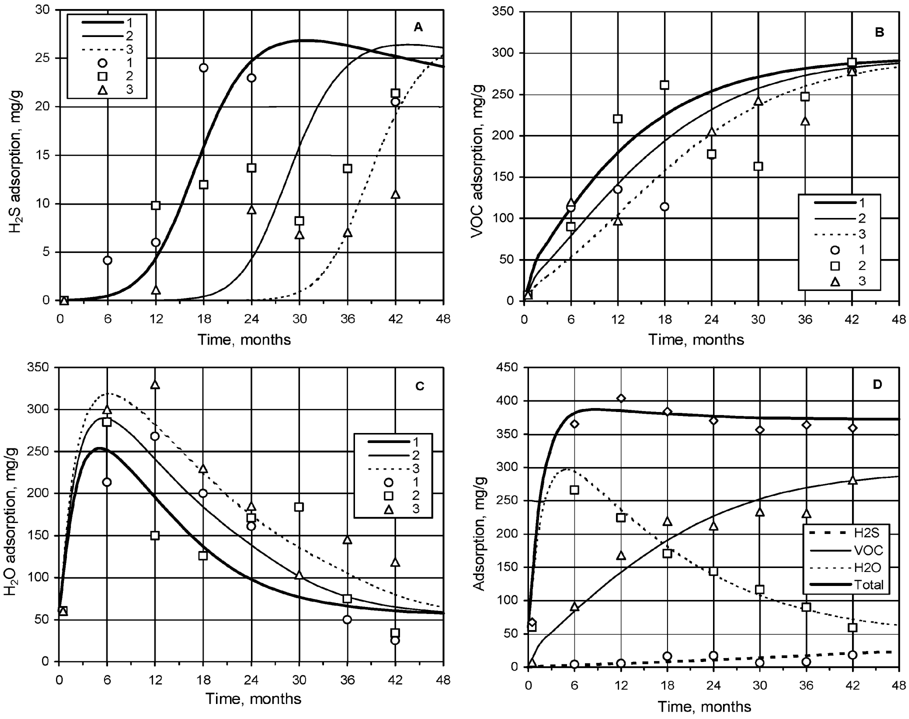

Figure 2. Dependence of H_2S (A), VOC (B) and H_2O adsorption (C) on time and the dependence of the average amount adsorbed (total) and that of each component on time (D). Experimental data is represented as points and calculated—as lines.

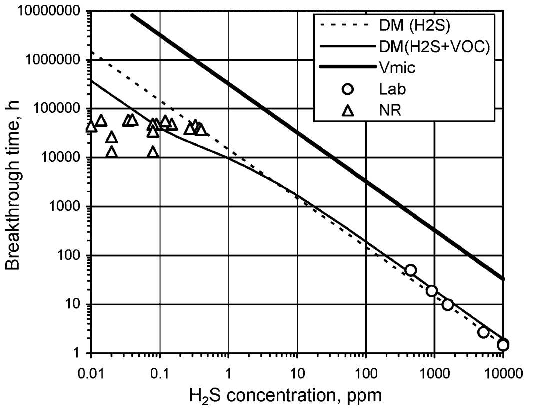

Figure 3. Dependence of the breakthrough time on inlet concentration of H_2S. Thin solid line and dashed line correspond to breakthrough time predicted by dynamics models (DM) for multicomponent (H_2S + VOC) and one component (H_2S) adsorption. Thick solid line predicts the amount adsorbed based on the micropore volume. Points represent the experimental data from the dynamics tests at high H_2S concentrations (Lab) and field conditions (NR).

If it is taken into account, the nonlinear dependence of the breakthrough time versus concentration is observed in the range of H_2S concentrations where competitive adsorption takes place. The results of these calculations are collected in Fig. 3 in comparison with experimental data and "working" line determined based on the micropore volume only. This volume limits the amount adsorbed. The best result is obtained for the model with multicomponent adsorption.

Conclusion

The method to evaluate the "real" breakthrough time and capacity of activated carbon at low concentration of H_2S was developed. The predicted values are in the range of experimentally observed data for the real life test at North River WPCP. To improve the predictions, the design of accelerated experimental procedure taking into account the competitive character of H_2S and VOCs adsorption is required.

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