Adsorption of Methylene Blue and Acid Blue 40 on Titania from Aqueous Solution

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Langmuir type adsorption was observed for two systems: methylene blue (MB) on TX titania and acid blue 40 (AB40) on P25 titania at an ambient temperature of (23 ± 2) °C and ambient pH initially at 4.6 ± 0.2 for P25 titania and 7.8 ± 0.2 for TX titania. Based on a Langmuir analysis, values for maximum surface coverage, $N_{\max}$, and adsorption intensity, b, are 1.6×10^{-5} mol MB·g^{-1} and 3.6×10^{4} L·mol^{-1}, respectively, for TX titania. An $N_{\max}$ value of 5.0×10^{-5} mol AB40·g^{-1} was determined for P25 titania. The TX titania adsorption surface area is estimated to be 12 m^{2}·g^{-1} based on maximum adsorption of methylene blue. Results of gel electrophoresis on both dyes at pH values of 4 and 9 indicate that methylene blue remains cationic and acid blue 40 remains anionic in this pH range. Single-point adsorption experiments at selected pH values other than ambient were performed. Experimental evidence clearly indicates that electrostatic attraction is a reasonable explanation for the observed adsorption process in the MB/TX system. Although the evidence is less conclusive, electrostatic attraction may also influence the adsorption process of the AB40/P25 system.

Introduction

The chemistry and interaction of molecules and ions at the surface/solution interface has been the subject of recent texts, chapters, and articles,[1−7] and the adsorption of organic molecules is of interest as it concerns titania particulates[8−13] and their role in photodecomposition and photocatalysis. Identifying characteristics of or manipulating the chemistry of aqueous particulate systems has become an interesting application of organic ion adsorption. Experimental investigations have included dye adsorption to sensitize photodegradation of organic solutes,[14−17] investigations of particulate surface modifications,[18,19] surfactant adsorption to alter surface charge and solute solubility in the vicinity of the particulate surface,[20] and adsorption to directly probe surface phenomena.[21−23] Clearly, ionic organic dye adsorption could be a useful area of investigation as well, although not a great deal of fundamental data have been published according to a recent review.[2]

The pH and ionic strength of solutions determine the surface characteristics of particulates introduced into those solutions, including the surface charge.[1,2,24−26] In general, hydrated oxide surfaces are viewed as amphoteric materials that respond to the bulk solution pH. The point of zero net proton charge, PZNPC, is a unique pH value that equalizes the number of protonated and deprotonated surface sites, resulting in a net neutral surface charge. At pH values below the PZNPC, the hydrated surface is protonated and therefore has an acquired positive charge. At pH values greater than the PZNPC, the hydrated surface is deprotonated, thereby acquiring a negative charge.

Ionic dye adsorption from solution onto particulates has been shown to be adequately described by the Langmuir model,[2,14,15,18,27−29] and the model's basic assumptions are consistent with the less well defined ionic nature of the particulate surface after hydration.[2] Typically, the moles of adsorbed dye per gram of adsorbent, N, rapidly increases reaching a plateau value as the equilibrium concentration of unadsorbed dye, $[\mathrm{Dye}]_{\mathrm{eq}}$, increases. This plateau value, $N_{\max}$, corresponds to an assumed single-layer full surface coverage by adsorbate molecules. The data trends just mentioned are well represented by eq 1, which defines the relationship among N, $N_{\max}$, $[\mathrm{Dye}]_{\mathrm{eq}}$, and a fourth parameter, b, a measure of the intensity of adsorption[1] which is defined as the ratio of moles of adsorbed dye to moles of solution dye.

$$N = (N_{\max} b\,[\mathrm{Dye}]_{\mathrm{eq}})/(1 + b\,[\mathrm{Dye}]_{\mathrm{eq}}) \qquad (1)$$

Recasting eq 1 in a linear form so that values for $N_{\max}$ and b can be obtained as the slope and intercept from a plot of $[\mathrm{Dye}]_{\mathrm{eq}}/N$ versus $[\mathrm{Dye}]_{\mathrm{eq}}$ results in eq 2.

$$[\mathrm{Dye}]_{\mathrm{eq}}/N = 1/(N_{\max} b) + (1/N_{\max})\,[\mathrm{Dye}]_{\mathrm{eq}} \qquad (2)$$

Full adsorption experiments were performed for acid blue 40 (AB40) and methylene blue (MB) onto two commercial forms of titania particulate from aqueous solution under conditions of ambient temperature and pH. Ambient conditions were chosen as a logical beginning in the study of the TX and P25 titania systems. Several single-point adsorption experiments at selected pH values were also performed in an effort to understand the relevant adsorption processes. The data suggest a pattern of adsorption based on electrostatic attraction as has been observed in other work.[8−23] This may be the first reported work using the TX titania adsorbent as no literature reference was found.

Experimental Section

Methylene blue chloride was used as received from Fisher Scientific. Acid blue 40 was obtained as a sodium

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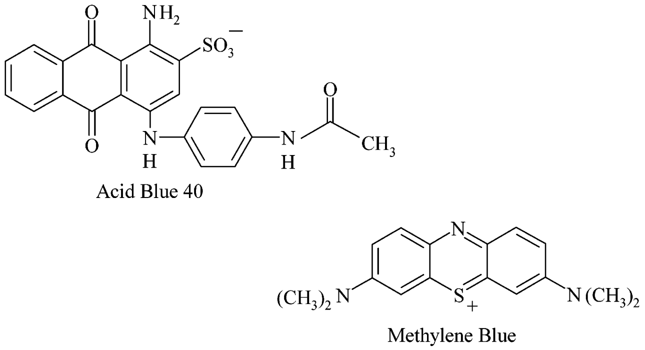

Figure 1. The structures of the ionic dyes methylene blue and acid blue 40.

salt from Aldrich and recrystallized twice from ethanol with the addition of diethyl ether to initiate precipitation. The structures of the two dyes are shown in Figure 1. The water (18 MΩ·cm resistivity) used to prepare the aqueous solutions was obtained from a Barnstead NANOpure II filtering system. The pH of this water was in the range of 5.5 to 6. Dye solubility in water limited the stock solution concentrations and thereby limited the range of initial dye solution concentrations. Gel electrophoresis was performed on each dye at pH values 4 and 9. The protein gel was prepared using buffer solution: diphthalate buffer at pH 4 and boric acid/sodium hydroxide buffer at pH 9. Each gel plate was immersed in buffer, the wells were loaded with dye dissolved in buffer, and the electrophoresis was performed for 85 min at 40 V.

The particulates used in this study were two commercial forms of titanium dioxide: TX titania powder purchased from EM Science and P25 titania donated by Degussa Corp. Each particulate sample was used as received and stored at ambient lab conditions. The P25 titania adsorbent is well characterized in the literature[2,14−17] with a Brunauer−Emmett−Teller (BET) surface area of 50 $m^2 \cdot g^{-1}$ and a PZNPC typically in the pH range 6 to 6.6. The other adsorbent particulate, TX titania, has a nitrogen gas BET surface area of 10 $m^2 \cdot g^{-1}$, as determined by a commercial lab, but has not been characterized in terms of PZNPC. If TX titania is typical, its PZNPC will be less than 7 as reported for most other titanias.[2] The solution volume/titania mass ratios used throughout were 100 to 1 for TX titania and 200 to 1 for P25 titania. As solution volumes were 10.0 mL in all cases, target masses for TX were 0.1000 g and for P25 were 0.0500 g as measured on a Mettler H10 balance (routine precision of ±0.0001 g).

All pH measurements performed used a calibrated Orion model 420A pH meter equipped with a Triode electrode. The ambient pH of P25 titania in water is 4.6 ± 0.2 and that of the TX titania is 7.8 ± 0.2, with both values obtained before the introduction of dye. The ambient pH was assumed to result from residual acidity or basicity from the manufacture of the two brands of titania.[2]

For adsorption work, stock solutions of each dye were prepared at concentrations of typically 8×10^{-3} M for acid blue 40 and 1×10^{-3} M for methylene blue. Various initial concentrations, $[\mathrm{Dye}]_i$, were prepared from stock solutions and water to give a final total volume in each plastic centrifuge tube of 10.0 mL. Stock solutions were prepared at different concentrations so as to provide a wide range of $[\mathrm{Dye}]_i$ values and to ensure the aliquot volumes of stock solution used to prepare $[\mathrm{Dye}]_i$, regardless of the concentration, were consistent and matched the glass fixed-volume pipets used in this work. The water, at least 1.0 mL in every case, was added to the tubes immediately after the appropriate mass of particulate to allow surface hydration to occur, establishing the ambient system pH prior to the introduction of dye. All volume transfers were performed using glass fixed-volume pipets. Tubes were vigorously shaken by hand and then attached to a rotating mixer (1 Hz) that inverted each tube once during each rotation.

Following at least 2 h of mixing, the tubes were centrifuged and a volumetric aliquot of solution was removed. The 2 h mixing time was chosen for convenience but was confirmed to provide adequate equilibration for both systems by the observation of no change, within experimental error, in the solution absorbance at 1, 2, 3, and 4 h intervals. Aliquots were either introduced directly into a plastic cell or diluted with an appropriate volume of water to allow for Beer's Law concentration analysis on a Perkin-Elmer Lambda 3 spectrophotometer. The values for the molar extinction coefficients, ϵ, obtained from linear standard calibration curves, are 8.42×10^4 $L \cdot mol^{-1} \cdot cm^{-1}$ ($\lambda_{max} = 664$ nm) for methylene blue in water and 8.26×10^3 $L \cdot mol^{-1} \cdot cm^{-1}$ ($\lambda_{max} = 617$ nm) for acid blue 40 in water. The values for methylene blue compare well to those in the literature[16] ($\lambda_{max} = 661$ nm and $\epsilon = 8.4 \times 10^4$ $L \cdot mol^{-1} \cdot cm^{-1}$). The literature λ_{max} value[16] of 611 nm for acid blue 40 compares reasonably well with our value. However, our molar extinction coefficient shows an increase over the literature value[16] of 5.1×10^4 $L \cdot mol^{-1} \cdot cm^{-1}$, presumably due to enhanced purity as a result of recrystallization. The visible absorption spectra obtained from dye taken from each tube after mixing were identical to those of their respective stock solutions.

The analysis just described leads to values for the equilibrium concentration of dye remaining in solution after adsorption, $[\mathrm{Dye}]_{eq}$. The difference between the values of $[\mathrm{Dye}]_i$ and $[\mathrm{Dye}]_{eq}$ for each experiment is assumed to be due entirely to the dye removed by adsorption to the particulate surface. Equation 3 describes how N is obtained experimentally.

$$([\mathrm{Dye}]_i - [\mathrm{Dye}]_{eq})V_s/\text{mass titania} = N \tag{3}$$

Here, V_s is the solution volume and mass titania is the number of grams of particulate used. At least three different stock solutions contributed to the overall data sets for each adsorbate/adsorbent system resulting in a series of single adsorption experiments over a wide range of $[\mathrm{Dye}]_{eq}$ values. Ambient temperature for all experiments was (23 ± 2) °C.

Results and Discussion

Manufacturing processes are known to affect the surface characteristics of particulates,[31] and residual acidity or basicity is a common contamination for many particulate systems.[2] When TX titania is introduced into water, the measured solution pH increases to 7.8 ± 0.2 indicating residual basicity. The measured pH value for P25 titania when introduced into water decreases to 4.6 ± 0.2 indicating a residual acidity. As a result of the pH location of the PZNPC for both particulates as stated in the Experimental Section and their residual acidity or basicity giving rise to ambient pH, we can conclude that the TX titania particulate acquires a negative surface charge when first introduced into water and P25 titania acquires a positive surface charge when first introduced into water. The surface charge should change to predominately positive for TX as the solution pH changes across the PZNPC to pH values lower than 6. For P25 slurries, the surface charge should change to predominately negative as solution pH changes across

Table 1. Numerical Values of $[MB]_{eq}$, N, and $[MB]_{eq}/N$ Obtained for the MB/TX Adsorption System[a]

10^4 $[MB]_{eq}$	$10^5 N$	$[MB]_{eq}/N$	10^4 $[MB]_{eq}$	$10^5 N$	$[MB]_{eq}/N$
$mol{\cdot}L^{-1}$	$mol{\cdot}g^{-1}$	$g\ TX{\cdot}L^{-1}$	$mol{\cdot}L^{-1}$	$mol{\cdot}g^{-1}$	$g\ TX{\cdot}L^{-1}$
0.0044	0.030	1.5	1.9	1.2	16
0.0053	0.019	2.8	2.1	1.4	15
0.0061	0.041	1.5	2.5	1.3	20
0.0070	0.051	1.4	2.9	1.5	19
0.046	0.47	0.98	3.2	1.5	21
0.16	0.95	1.7	4.4	1.4	32
0.23	0.87	2.6	4.7	1.6	30
0.72	1.2	6.0	5.3	1.6	33
0.79	1.1	7.2	5.3	1.5	36
1.4	1.3	11	6.0	1.5	40
1.5	1.3	11	6.8	1.5	45

[a] Error analysis is fully discussed in the text.

its PZNPC of 6.0 to 6.6 to higher pH values. During dye equilibration, the ambient pH changes to a lower value of 7.3 ± 0.2 for TX at the highest MB surface coverage. For the P25, the ambient pH changes to 6.8 ± 0.2 during equilibration, also for maximum coverage of AB40. Such changes may contribute to a loss of precision in the adsorption experiments as the dye/titania system adjusts to new pH values.

Because acid blue 40 is a sodium salt and methylene blue is a chloride salt, it is reasonable to assume that acid blue 40 is anionic and methylene blue is cationic. However, there is a possibility that one or both dyes could respond to changes in pH by protonation of amine functionalities within the molecule (see Figure 1). A survey of various aniline derivatives, acid/base models for these dyes, reveals that pK_b values are in the range 10 to 12. Only at low pH would the amine functionalities on the dyes be expected to protonate. Since methylene blue is already cationic, no change in ion charge should occur upon protonation. For acid blue 40, low pH may cause some protonation of amine groups in the dye, resulting in a change in net ion charge.

As information on the specific acid/base properties of these dyes was not found, gel electrophoresis was undertaken for both dyes at the extremes of the pH range encountered in the adsorption isotherm experiments in an attempt to verify the ion charge. At pH 4, acid blue 40 was observed to move toward the positive terminal while methylene blue was observed to move toward the negative terminal. At pH 9, the same results were observed although the response of acid blue 40 was not as pronounced as at the lower pH, possibly indicating a change in dye structure. However, because the pH of the AB40/P25 system does not go above 6.8 ± 0.2 and that of the MB/TX system does not go below 7.3 ± 0.2, we infer that acid blue 40 remains anionic and methylene blue remains cationic during the adsorption isotherm experiments. The visible absorption spectra obtained at both pH 4 and 9 for each dye are unchanged, and we infer that the Beer's Law analysis will not be affected by these different pH conditions.

The values of equilibrium concentration, extent of adsorption, N, and the data used for the linear fit are listed in Table 1 for the adsorption isotherm of methylene blue onto TX titania and in Table 2 for the adsorption isotherm of acid blue 40 onto P25 titania. Figure 2 represents the adsorption isotherm data of methylene blue from aqueous solution on TX titania found in Table 1. The data follow the rapid increase and plateau typical of a Langmuir adsorption isotherm. Shown in Figure 3 is the strong linear trend in the data when plotted according to eq 2. This provides further evidence for the applicability of the Langmuir adsorption model to this system. Figures 4 and 5 represent the adsorption isotherm data for acid blue 40 from aqueous solution on P25 titania found in Table 2, a system studied previously for its photodecomposition kinetics.[9] Once again, the data trend of Figure 4 and the excellent linear fit of the data in Figure 5 are typical features of Langmuir type adsorption. The error bars in Figures 2 and 4 are set at 10% as discussed below. The ±10% error value then applies to the N and the $[Dye]_{eq}/N$ data of Tables 1 and 2. The error in the $[Dye]_{eq}$ values given in Tables 1 and 2 is estimated by replicate measurement to be less than 3%.

Table 2. Numerical Values of $[AB40]_{eq}$, N, and $[AB40]_{eq}/N$ Obtained for the AB40/P25 Adsorption System[a]

10^3 $[AB40]_{eq}$	$10^5 N$	$[AB40]_{eq}/N$	10^3 $[AB40]_{eq}$	$10^5 N$	$[AB40]_{eq}/N$
$mol{\cdot}L^{-1}$	$mol{\cdot}g^{-1}$	$g\ AB40{\cdot}L^{-1}$	$mol{\cdot}L^{-1}$	$mol{\cdot}g^{-1}$	$g\ AB40{\cdot}L^{-1}$
0.0022	0.076	2.9	3.2	4.6	70
0.0036	0.98	0.37	3.8	5.0	76
0.040	3.0	1.3	4.4	5.2	85
0.13	5.0	2.6	5.3	5.0	110
0.29	4.8	6.0	5.8	5.0	120
0.43	5.0	8.6	6.6	5.2	130
0.92	4.2	22	7.0	5.1	140
2.1	5.0	42			

[a] A full discussion of error analysis is provided in the text.

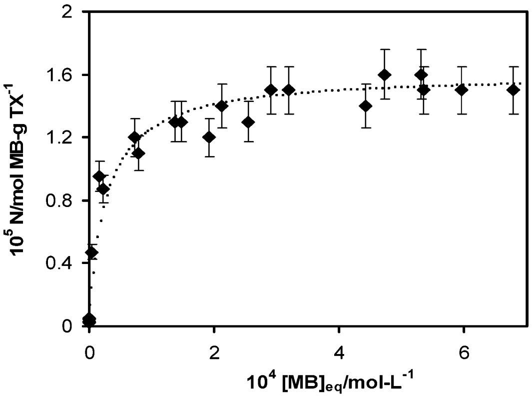

Figure 2. Adsorption isotherm for methylene blue onto TX titania from aqueous solution at ambient pH. A Langmuir curve, eq 1, was generated using $N_{max} = 1.6 \times 10^{-5}$ mol MB·g^{-1} and $b = 3.6 \times 10^4$ L·mol^{-1} and is overlaid on the data. Error bars are set at ±10%.

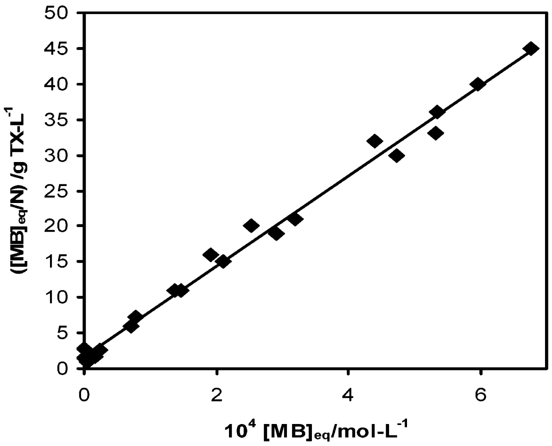

Figure 3. Adsorption data of methylene blue onto TX titania from aqueous solution recast in the linear form of the Langmuir model, eq 2. Slope and intercept values result in the data presented in Table 3.

Slope and intercept analyses of the linear data fits shown in Figures 3 and 5 lead to the values for N_{max} and b

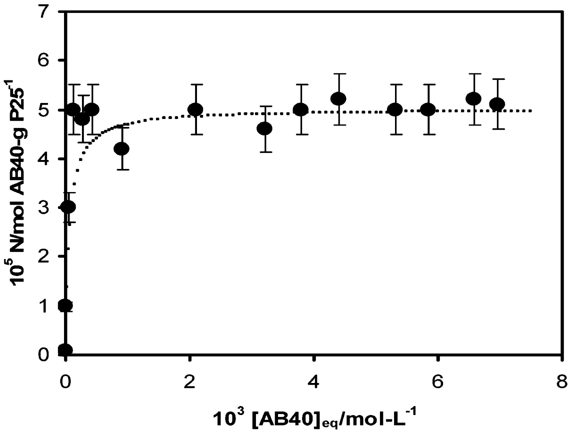

Figure 4. Adsorption isotherm for acid blue 40 onto P25 titania from aqueous solution at ambient pH. A Langmuir curve, eq 1, is generated using $N_{max} = 5.0 \times 10^{-5}$ mol AB40·g^{-1} and $b = 1.5 \times 10^5$ L·mol^{-1} and is overlaid on the data. Error bars are set at ±10%.

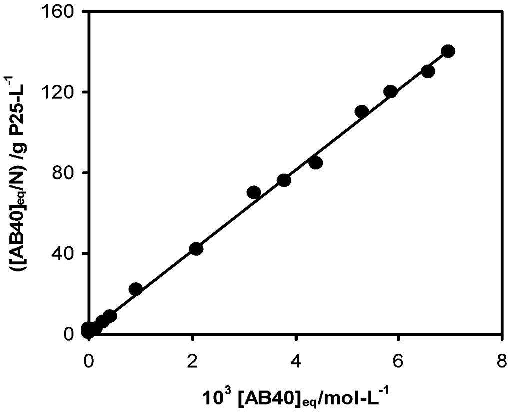

Figure 5. Adsorption data of acid blue 40 onto P25 titania from aqueous solution recast in the linear form of the Langmuir model, eq 2. The slope value results in the data presented in Table 3.

Table 3. Langmuir Parameters Obtained from the Linear Regressions Shown in Figures 3 and 5[a]

	10^5N_{max}/mol·g^{-1}	$10^{-4}b$/L·mol^{-1}	R^2
MB/TX	1.6 (0.2)	3.6 (0.9)	0.9928
AB40/P25	5.0 (0.5)		0.9981

[a] The error associated with each number is given in parentheses and discussed in the text.

reported in Table 3. The R^2 values, being very close to 1, reflect the strong linear trends seen in both Figures 3 and 5. A standard deviation error analysis of the data with respect to the intercept results in the error listed in parentheses for the b value calculated for the MB/TX system. A discussion of the error analysis associated with the N_{max} values follows. The N_{max} and b values for both systems were used to generate Langmuir curves which have been overlaid on the data in Figures 2 and 4. A “Q test” was performed on each data set relative to these generated curves, and data points were rejected that fell statistically outside of the set. Error bars associated with the data points that remained were increased until the generated curve fell within error for almost all data. For the MB/TX system, adjusting the N_{max} value to greater than ±10% of the value listed in Table 3 or adjusting the b value to greater than the error reported in Table 3 generated Langmuir curves which did not adequately represent the data of Figure 2. For the AB40/P25 system, adjusting the N_{max} value to greater than ±10% of the value shown in Table 3 generated curves that did not adequately represent the data of Figure 4. However, the b value obtained from the intercept of Figure 5 generated a poor fit to the data of Figure 4. The b value was adjusted until the curve that is shown in Figure 4 was generated. This value of b is 7 times greater than the b value determined from the intercept shown in Figure 5 indicating a very large and substantial error. Consequently, no result for a b value for the AB40/P25 system is reported in Table 3. The loss of precision in these data is attributed to three sources: additive volume error associated with small aliquots used throughout the procedure, changing pH values as discussed earlier, and the 3% error associated with the [Dye]$_{eq}$ values obtained from the Beer’s Law calibrations. The additive volume error becomes significant at small aliquot volumes, which accounts for the larger error in the intercepts and consequently the b values.

The maximum molar adsorption capacities of P25 titania and TX titania shown in Table 3 cannot be compared directly because the values are based on different adsorbate molecules. Employing a method used previously,[27] a flat adsorption area of 1.2 nm^2 per methylene blue molecule and the value of N_{max} for methylene blue given in Table 3 combine to predict a value for the adsorption surface area of TX titania of approximately 12 m^2·g^{-1}. Similarly, assigning a reasonable value for the flat adsorption area of 1.5 nm^2 per acid blue 40 molecule (25% larger than the area assigned to MB based on the structures shown in Figure 1) and using the value of N_{max} for AB40/P25 given in Table 3, an adsorption surface area of 45 m^2·g^{-1} for P25 titania is calculated. The surface area values for both TX titania and P25 titania calculated from dye adsorption are in general agreement with their respective BET surface areas stated earlier in the Experimental Section.

No interpretation is possible for the adsorption intensity, b, in Table 3 without refinement of the experimental design to reduce error. The b value reported for the MB/TX system is, however, similar to the b value of 5×10^4 L·mol^{-1} obtained for the anionic dye rose bengal adsorbed onto P25 titania.[14]

To investigate the role electrostatic attraction may play in the adsorption processes for these dye/particulate systems, single-point adsorption experiments were performed. Methylene blue was introduced into a TX solution with the pH fixed at 2.4, achieved by adding a small volume of 6 M HCl. The $[MB]_i$ for this experiment was set at 7.0×10^{-4} mol·L^{-1}, which should result in maximum adsorption and therefore a substantial change in the methylene blue concentration. Within error, there was no measurable difference between $[MB]_i$ and $[MB]_{eq}$, indicating no adsorption occurred at this pH. Methylene blue, assumed to be cationic over the pH range of 4 to 9 based on the electrophoresis data provided earlier, should remain positively charged at pH 2.4 considering the dye structure (see Figure 1). At this solution pH, the dominant surface charge for TX should be positive, instead of negative as in the ambient pH experiments of Table 1, thereby leading to the subsequent loss of attraction for the cationic methylene blue. This experimental evidence clearly points to electrostatic attraction as a reasonable explanation for the observed adsorption behavior of the MB/TX system. The AB40/P25 results were not conclusive. Acid blue 40 at an initial concentration of 1.2×10^{-3} mol·L^{-1} was introduced into a P25 solution with the pH fixed at 12.6, achieved by adding a small volume of 6 M NaOH. At this pH, the P25 surface should possess a dominant negative charge and therefore no attraction for the anionic acid blue 40 dye. The value obtained for $[\mathrm{AB40}]_{\mathrm{eq}}$ of 6.9×10^{-4} mol·L^{-1} indicates a measurable loss, outside of error, of AB40 from solution. As was reported earlier in this paper, the electrophoresis of this dye at pH 9 may have indicated a change in structure. Although no such change was indicated by inspection of the absorption spectra in this single-point experiment, it is reasonable to assume that at this higher pH, some if not all of the AB40 loss from solution is due to degradation of dye instead of adsorption to P25. To resolve this question, efforts are underway to refine our experimental technique to give greater control over pH and to conduct experiments to determine the extent of dye decomposition at high pH. Information addressing the acid/base character or reactions of both dyes, which would certainly have aided in our interpretation, was not found in the literature.

The role of electrostatics and dye structure on the adsorption processes of TX and P25 titania is the subject of continuing study in this lab.

Conclusions

The Langmuir adsorption model is an adequate representation for the adsorption of the two organic ionic dyes, methylene blue and acid blue 40, onto two commercial forms of titania, TX and P25. Experimental evidence indicates that electrostatic attraction is a reasonable explanation for the adsorption of the methylene blue on TX titania. Electrostatic attraction is also indicated as an influence on the adsorption of acid blue 40 on P25 titania, but the evidence is less complete. The maximum adsorption surface area of P25 titania, 45 m^2·g^{-1}, is greater than that for the TX titania surface, 12 m^2·g^{-1}, by a factor of 3.8 based on surface coverage of the two dyes. Residual basicity in the TX titania leads to a negative surface charge when the particulate is introduced into water.

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Note Added after ASAP Posting. This article was released ASAP on 4/29/2003. The column heads in Table 2 were changed. The paper was reposted on 6/17/2003.

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