

Cation Exchange Properties of Pine Bark Growing Media as Influenced by pH, Particle Size, and Cation Species

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Abstract. Pine bark cation exchange capacity (CEC) (by Ba/Mg exchange on four particle size fractions) increased regularly from 38 to 98 meq/100 g between pH 4 and 7. Decreasing particle size from <2.38 to <0.05 mm did not result in the expected large increases in bark CEC. The Ba/Mg CEC of unsieved bark samples was less than that determined by the weighted average of component size fractions. Monovalent/monovalent-determined CEC was higher than Ba/Mg, indicating that a number of differing charge-specific sites are involved. The pH-dependent CEC increase between pH 4 and 7 was greater for divalent exchange than for monovalent. Ammonium/K CEC was higher than K/NH₄ CEC, probably due to enhanced NH₄ adsorption by carboxyl groups. Infrared analysis of pine bark revealed that surface functional group composition is similar to soil organic matter. The accurate measurement of CEC in pine bark is complicated by solution pH and ionic strength, as well as by the cations employed for exchange.

The use of ground pine bark as a potting medium has become increasingly popular in the southeastern United States in recent years. Pine bark is inexpensive relative to peatmoss, has good physical properties, significant CEC, and is generally free of toxic heavy metals at low pH. Recently, growing concerns over the potential threat of greenhouse and nursery industries to local groundwater quality have prompted studies into the basic ion retention and nutrient supply characteristics of pine bark (2, 5). The basic surface properties and cation selectivity of pine bark potting media are poorly understood.

The organic surfaces of pine bark potting media would be expected to behave as totally pH-dependent or constant potential surfaces (6). The measured CEC or surface charge therefore will depend not only on pH, but should increase with the ionic strength of the bathing solution and cation valence as well. This, of course, assumes ideal exchange behavior, which seldom is observed in practice. Soil organic matter has been shown to adsorb Ca preferentially over Na (7), and ammonium (NH₄) fixation by carboxyl and phenolic hydroxyl groups has been reported by Burge and Broadbent (1). Recent work by Foster et al. (2) on a pine bark medium indicated that substantial amounts of NH₄ were bound by pine bark and that cation adsorption preferences varied with pH.

A better understanding of the basic surface chemistry and cation exchange properties of pine bark media would allow manipulation of fertilizer solution pH and ionic composition to maximize nutrient retention and plant availability. The major objective of this study was to determine the interactions among solution pH, cation species, bark particle size, and measured CEC. A further objective was to characterize the functional group composition of ground pine bark via infrared and potentiometric titration analyses.

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Materials and Methods

A large sample of milled pine bark was sieved through a 6.35-mm screen to remove extremely coarse particles and then sieved again into the following particle size classes: 6.35–2.38 mm; 2.38–1.19 mm; 1.19–0.05 mm; and <0.05 mm. The CEC of each size fraction as influenced by pH was determined using a modification of the procedure used by Helling et al. (3). A multirange buffer was prepared consisting of 0.10 N mono-chloroacetic acid (MCA, pK = 2.87), 0.10 N Ba(OAc)₂ (pK = 4.76), 0.40 N BaCl₂, and 0.20 N Hepes (pK = 7.5). Hepes is a zwitterionic buffer commonly used in biomedical research and was used as a substitute for *p*-nitrophenol, which is exceedingly toxic. The reader is cautioned that MCA is also toxic. Batches of buffer solution then were adjusted to pH 4, 5, 6, and 7 using HCl or Ba(OH)₂. Ten grams of bark from each size fraction were equilibrated with each buffer by applying solution to the top of 7.5 × 2.5 cm PVC columns filled with bark using a peristaltic pump with a flow rate of 60 ml·hr⁻¹ until leachate pH stabilized. Samples then were washed with 200 ml of pH-adjusted BaCl₂, followed by 300 ml of distilled water to remove excess salts. Adsorbed Ba was then displaced with pH 5 N Mg(OAc)₂ until Ba was not detected in the leachate.

In the second phase of the ion exchange experiment, 10-g samples of unsieved bark were buffered to pH 4 and 7 with the multirange buffer, saturated with BaCl₂, and then displaced again with Mg(OAc)₂. The columns then were washed to remove salts and saturated with pH 4 or 7 0.5 N KCl or NH₄Cl. Leachates from this saturation step were analyzed for Ba that was not displaced by the previous Mg solution but was displaced by the monovalent ions. The NH₄ and K saturated columns then were washed again to remove salts and displaced with the opposite pH 5 N monovalent cation solution. This procedure resulted in the following cation saturation exchange sequences: Ba/Mg, K/NH₄, and NH₄/K. For all exchange experiments, Ba and K in solution were analyzed by atomic absorption spectrophotometry and NH₄ with an ion-specific electrode.

All CEC procedures developed for this experiment were initially run several times to check lab precision, perfect buffer equilibrations, and eliminate background interferences in final cation determinations. All CEC data reported are average values of final duplicate runs. The SES of all CEC estimates (Tables 1

and 2) were all <10% of their respective mean values, and the vast majority were <4%. The variability that did occur between duplicate runs is largely attributable to small variations in buffer pH between the two samples (i.e., pH 4.01 vs. 3.95 for a pH 4.00 run).

In an effort to characterize the surface properties of the bark further, a 0.5-g sample of the <0.05 mm fraction was acid-washed, equilibrated with 50 ml of N KCl, and then stirred and titrated potentiometrically with 0.039 N NaOH with a Radiometer automatic titration system. Two additional <0.05-mm bark samples were equilibrated with N KCl and N CaCl₂, washed, dried, and then pressed into KBR pellets for infrared surface analysis with a Perkin-Elmer Model 283 infrared spectrophotometer.

Results and Discussion

As expected, whole-bark CEC increased in a regular fashion between pH 4 and 7, with an average increase of 20 meq per 100 g per pH unit (Table 1). Values reported as "whole-bark CEC" are based on the weighted averages of the various size fractions. This regular, nearly linear, response indicates that there are probably a number of different acid carboxylic (R-COOH) groups that deprotonate across this pH range. An unexpected result, however, was that CEC on a mass basis (meq·g⁻¹) did not show a strong inverse correlation with particle size (Table 1) between <2.38- and <0.05-mm size fractions. There was only a slight decrease in CEC/g with increasing particle size at all pH levels through the 1.19–2.38 mm fraction, before

it dropped significantly in the very coarse 2.38–6.35 fraction. Although the finer fractions did dominate total whole bark CEC, this domination was due primarily to their higher percentage weight. This phenomenon may indicate that cation exchange is not totally a surface exchange phenomena in these materials and that significant internal exchange sites may exist. This hypothesis also is supported by the results of the potentiometric titration analysis (Fig. 1). Despite the fact that a weak base was used at a very slow titration speed (1.25 ml·min⁻¹), the equilibrium pH in the reaction vessel dropped from 8.2 to 5.8 within minutes after base addition ceased. Such behavior indicates diffusion-controlled reactions, physically isolated from the bulk bathing solution. The total bark acidity titrated to pH 8.2 was only 24 meq/100 g, a fraction of the measured CEC. The presence of significant amounts of reactive functional groups on internal surfaces that react only slowly with the bulk bathing solution is a probable explanation.

Another potential explanation for the lack of strong particle size effects could be that all of the size fractions examined were fairly coarse and therefore did not differ greatly in specific surface area. In mineral soils, exponential increases in specific surface area and associated CEC are not apparent until equivalent particle diameter approaches 0.005 mm or less (8) and the particles begin to behave as colloids. However, there is certainly a significant difference in specific surface area between the <0.05- and 1.19–2.38-mm bark fractions used in this experiment; thus, the internal site hypothesis is more plausible.

Mass specific CEC (meq·g⁻¹) increased ≈100% between the

Table 1. Effect of pH and particle size fraction on pine bark media CEC as measured by Ba/Mg exchange.

Size fraction (mm)	Weight (%) of whole bark sample	Mass specific charge (meq·g ⁻¹)	Total charge of size fraction (meq/100 g of whole bark) ²
<i>pH 4</i>			
<0.05	38	0.44	16.7
0.05– 1.19	28	0.39	10.9
1.19– 2.38	20	0.37	7.4
2.38– 6.35	14	0.22	3.1
			Total CEC = 38.1
<i>pH 5</i>			
<0.05	38	0.65	24.7
0.05– 1.19	28	0.58	16.2
1.19– 2.38	20	0.67	13.4
2.38– 6.35	14	0.29	4.1
			Total CEC = 58.4
<i>pH 6</i>			
<0.05	38	0.83	31.5
0.05– 1.19	28	0.75	21.0
1.19– 2.38	20	0.76	15.2
2.38– 6.35	14	0.42	5.9
			Total CEC = 73.6
<i>pH 7</i>			
<0.05	38	1.15	43.7
0.05– 1.19	28	1.00	28.0
1.19– 2.38	20	0.94	18.8
2.38– 6.35	14	0.53	7.4
			Total CEC = 97.9

²All SES <10% of respective means.

Table 2. Effect of cation type and pH on measured CEC.

Satur./disp. cations	CEC (meq/100 g) ^z		pH-dependent charge increase (%)
	pH 4	pH 7	
<i>Divalent/divalent exchange</i>			
Ba/Mg	31	74	139
<i>Residual Ba after divalent exchange^y</i>			
Ba/K	3	12	300
Ba/NH ₄	3	14	367
<i>Monovalent/monovalent exchange</i>			
NH ₄ /K	48	93	94
K/NH ₄	40	67	68

^zAll SES for CEC measurements <10% of respective means.

^yThese values represent the meq of Ba exchangeable to monovalent cations remaining after Mg displacement of the Ba-saturated columns.

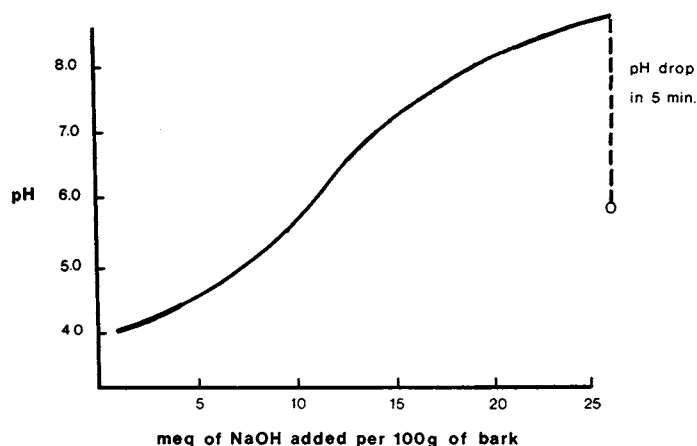


Fig. 1. Potentiometric titration curve for <0.05-mm bark sample in KCl. Titration rate = 0.05 meq NaOH/min.

very coarse (2.38–6.35 mm) and finest (<0.05 mm) fractions at all pH values, indicating that while there is a pronounced effect of pH on total charge, all size fractions behave similarly and probably contain a similar mix of reactive functional groups. The titration curve shown in Fig. 1 exhibits a pronounced buffering inflection around pH 5.8. This is also the level that the equilibrium pH of the bark/KCl mixture returned to within minutes after reaching pH 8.2. Apparently, solution acidity in this material is strongly controlled by a functional group(s) with a pK around 5.8, once more acidic groups with lower pKs have been deprotonated.

The results of the various cation exchange combinations reveal strong differences in the affinity of pine bark for various cations (Table 2). The CEC determined by Ba/Mg exchange increased from 31 meq/100 g at pH 4 to 74 meq/100 g at pH 7. These CEC values, determined on unsieved samples, are considerably lower than the weighted averages determined from the individual size fractions (Table 1). This discrepancy may be due to differences in particle packing arrangement, void sizing, and particle interactions between the poorly sorted sieved bark fractions and the well-sorted whole samples. All of these factors may have affected solution flow through the columns and/or exchange kinetics.

When the Mg-saturated columns from the Ba displacement step above were then saturated with K and NH₄, an additional

3 meq of Ba were displaced by both monovalent cations at pH 4. At pH 7, 12 and 15 meq of unexchanged Ba were removed by K and NH₄, respectively. Barium has a smaller hydrated radius and therefore higher charge density than Mg and was therefore not completely removed from the exchange sites by the Mg-displacing solution. The smaller radii monovalent cations, however, displaced this tightly bound Ba. The proportional increase (400%) in Ba retained against Mg between pH 4 and 7 was much larger than the associated increase in total CEC.

The NH₄/K and K/NH₄ exchanges resulted in somewhat similar values at pH 4 (48 vs. 40 meq/100 g), but at pH 7 the NH₄/K combination resulted in almost 50% more apparent CEC than K/NH₄ exchange. The strong affinity of carboxyl groups for NH₄ (1) may be responsible for this difference, but the fact that the NH₄ remains exchangeable to a KCl solution indicates that this portion of the NH₄ is not truly "fixed". The majority of carboxylic functional groups dissociate above pH 4 and therefore would be expected to increase NH₄ adsorption much more at pH 7, as these data indicate. This activity does not preclude the possibility that significant amounts of applied NH₄ may be fixed as well. Regardless of the mechanism, these data indicate that different sites are involved in cation adsorption. The increase in CEC between pH 4 and 7 was much greater for Ba/Mg exchange than either of the monovalent/monovalent exchange combinations. This difference also indicates that different sites are involved in cation exchange in pine bark media. These differences may be due to steric or charge density effects on the exchange surfaces in addition to the possibility of specific NH₄ sites.

If these surfaces behaved as ideal constant potential surfaces, as discussed previously, divalent exchange should have resulted in higher measured CEC than monovalent exchanges. It should also be pointed out that these experiments were run at much higher ionic strengths than normally encountered in the field or greenhouse, so the measured surface charge is correspondingly higher. For example, Foster et al. (2) determined the cation adsorption potential of the same bark material used in this experiment, but at much lower ionic strengths, and found that both K and NH₄ were adsorbed in much lower amounts than reported here. It is also possible that the buffer solution itself may have influenced surface charge, but that effect should be constant over all exchanges at a given pH.

During the course of the cation exchange procedures, we noted that some of the leachates leaving the columns were colored brown by soluble organics. When Ba/Mg exchange was being carried out, the Mg(OAc)₂ displacing solution was colored, but, during the monovalent/monovalent exchanges, the distilled wash step between cation saturation and displacement was colored. Thus, at least some of the cation adsorption in this material may be accomplished by displacement of soluble organics, or the cations may affect the dispersion of the soluble organics differently.

Infrared spectroscopic analysis of Ca and NH₄ saturated bark samples (Fig. 2) revealed that the external surfaces of ground bark are similar in composition to soil organic matter (4). Strong adsorption bands associated with dimeric and polymeric OH stretching (3442 cm⁻¹), aliphatic C–H stretching (2923 cm⁻¹), COOH stretching (1617 cm⁻¹), and associated bending and rocking bands of carboxyls, aldehydes, and phenolic groups at lower wave numbers were evident. Compared with the Ca-treated bark, all peaks observed with the NH₄ saturation were sharper and more distinct, but no significant peak shifts were observed

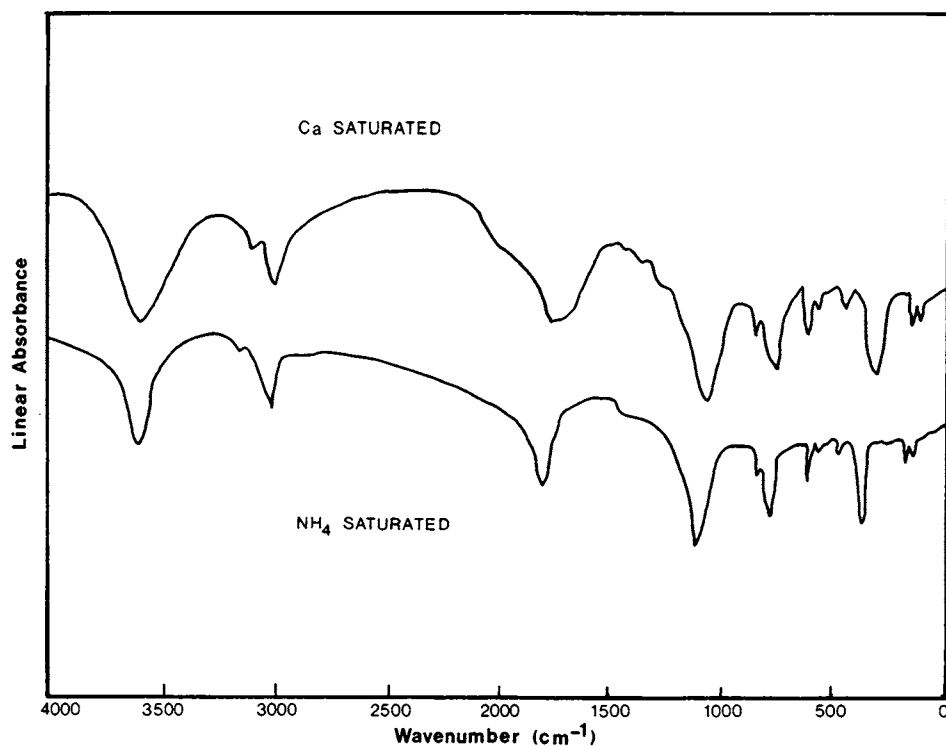


Fig. 2. Infrared spectroscopic analysis of Ca- and NH_4 -saturated ground bark samples.

that might indicate the formation of specific NH_4 complexes with functional groups.

It is apparent from these data that cation exchange in pine bark involves more than one type of exchange site and that the sites react differently to changes in pH. Significant amounts of internal functional groups and/or exchange sites, which interact more slowly with bulk solution than external sites, probably exist in pine bark. Ammonium appears to be adsorbed to a greater degree than K. Divalent CEC increases faster than monovalent CEC as pH increases, so it may be possible to manipulate fertilizer solutions to enhance the adsorption of divalent cations. Cation exchange may occur to some extent concurrently with the displacement of organics, but the mechanisms and sites are unknown. These surfaces contain the same general functional groups as soil organic matter and exhibit similar overall pH-dependent CEC. Care should be taken in the interpretation of pine bark CEC data, since the surface charge responds not only to pH, but to the ionic strength of the bathing solutions and cation species as well.

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