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Colloids and Surfaces
A: Physicochemical and Engineering Aspects 107 (1996) 297–307

COLLOIDS AND SURFACES A

Role of organic acidity in sorption of natural organic matter (NOM) to oxide surfaces

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Received 1 March 1995; accepted 21 July 1995

Abstract

Very strong organic acids (acid groups ionized at pH 3.0) represent a significant portion of the total acidity (4–25%) in samples of organic matter isolated from two lakes, a landfill leachate, and a Krafft mill effluent. On the basis of model compound behavior and established complexation constants, these very strongly acidic groups are predicted to be the key to the formation of strong surface complexes between organic molecules and oxide surfaces. This prediction was confirmed for the sorption of aquatic natural organic matter (NOM) on to preformed iron oxide surfaces. A significant fraction of the carboxylic acidity in polymeric analogs to NOM is due to weak acids (which ionize above pH 8.0). If a portion of the weak acidity in aquatic NOM currently attributed to phenols were actually due to carboxylic acids, significant discrepancies in the understanding of NOM behavior could be reconciled.

Keywords: Acidity; Adsorption; Iron oxide; Natural organic matter; Organic acids; Oxides; Surface complexation

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1. Introduction

Natural organic matter (NOM) plays an important role in particle coagulation, weathering of minerals and contaminant transport. Since complexing carboxylic and phenolic groups are considered key to NOM behavior in these processes, the use of potentiometric titrations to define the role of acidity in NOM reactions has been commonplace in recent years. However, on closer examination, the accurate determination of acidic functional groups by potentiometric titration is problematic. Moreover, in several instances the data interpretation is inconsistent with independent results from nuclear magnetic resonance (NMR) and studies of model compound behavior. With these problems in mind, this work re-examines the role of organic acidity in sorption reactions between aquatic NOM and preformed oxide surfaces.

1.1. Characteristics of organic matter acidity

In previous work examining the role of organic acidity in the sorption of NOM on to oxide surfaces, the most common means of quantifying acidic groups has been through direct titration. In a typical analysis the sample is adjusted to about pH 3.0, degassed, and titrated with a strong base [1]. Base consumption in excess of that for titra-

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SSDI 0927-7757(95)03371-8

tion of an appropriate blank is attributed to deprotonation reactions

$$\mathrm{RCOOH} + \mathrm{OH^-} \leftrightarrow \mathrm{H_2O} + \mathrm{RCOO^-}$$

(carboxylic acids)

$$\text{Ø–OH} + \mathrm{OH^-} \leftrightarrow \mathrm{H_2O} + \text{Ø–O}^- \quad \text{(phenols)}$$

Because acidity constants of simple carboxylic acids are typically in the range $3 \leqslant \mathrm{p}K_a \leqslant 6$, and those of phenolic groups are typically in the range $8 \leqslant \mathrm{p}K_a \leqslant 12$, base consumption below pH 8 is typically attributed to carboxylic groups (strong acidity) while base consumption at pH above 8 is attributed to phenols (weak acidity) [2,3].

Several workers [1,4–8] have noted that direct aqueous titrations with a pH 3.0 starting point would underestimate the acid content in NOM samples, since all acid groups that protonate below pH 3.0 or ionize above pH 11.0 are not "counted" by the method. This observation is supported by the work of Hatcher et al. [9] and Ephraim et al. [10], who demonstrated that independent estimates of carboxylic acidity by NMR or non-aqueous titrations approximately equaled the sum of the carboxylic and phenolic acidity as determined by direct titration. It is noteworthy that these results also call into question the traditional assignment of functional groups by these analytical techniques, since at least some "phenolic" groups quantified by direct titration appear to be counted as "carboxylic" groups by NMR and non-aqueous titrations.

1.2. Role of functional groups in sorption to oxides

Sorption of organic matter on to oxides is an important reaction in water treatment and natural systems. The primary adsorption mechanism is thought to be surface coordination, with functional groups of organic matter exchanging with oxide surface hydroxyl groups. Due to the multiplicity of functional groups on each NOM molecule, the molecules may be capable of coordinating with a number of surface sites at once [11], although Tipping [12] has suggested that no more than a few surface bonds form with any one humic molecule.

The removal of NOM from solution by coagulation or by sorption to iron and aluminum hydroxides typically reaches a maximum near pH 5, with minimal removals at pHs greater than about 9. A significant fraction of the NOM (often about 30–60% of the total) cannot be sorbed to oxide surfaces at any pH [13]. Davis suggested that these molecules might lack ligands capable of coordinating with the oxide surface [11].

Considerable effort has been expended in determining the type of ligands involved in surface complex formation, with a special focus on the relative role of carboxylic versus phenolic acidity. The conclusions obtained appear to depend on the type of experimental method or analysis used (Table 1). For instance, on the basis of model compound behavior, the general pattern for sorption of NOM on to oxides is more consistent with that of molecules which bind to the surface through the carboxylic acid group than those that bind through the phenolic group. As with NOM, maximum sorption of model compounds forming oxide complexes through the carboxylic group occurs at pH 3.5–5.5, whereas maximum sorption for model compounds forming complexes with phenolic ligands is near pH 9 [14]. Other work also supports the notion that carboxylic groups are of primary importance in forming oxide surface complexes. Benjamin et al. [15] used NMR to determine that NOM sorbing to oxide surfaces has a higher carboxylic acid content than does the fraction of NOM not sorbing to oxides. Similarly, FT-IR analysis by Gu et al. [16] indicated that surface–carboxylic acid bonds are formed when NOM sorbs to oxide surfaces

On the other hand, workers relying on direct titration with a pH 3.0 starting point have reached a contrary conclusion (Table 1). For instance, defining carboxylic acids as those titrated from pH 3–8, Davis [11] and Kim et al. [17] found no difference in carboxylic content of soluble organics before and after some of the NOM was removed from solution by sorption on aluminum oxides; by contrast, weak acid groups (i.e. phenols) were sorbed preferentially. On the basis of this finding, Davis concluded that weak acidity (phenolic groups) dominates surface complex formation between NOM and hydroxide surfaces, whereas strong acidity (carboxylic groups) appears to be relatively unimportant. Using similar analytical approaches, Gu et al. [18] noted that carboxylic

Table 1
Summary of research into role of NOM activity in sorption to oxide surfaces.

Sample	Conclusion	Method	Ref.
NOM	Carboxyls sorb to oxides preferentially	NMR	[15]
Simple acids	Carboxyl groups dominate sorption, salicylic- and phthalic-type moeties from strong surface complexes	Reference samples	[14, 16]
NOM	Carboxyl groups important in oxide surface complex formation	FT-IR	[16]
NOM	Oxides preferentially remove phenols, no preferential removal of carboxyl groups	Direct tritration	[30, 16–19]

acid groups were not preferentially sorbed to oxide surfaces for NOM isolated from a wetlands pond, and Collins et al. [19] reported that organics removed during alum coagulation had an even lower carboxylic acid content than the organic matter that was not removed. Once again, it is noteworthy that the results from NMR and other examinations do not agree with these interpretations based on direct titration techniques. Any problems in classifying acidity by direct titration would contribute to these discrepancies.

In this work, the possibility that weak acids in NOM might be carboxylic acids was explored. Titrations were conducted with a series of polymeric model compounds to examine the role of polyacidity and molecular weight on pK_a values of carboxylic acids. Moreover, the role of very strong acids (i.e. those that ionize below pH 3.0) in NOM sorption to oxide surfaces was carefully examined. As mentioned previously, very strong acidity is not typically quantified during direct titrations.

2. Experimental

2.1. Materials

Samples of organic matter were obtained from a kraft mill (paper manufacturing) effluent, a municipal landfill leachate, and Lake Pleasant and Lake Washington (both in Seattle, WA). The leachate sample was diluted 1:5 with deionized-distilled water before use in the experiments. The Lake Pleasant and Lake Washington NOM was collected in mid-June of 1988 and was concentrated by reverse osmosis (better than 85% recovery as measured by total organic carbon (TOC)).

The two NOM concentrates, the kraft effluent, and the diluted leachate were all passed through cation exchange resin in the sodium form until calcium concentrations were less than 0.05 mg l^{-1}, and then through a 0.45 μm pore size filter prior to use in the experiments. Additional details of the isolation procedure are provided elsewhere [20]. Total organic carbon (TOC) concentrations of the stock solutions were 925 mg l^{-1}, 1150 mg l^{-1}, 760 mg l^{-1}, and 527 mg l^{-1} in the Lake Washington, Lake Pleasant, landfill leachate, and kraft mill effluent samples, respectively. Samples of styrene–maleic anhydride polymer with a number-average molecular weight (*MW*) of 50 000 (American Cyanamid, Wayne NJ), polymaleic acid with $MW = 1000$ (Polysciences, Warrington PA) and polyacrylic acid of $MW = 10000$ (Polysciences, Warrington PA) were used in some titrations as received from the manufacturer. All titrations with the polymers were conducted at 0.1 M $NaNO_3$ at 500 mg polymer per liter concentrations.

2.2. Experimental procedures

Organic acidity was determined using a modified direct titration from pH 2 to 11 as described by Edwards and Benjamin [21]. In some experiments, very strong organic acidity (i.e. acids that are deprotonated at pH 3.0) was determined via a charge balance using the method of Dempsey and O'Melia [7]. In this method, the concentrations of the major dissolved inorganic anions and cations are quantified (Table 2), and the concentration of ionized organic functional groups is assumed to balance the excess of cationic over anionic charge. The charge balance allows the quantification of very strong acids with a higher degree of precision than can be attained by direct titrations [7,21]. Inorganic anion concentrations were determined by ion chromatography (Dionex, ASA5, Sunnyvale, CA), and cation concentrations were determined by inductively coupled plasma (ICP)-emission spectroscopy (JY Model 50P, Instruments SA, Edison, NJ). Total organic carbon was determined by triplicate analysis on a carbon analyzer (model 700, OI, College Station Texas).

Amorphous iron hydroxide solids were freshly precipitated 3 h before use from solutions containing 0.083 M $Fe(NO_3)_3$, by dropwise, quantitative addition of 5 N carbonate-free NaOH. Prior to their use in experiments, particles were subjected to three cycles of rinsing in deionized water and centrifugation.

In the NOM adsorption experiments, a predetermined dose of rinsed iron hydroxide was concentrated by centrifugation at 3000 rev min^{-1} for 3 min. The supernatant liquid was decanted and replaced with 50 ml of pH-adjusted solution containing the organic matter. The solids were resuspended with a magnetic stir bar, the pH was maintained at the target value by incremental additions of acid (0.1 M HCl) or base (0.1 M NaOH), and the solution ionic strength was adjusted by the addition of either 0.01 or 0.1 M NaCl. The sample was allowed to equilibrate for 0.5 h, after which the suspension was centrifuged at 3000 rev min^{-1} for 3 min to separate the dissolved organic matter from the adsorbed organic matter. The organic matter remaining in the solution was then characterized by titration and TOC analysis. In experiments at pH 6.0 with each different NOM sample, no soluble Fe^{2+} could be detected in the solution after 3 h, suggesting that reductive dissolution reactions were not significant in these aerated systems.

3. Results and discussion

The results are organized into three sections, beginning with an examination of acidity in the isolated organic matter samples and in polymeric model compounds. Thereafter, the relationship between the pK_{a1} of organic acids and their tendency to form complexes with soluble iron and aluminum is discussed. Finally, the role of acidity in forming oxide surface complexes is considered directly.

3.1. Acidity of organic matter and model polymers

For the purposes of this work, organic acidity is categorized into three groups: very strong acids are defined as those that are deprotonated at

Table 2
Ionic composition of sample stock solutions[a]

Parameter/ion	Landfill leachate	Kraft	Lake Washington	Lake Pleasant
pH (pH units)	5.1	5.0	5.1	6.2
TOC (mg l)	760	527	925	1150
Cl^-	12.3	5.2	15.2	38.9
N_3^- [b]	0	0	0	2.0
SO_4^{2-}	0.7	0.3	0.5	1.2
NA^+	29.6	9.1	21.5	52
Fe[c]	0.1	0.1	0.6	0.5
K^+	<0.1	<0.1	<0.1	0.8
ΣCa, Mg, Al	<0.1	<0.1	<0.1	<0.1
Net organic anionic charge	16.7	3.6	6.4	11.2

[a] All in milliequivalents per litre unless otherwise indicated.

[b] Added as a preservative.

[c] Assumed to be present as Fe^{3+} in charge balance.

pH 3.0, strong acids are those that are protonated at pH 3.0 and deprotonated at pH 8.0, and weak acids are those that are protonated at pH 8.0 and deprotonated at pH 11.0. Total acidity is defined as the sum of the very strong, strong, and weak acidity.

The titration curves for all the samples are shown in Fig. 1a. Total organic acidity in the two lake NOM and the kraft effluent samples ranged from 10.7 to 14.1 meq g^{-1} TOC (12.7–16.8 acid groups per 100 carbon atoms). Of this, 15–22% was present as very strong acidity, 64–75% as strong acidity, and the remaining 9–17% was attributable to weak acids (Fig. 1b). By contrast, the landfill leachate contained 36 meq g^{-1} TOC (43 acid groups per 100 carbon atoms) with 82% present as strong acids. The characteristics of the landfill NOM are consistent with the very high concentrations of volatile fatty acids such as acetate (50 acid groups per 100 carbon atoms) that commonly comprise much of the TOC in such samples [22].

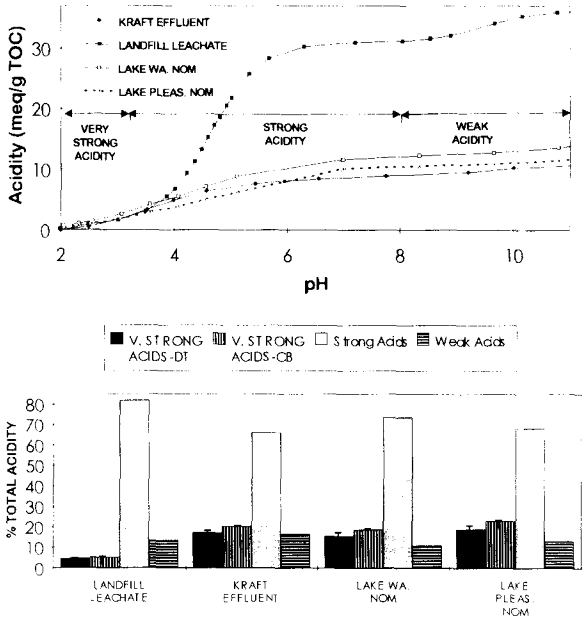

Fig. 1. (a) ionized organic acidity as a function of pH in four heterogeneous samples of organic matter as determined by direct titration from pH 2.0. (b) grouping of organic acidity in the four samples. Very strong acidity was determined by charge balance (CB) and direct titration (DT). Error bars indicate 1 standard deviation on replicate samples.

The estimate of very strong acidity based on the charge balance was between 15 and 23% larger than that based on direct titration. Whereas the charge balance detects all ionized organic acid species in solution at pH 3.0 (i.e. all of the very strong acids), the direct titration only detects acid groups that ionize between pH 2.0 and 3.0 and not those that ionize below pH 2.0. Thus, it appears that about 20% of the very strong acidity in each sample was ionized at pH 2.0. Standard deviations were higher for the determination of very strong acidity by direct titration owing to the small difference between the pH of the sample and the blank solution [21]. Estimates of very strong acidity based on the charge balance are generally considered to be more accurate than those based on direct titration at pH below 2.0 [21]; thus, the charge balance estimates will be used for the remainder of the discussion.

As mentioned earlier, some inconsistencies in the interpretation of organic acidity data could be reconciled if the weak acids in NOM were primarily carboxylic, and not phenolic. To explore this hypothesis in greater detail, direct titrations were conducted on two types of organic polymers: polyacrylic acid and polymaleic acids. These polymers contain only carboxylic acidity. For the polyacrylic acid polymer of $MW = 10000$ (in which no two carboxyl groups are located on adjacent carbon atoms), nearly all carboxyl groups ionize as strong acids (Fig. 2): about 85% of the carboxyl groups are ionized at pH 8.0.

In contrast, consider the styrene–maleic acid copolymer with a number-average $MW = 50000$ (Fig. 2), for which every carboxylic acid group is adjacent to another carboxylic acid group in a paired arrangement. For monomeric maleic acid, pK_{a1} and pK_{a2} are 1.8 and 6.1, respectively [23]. However, in the copolymer, only one carboxyl group on each maleic acid unit is deprotonated at pH below 7.0. The remaining carboxyl group in each pair, or 50% of the total carboxylic acidity in the sample, is deprotonated between pH 7 and 11.

Thus, the maleic acid carboxyl groups are two to three orders of magnitude less acidic in the copolymer than in the monomer. This is not solely a function of molecular weight, as illustrated by the similar results obtained for polymaleic acid of

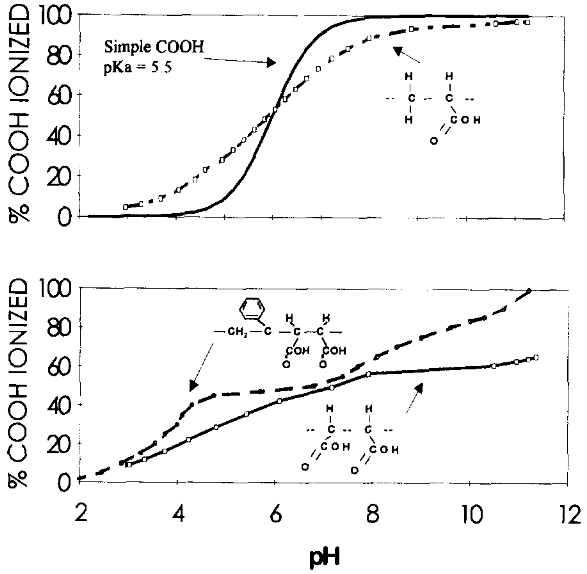

Fig. 2. Upper: titration curve of polyacrylic acid polymer (MW = 10000) and a theoretical titration curve for an ideal, simple carboxylic acid with $pK_a = 5.5$. Lower: titration curve of a maleic acid styrene copolymer (MW = 50000) and polymaleic acid (MW = 1000). The repeating units for the polymers are as illustrated. For the maleic acid polymers, no more than 60% of the carboxyl groups are ionized below pH 7.0.

MW= 1000, in which only about 60% of the carboxylic acidity is ionized at pH 8.0. In fact, on this molecule only about 70% of the carboxyl groups are ionized at pH 11.0. Similar results have been reported for other maleic acid copolymers [24], and the general observation that polymerization of acids generates molecules with weaker acidity is well established [25,26]. Since analogous paired carboxylic acid structures are believed to be present in NOM [4], analogous reasoning could apply to carboxylic acidity in these molecules as well.

As a final point, the same factors that decrease the acidity of carboxyl groups and make them titrate as weak acids probably affect phenolic groups and raise their pK_a to well above that of phenol itself ($pK_a = 9.9$). This effect could cause such groups to remain almost completely unionized in a direct titration to pH 11. In fact, if many phenolic groups on NOM occur in salicylic-type moieties (as suggested by Schnitzer and Khan [27]), most phenols would not even be detected by direct titration with a pH 11 endpoint (even in the absence of the acid weakening effects discussed above), since the pK_a of the phenolic group in salicylic acid is 13.4.

In sum, the above discussion suggests that the acidity of many carboxylic and phenolic groups in NOM is likely to be lower than that of their simple monomeric analogs. Given the evidence cited above for polymeric model compounds (in which paired carboxyl groups in moderate molecular weight molecules titrated as weak acidity), it seems reasonable·to suspect that some weak acidity in NOM is carboxylic and not phenolic.

3.2. *Very strong acidity and formation of soluble organic–metal complexes*

The previous results highlighted some important aspects of weak acidity in NOM; however, the literature review also noted that very strong acids (i.e. acids ionized pH below 3.0) are typically "missed" during conventional titration analysis. While there has been a tendency in the literature to group and discuss carboxyl groups without consideration of acidic strength, these very strong acids may be of special importance in key NOM reactions.

Qualitatively, a number of workers [14,16,18,27,28] have demonstrated that organic acids containing paired functionalities (i.e. phthalic, salicylic and oxalic acid, all with pK_{a1} below 3.0) sorb more strongly to oxide surfaces than monoprotic acids (i.e. acetic, benzoic acid, $pK_a = 4.2$–4.7). Comparison of the pK_{a1} values of such species suggests that, due to the presence of the adjacent acid group, strongly sorbing organic molecules might tend to have a lower pK_{a1} than weakly sorbing acids.

This hypothesis was explored more formally using established equilibrium constants for simple monoprotic and diprotic carboxylic acids [29]. According to Kummert and Stumm [14], the strength of surface complexation between organic ligands and oxide surfaces is related to the strength of the corresponding complexation reaction in solution

$$H_2L + Fe^{3+} \rightarrow FeL + 2H^+ \quad \text{(diprotic acid)}$$

$$HL + Fe^{3+} \rightarrow FeL + H^+ \quad \text{(monoprotic acid)}$$

In the above reactions, at a fixed pH and Fe^{3+} concentration, the tendency of metals and organic ligands to form solution complexes is proportional to the ratio [Fe–L][/HL] or $[\text{Fe–L}]/[H_2L]$, depending on whether the acid is monoprotic or diprotic. Similar reactions are possible between Al^{3+} and organic ligands.

The strengths of soluble complexes between iron or aluminum and simple carboxylic acids generally increase with the strength of the acid (Fig. 3). That is, as log K_{a1} of the organic ligand becomes less negative, the tendency to form organic ligand complexes actually increases for both Al^{3+} and Fe^{3+}. The expectation, then, is that the stronger carboxylic acids are more important than weaker carboxylic acids when the formation of oxide–surface complexes is examined.

3.3. Sorption of organic matter to oxides

Batch experiments were conducted with preformed oxides to elucidate the role of organic acidity in sorption reactions. By comparing measurements of soluble organic acidity before and after sorption, the number and strength of acids sorbed to the oxide surface could be calculated by difference.

Adsorptive removal of organic matter followed similar trends in each sample tested (Fig. 4). At low sorbent (ferric hydroxide) doses, corresponding to high sorbate:sorbent ratios, removal of TOC increased steadily and approximately linearly with oxide concentration. As a result, for each type of sample investigated, the low adsorbent dose experi-

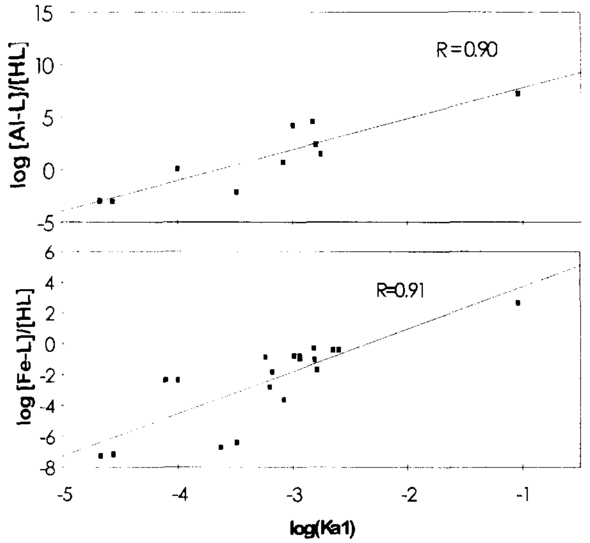

Fig. 3. The tendency to form solution complexes increases with the K_{a1} value of the complexing organic acid. In the figure, for diprotic acids [Me–L]/[HL] is $[\text{Me–L}]/[H_2L]$ as per treatment described in Ref. [14]. The analysis includes all data for simple monoprotic and diprotic carboxylic acids with appropriate complexation constants for Al^{3+} and Fe^{3+} in Ref. [29]. Conditions for calculation: pH 6.0; 10^{-12} M Fe^{3+}; 10^{-6} M Al^{3+}.

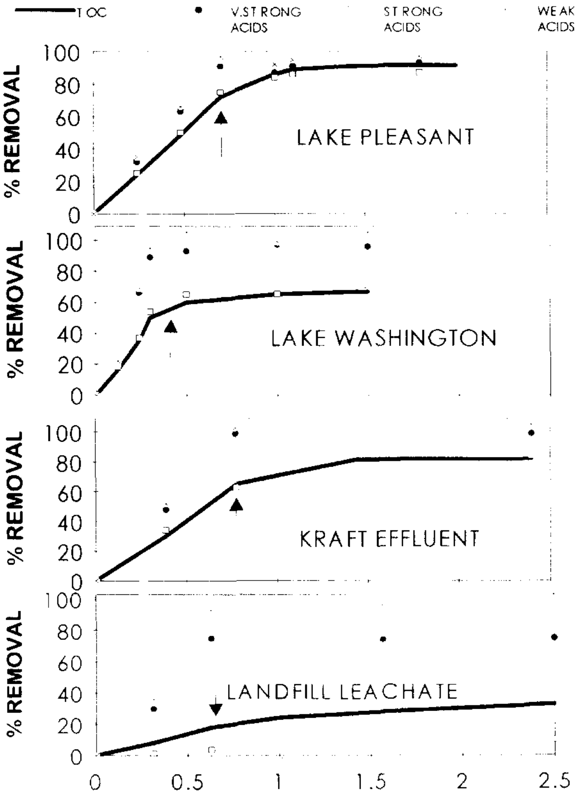

Fig. 4. Percentage removals of TOC, very strong acidity, strong acidity and weak acidity by sorption on to the indicated dose of preformed iron hydroxide. Arrows indicate the highest iron concentration at which the linear sorptive removal of color was observed in preliminary experiments. This point corresponds closely to the highest dose at which linear removal of TOC occurred and the lowest dose attaining 100% removal of very strong and weak acidity. Initial conditions: pH 6.0; I = 0.01M as NaCl.

ments could be characterized by an approximately constant TOC adsorption density: 0.29 mol TOC, 0.84 mol TOC, 1.02 mol TOC and 1.66 mol TOC per mole iron for the leachate sample, kraft effluent, Lake Pleasant NOM, and Lake Washington NOM samples, respectively. When the sorbent:sorbate ratio exceeded some critical value, however, NOM removals reached an upper limit and rather abruptly became independent of ferrihydrite dose. The maximum fraction of the organic matter that could be removed varied from sample to sample.

For the kraft mill effluent and the two lake NOM samples, the fractional removal of strong acids was approximately equal to the fractional removal of TOC. In contrast, both very strong acids and weak acids were preferentially sorbed to the oxides at all iron doses (i.e. fractional removal of these subgroups was greater than fractional removal of overall TOC), and they were removed almost completely at high sorbent:sorbate ratios (to within the detection limit of ±6% in these samples). Both of these observations suggest that the weak and very strong acid groups directly facilitated sorption. Furthermore, the percentage adsorption of these two groups was very similar, and the adsorbent dose at which they were completely sorbed corresponded quite well to the dose at which removal of TOC reached its maximum value.

The results suggest that very strong acid groups are critical for the formation of strong surface complexes: at low sorbent:sorbate ratios (i.e. in the linear region of the isotherms) insufficient sorbent has been added to bind all the strong acids, and increasing the sorbent dose increases the amount sorbed approximately proportionally. At higher sorbent:sorbate ratios, relatively few strong acid groups (and therefore relatively few strongly binding adsorbates) remain in solution, and increasing the sorbent dose has a much smaller effect on the amount of NOM sorbed. This hypothesis is also consistent with the behavior of model compounds: as noted earlier, polyprotic organic acids with at least one very strongly acidic carboxylic group (i.e. oxalic, salicylic, phthalic acids) form strong surface complexes with oxides, while monoprotic compounds with strong acid groups (i.e. acetic, benzoic acid) do not [30].

In addition, as evidenced by the titration curve of the maleic acid copolymer, the very presence of weak acids on NOM molecules may indicate the presence of paired carboxylic groups. Thus, many of the weak acids in NOM might be carboxylic groups which, in isolation, would be characterized as moderately strong acids. However, because of association with a very strongly acidic carboxyl group residing nearby on the same molecule, and because of the energy required for conformational changes as the molecule becomes more highly charged, the acidity of the "second" acid group is decreased. That is, it becomes a weak acid group. If the paired acid groups were a key factor in sorption, both very strong and weak acid groups would be preferentially removed when NOM was exposed to an oxide surface, as was observed.

Consideration of the above points might also explain the anomalous partitioning of acid groups in the leachate sample, for which 16% of the very strong acids did not sorb at any ferric hydroxide dose. As noted earlier, this sample probably contained high concentrations of simple carboxylic acids. In the range pH 4–6, the leachate sample contained approximately 20 meq more acidity per gram TOC than the other samples. As a limiting hypothetical case, we can assume that all this acidity is attributable to simple carboxylic acids (such as acetic) with a pK_a of 4.7. In such a case, approximately 1.9% of the acid groups, or 0.38 meq g^{-1} TOC, would be ionized at pH 3.0. In a charge balance analysis, those groups would be identified as very strong acids, accounting for about 23% of the very strong acidity in this sample (1.65 meq g^{-1} TOC). These simple monocarboxylic acids are not expected to sorb strongly to the oxide surface, which could explain the result that, in this sample only, a significant fraction (16%) of the strong acidity did not sorb. The discrepancy between the hypothetical calculation and the actual result (23% vs. 16%) probably reflects errors in the estimate of the simple acid concentration and the fact that some relatively small fraction of those compounds can sorb.

Though different conclusions were reached in each work, it is noteworthy that our interpretation of the sorption results is also consistent with Davis' observations that, when humic acids sorbed on to aluminum oxides, strong acids were not preferentially removed and weak acids appeared to be important in surface complex formation [11]. Very strong acidity was not analyzed by Davis. The current work affirms and extends that finding to indicate that (1) very strong acids are important in surface complex formation; and (2) weak acids might be carboxyl groups associated with very strong acids on high molecular weight molecules, and are therefore likely to be present on strongly sorbing molecules even if they are not directly involved in complex formation.

3.4. Conceptual model of NOM removal through sorption on to oxides

The key parameter in this analysis is the type of organic ligands present (in organic molecules) and the relative strength of their binding to oxide surface sites. In the discussion that follows, these ligands are broadly classified as non-sorbing, weakly sorbing, or strongly sorbing. Non-sorbing ligands are incapable of surface complexation. Weakly sorbing ligands may be sorbed onto oxides surfaces but the extent of removal is dependent on solution concentration (e.g. benzoic acid). Strongly sorbing ligands form strong surface complexes and are nearly completely removed from solution unless the surface is completely saturated (e.g. phthalic-, salicylic-, and oxalic-acid-type ligands). The conceptualization further assumes that the sorptive behavior of a molecule is dominated by the strongest sorbing ligand present.

For the purposes of this discussion, sorptive removal is divided into three zones (Fig. 5). In the first zone, the removal of color or organic matter is proportional to the amount of surface provided, and some strongly sorbing NOM remains in solution. This zone is characterized by the presence of some very strong and weak acids remaining in solution. In the second zone, oxide surface concentrations exceed that required to remove all strongly sorbing ligands, and adsorption density gradually decreases as more surface becomes available. In this zone, a portion of the strong acidity was removed concurrently with TOC in this work, suggesting that some of these acids are weakly sorbing ligands. In the third zone, all strong and weakly binding ligands have been removed from solution, and little or no additional removal of TOC or acidity is observed at higher oxide surface concentrations.

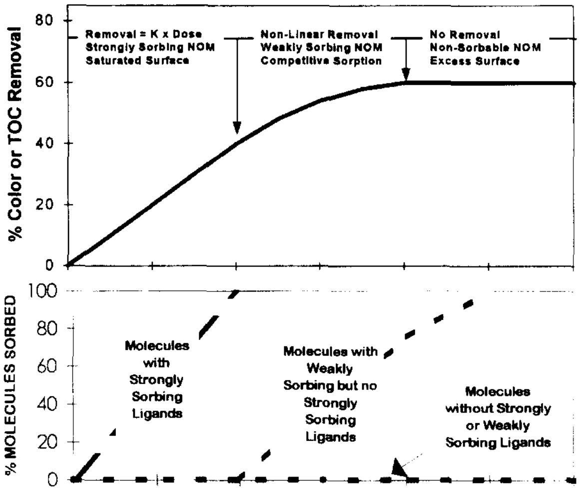

Fig. 5. Generalized zones of TOC removal observed in heterogeneous collections of NOM (upper figure). It is speculated that the various zones of removal correspond to the presence, in solution, of molecules with strongly sorbing ligands, molecules with weakly sorbing but no strongly sorbing ligands, and molecules without sorbing ligands (lower figure).

The percentage of molecules within each class and the oxide surface concentration corresponding to each zone of removal depend on the specific sample tested. Of course, this analysis attributes all heterogeneities in NOM–surface complexation exclusively to NOM, whereas variations in oxide surface sites and surface coverage will also be important under some circumstances [18]. Nevertheless, among the parameters that could influence the strength of NOM binding to oxide surfaces, that due to differing ligands was clearly dominant in this investigation.

3.5. Future work

Future work should carefully re-examine possible implications of misclassifying carboxylic/phenolic acidity as determined by direct titration. For instance, work on ozonation of NOM has consistently found that "phenolic" acidity (determined by direct titration) increases markedly during ozonation [21,31]. This is very surprising given ozone's extreme destructive reactivity with phenolic-type moieties [32]. Once again, the results are reconciled if carboxylic acid weak acidity, and not phenolic acidity, is produced during ozonation. The production of paired carboxylic acid structures like oxalate during ozonation is well accepted [21], and their occurrence in moderate molecular weight structures could increase weak acidity after ozonation.

Similarly, the importance of very strong acids in key NOM reactions with oxide surfaces should be examined in greater detail. For example, Stone [33] and LaKind and Stone [34] have demonstrated that polyprotic organic acids containing acidic functional groups in ortho positions (e.g. salicylic acid, catechol, oxalate) dissolve oxides much more rapidly than do polyprotic organic acids without ortho functional groups (resorcinol, hydroquinone, 4-hydrobenzoic acid) or monoprotic acids (phenol) [35,36]. Because strong binding of organic matter to oxide surfaces is a crucial first step in ligand-promoted and reductive dissolution of oxides by NOM, very strongly acidic groups in NOM are probably key in promoting such reactions.

4. Conclusions

Very strong organic acid groups (acid groups that are partially deprotonated at pH below 3.0) can represent a significant portion of total organic acidity in heterogeneous collections of natural organic matter. These very strong acid groups appear important in controlling the formation of surface complexes between organic matter and oxide surfaces.

Weak acid groups in NOM (i.e. those which are partially protonated at pH 8.0) might be weak carboxylic groups on high molecular weight organic molecules. This interpretation is consistent with the sorption behavior of simple acids, the titration behavior of model compounds, and the results of NMR spectroscopy.

At high ratios of oxide adsorbent to NOM, organic matter with very strong acid groups is strongly sorbed in comparison to organic matter without very strong acid groups. The removal of organic matter is linearly related to sorbent concentration (site-limited) until essentially all very strong organic acid groups are removed from solution. At higher oxide surface concentrations, sorptive removal of TOC becomes less sensitive to sorbent dose and ultimately reaches a maximum value that cannot be increased with higher surface concentrations.

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