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Humic acid preparation, properties and interactions with metals lead and cadmium

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Abstract

Humic acid (HA) extracted from soil is investigated in terms of its cation exchange capacity (CEC), zero point of charge (zpc), oxygen containing functional group content, scanning electron microscope (SEM) images, and pH. The CEC of HA that was dried was approximately half the CEC of hydrated HA. Metal retention by HA was studied by conducting 24 h batch equilibrium tests with lead (Pb, as $PbCl_2$) and cadmium (Cd, as $CdCl_2$) and HA at pH 4 and 6, and with a mixture of HA, mackinawite and kaolinite. The reactivity of the HA towards Pb and Cd was reduced when it was combined with the mackinawite and kaolinite. The mackinawite raised the pH and dissolved some of the HA, until sufficient reactions between the metals and mixture lowered the pH enough for the dissolved HA to solidify and remove more metal from solution. HA bonding with the mackinawite and kaolinite reduced the HA sites available for metal uptake. The functional group content of the HA provided indications regarding the origin of the HA, the extent of humification and the presence of less decomposed fractions. The CEC of the HA could conservatively predict the amount of metal uptake. Low pH conditions are favorable for metal removal from solution by HA because the zpc of the HA was below pH 0.5 and because at higher pHs HA begins to dissolve. HA, especially in the hydrated phase, may represent an important material for metal removal from waters and wastewaters containing metals.

Keywords: Wet humic acid; Lead; Cadmium; pH effects; Cation exchange capacity

1. Introduction

Industrial effluents are contributing to increasing concentrations of metals being discharged to the environment. Since these metals are not biodegraded they need to be removed from waters and wastewaters and adsorption onto various media is generally the referred treatment (Mohammad and Najar, 1997). Organic matter, such as found in sediments and surface soils, has natural and powerful adsorbent properties and because of this, humic acid (HA), which is the most abundant fraction of decomposed organic matter, has been the focus of much research. Sorption interactions of four forms of HA have been studied in depth and they include the dissolved phase, a solid phase coating on another material, a low pH powder (comparable in this study to the dried HA), and a sol-gel (Laor et al., 2002).

The oxygen containing functional groups in HA represent a quarter of the total molecular weight of HAs

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(Rashid, 1985). The carboxyl (COOH) group increases in abundance with humification (Rashid, 1985), reacts readily with metals (Spark et al., 1997; Barancikova et al., 1997), and gradually dissociates between pH 2.5 and 7 to form the carboxylate (COO^-) group (Perdue, 1985; Buffle, 1988; Spark et al., 1997). The phenolic hydroxyl (OH) group is more abundant in the early stages of decomposition (Yong and Mourato, 1988), is derived from lignin in woody plants (Rashid, 1985), reacts less with metals, and dissociates between pH 8 and 13.5 (Perdue, 1985). The COOH and phenolic OH groups account for the total acidity of HA (Schnitzer, 1982) while the alcoholic OH group is only weakly acidic and reacts minimally with metals (Yong et al., 1992).

The carbonyl ($C{=}O$) group increases in abundance with humification (Saito and Hayano, 1980; Lavti and Paliwal, 1981), is the main functional group in sediments (Rashid, 1985) and transforms into the COOH group under oxidizing conditions (Pillon et al., 1986) or when exposed to clay (Rashid, 1985).

The pH dependent surfaces of HA cause flocculation at low pH and dispersion at high pH (Flaig, 1971). SEM images of HA reveal smooth, compact shapes at pH 3 and rough, elongated and dispersed shapes at pH 7 (Senesi et al., 1996) and HA also begins to dissolve at higher pHs (Spark et al., 1997). HA may remove metals from solution at low pH but at high pH metal bonding with dissolved HA results in the formation of soluble metal humate species (Hatton and Pickering, 1980). It is also believed that small materials can become trapped inside voids within the HA molecules (Schulten and Schnitzer, 1995).

HAs are highly negatively charged and organic matter contributes towards the lowering of the zero point of charge (zpc) of soils (Van Raij and Peech, 1972; Morais et al., 1976). Kretzschmar et al. (1997) show kaolinite with a zpc at ≈ pH 4.8 and the same kaolinite containing only 0.25 wt.% HA with a zpc of ≈ pH 2.0. Approximately 80% of aquatic humus may be electrically neutral between pH 1.2 and 1.8 (Gjessing, 1976).

Metal uptake, pH and properties of the HA including CEC, zpc, functional group content and the HA phase are considered. Better understanding of the properties and behaviour of HA may lead to the development of metal removal applications in industry such as in wastewater treatment, in the use of reactive walls to intercept groundwater flow, and in the use of landfill liners.

2. Materials and methods

2.1. HA extraction, purification and ash content determination

The HA was obtained from a compost/topsoil from a low-lying area in Montreal. The year old compost had consisted of fertilizer and pesticide free lawn clippings and leaves. The HA was extracted form the soil and purified by removing suspended clays as described by Schnitzer and Preston (1986). Ash removal was not undertaken as harsh treatments and the use of strong acids can alter the surface chemistry of HA (Yong and Mourato, 1988). Instead the HA was washed for 1 h with 0.003 mol/L HCl (at pH 2.5) to wash out the soluble potassium that remained from the clay removal step. The HA was centrifuged and air-dried, causing it to shrink and solidify, so it was then ground with a mortar and pestle. The ash content was measured by combusting the HA (Hirata, 1992).

2.2. HA characterization

The pH 7 cation exchange capacity (CEC) of the HA was determined by the calcium acetate–calcium chloride displacement method (Sheldrick, 1984) both for samples that had been dried and for hydrated samples that were only centrifuged. The wet samples were dried and weighed afterwards since any difference in weight resulting from a change in the saturating cations would be negligible. All other characterization (and batch) tests were only conducted on the dried and powdered HA. The total acidity, the COOH groups, the total OH groups and the $C{=}O$ groups were measured (Schnitzer, 1982). Determination of the zpc of the HA (Van Raij and Peech, 1972) was attempted. 0.035 g of HA was mixed with 20 mL of 1.0, 0.1, 0.01 and 0.001 N solutions of NaCl and the samples were mixed for 1 h. Subsequently, 2 mL of 0.01 N NaOH or 1.0 N HCl were added every 2 min and the change in pH was recorded. A Japan Electro-Optics Laboratory (JEOL), model 6T100 scanning electron microscope was used to photograph the HA, and the pH of a mixture of 1 part of HA and 100 parts of distilled water was measured.

2.3. Determination of metal retention

Batch equilibrium tests were conducted at room temperature (22 °C) in duplicate, triplicate or quadruplicate. The solutions of Pb (as $PbCl_2$) and Cd (as $CdCl_2$) were adjusted with HCl to approximately pH 3.6 and 3.9 respectively to ensure that the metals were soluble. Batch tests with the dried HA were conducted under aerobic conditions, and batch tests with the HA, mackinawite and kaolinite were conducted under anoxic conditions.

For the batch tests with the HA and metals only, suspensions of HA and distilled water were adjusted to pH 4 and 6. 0.03 g HA was mixed with 30 mL of solution and metal concentrations of 50, 100, 250, 500, 750, 1000, 1500, 2000 and 2500 mg/L were tested. 24 h batch tests were conducted because this is a typical duration (Hatton and Pickering, 1980; Pilarski et al., 1995) and preliminary tests suggested that metal uptake would be approximately 90% complete within this time. The suspensions were centrifuged for 10 min at 6000 rpm and the supernatant metal concentrations were measured with a Perkin Elmer 3110 atomic absorption (AA) spectrometer. Metal uptake was taken as the difference between the metal added and the metal in the supernatant.

For the other batch tests 0.14 g HA, 0.1 g mackinawite and 14 g kaolinite were mixed with 140 mL of solution and the suspensions were tested at their natural pH. The metal concentrations were approximately 500, 1000, 1500, 2000 and 2500 mg/L. The mackinawite was prepared as described by Coles and Yong (2000) and the Flat D kaolinite was obtained from the Dry Branch Kaolin Company. A nalgene bottle that was half filled with distilled water, kaolinite and HA, was bubbled with high purity nitrogen gas to give a dissolved oxygen concentration of 0.3 mg/L. The mackinawite was added, the suspension pH was measured, the de-aerated metal solution was added to give zero air space, and the bottle was sealed with Parafilm, capped and placed on a roller for 24 h. The pH was again measured and the suspension was centrifuged to determine the supernatant metal concentration.

3. Results and discussion

3.1. Characterization tests

The ash content of the HA was 33.9% and the pH of the HA was 3.6. The dry, powdered HA had a CEC of 288 or 436 meq/100 g on an ash free basis, and the hydrated HA had a CEC of 533 or 806 meq/100 g on an ash free basis, while reported CEC values for soil HAs are between 300 and 787 meq/100 g (Lavti and Paliwal, 1981). The CEC of the hydrated HA is almost double that of the dried HA and is greater than typical values, so the hydrated HA appears to be significantly more reactive than the dried HA. Cox et al. (2000) observed that Hg adsorption by a wet carbonaceous material was double the Hg adsorption by the same material that had been dried and ground, and they concluded pore shrinkage during drying was inhibiting the entry of Hg^{2+} ions. Mohammad and Najar (1997) reported that undried tea could adsorb more Pb and Cd than dried tea. Shrinkage of the HA during drying could have resulted in less space available for cation exchange reactions.

Air-drying of the HA caused the HA particles to be strongly bonded together. Since water layers closest to a soil surface are the most difficult to remove, and clays can require temperatures in excess of 500 °C (Hillel, 1998), this bonding may be due to residual moisture held by the functional groups of the HA. Weak bonding within the hydrated HA could be due to interactions between the functional groups of HA and water molecules.

Overnight mixing of the dried HA with distilled water did not restore the HA to its pre-dried state and Cox et al. (2000) did not observe any swelling when their dried carbonaceous material was placed in water. The effects of the drying process do not appear to be readily reversible when the HA is brought into contact with water under moderate conditions of pH and temperature. In addition to the dissolved, powdered, sol-gel and solid coating HA phases, the hydrated HA could become an important adsorbent phase.

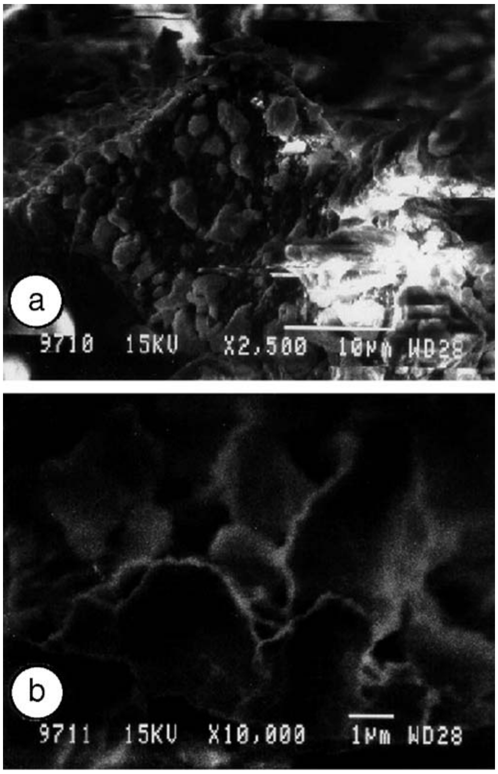

Fig. 1. SEM images of HA a) at 2500× magnification and b) at 10,000× magnification.

Table 1
Oxygen-containing functional groups in HA on an ash free basis and typical values for soil and sediment HA

Functional group	HA, ash free (meq/100 g)	Typical soil HA (meq/100 g)	Range sediment HA (meq/100 g)
Carboxyl, COOH	472	360	200–500
Phenolic OH	330	390	0–250
Alcoholic OH	648	260	0–300
Carbonyl, C═O	572	290	300–600

The SEM images of the HA (Fig. 1) reveal a material of closely packed, non-uniform shapes, ≥ 1 μm in size. The final washing of the HA at low pH could be responsible for the compact appearance of the HA and the relatively large, non-uniform shapes may be formed by the HA coating the ash.

The zpc for the HA was found to be below pH 0.5 because the experiment was stopped at this point. Gjessing (1976) reported values for the zpc of aquatic humus of between pH 1.2 and 1.8. Therefore, HA will be able to retain metals at very low pHs.

The functional group contents for the HA are reported in Table 1, along with typical values for soil HA (Schnitzer, 1978) and a normal range of values for sediment HA (Rashid, 1985). The alcoholic OH group content is high while the amounts of the other groups are reasonable. Higher COOH and C═O group contents and a lower phenolic OH group content indicate a well humified HA (Lavti and Paliwal, 1981; Yong and Mourato, 1988) whereas a high alcoholic content indicates the presence of poorly decomposed HA (Lavti and Paliwal, 1981). The HA is mostly well-humified but also contains some less decomposed organic matter, which may represent more recently added lawn clippings and leaves.

The COOH group content (312 meq/100 g) should be approximately the same as the pH 7 CEC of the HA (288 meq/100 g) (Buffle, 1988). The use of different methods to determine these values can account for the small variation. According to the dissociation of the phenolic OH groups (Perdue, 1985) the pH 13 CEC of the HA is 530 meq/100 g, and the expected increase in CEC with pH is observed.

3.2. Batch equilibrium test results and metal retention

For all batch tests, solutions Pb as $PbCl_2$ (adjusted to pH 3.6) and solutions of Cd as $CdCl_2$ (adjusted to pH 3.9) were used. For the batch tests with HA only, suspensions of HA and distilled water were initially adjusted to pH 4 and 6, and the results of these tests are

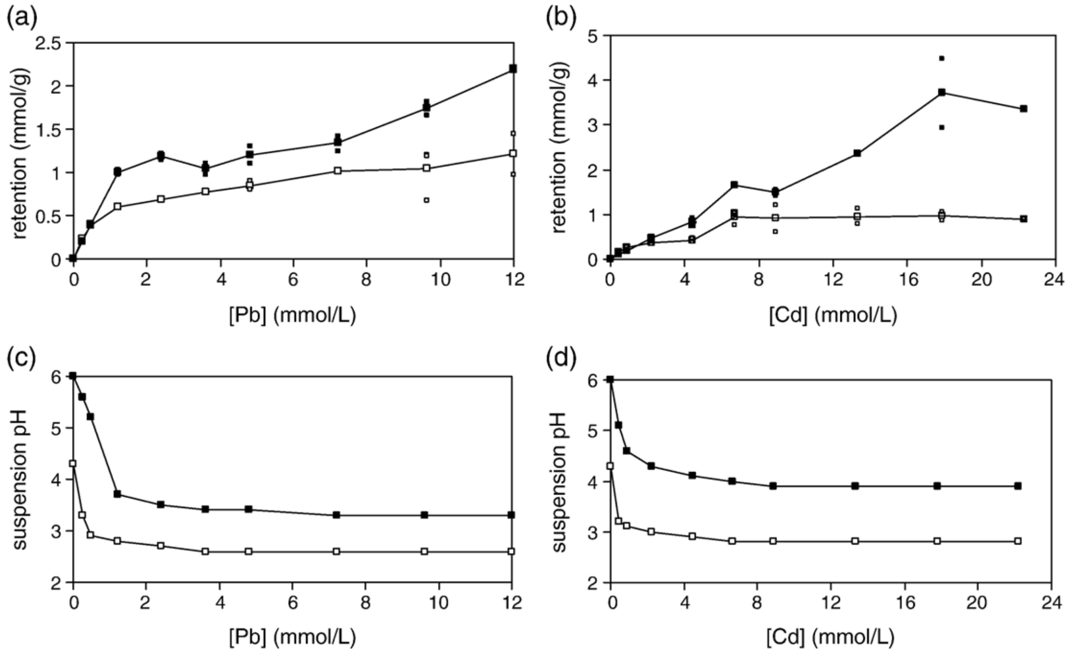

Fig. 2. a) Pb retention by HA at pH 4 (□) and pH 6 (■), b) Cd retention by HA at pH 4 (□) and pH 6 (■), c) final pHs of suspensions with Pb and HA, and d) final pHs of suspensions with Cd and HA, with all values as a function of the initial metal concentration.

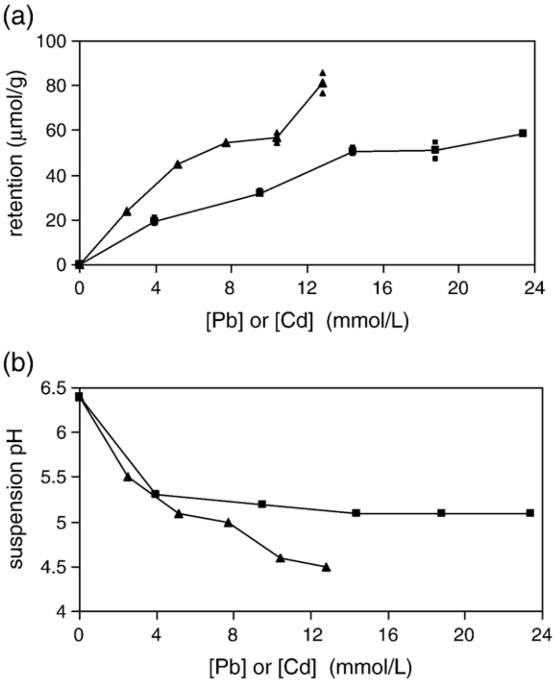

Fig. 3. a) Retention of Pb (▲) and Cd (■) by HA, mackinawite and kaolinite and b) final suspension pHs, as a function of the initial metal concentrations.

shown in Fig. 2. For the batch tests with mixtures of HA, mackinawite and kaolinite, the mixture was tested at its natural pH, and the results of these tests are shown in Fig. 3.

A visual comparison of the Pb and Cd retention can be observed from Fig. 2a and b where metal is plotted as a function of the initial metal concentration. The greater uptake at the higher pH may be attributed to 1) the greater negative charge of the HA as seen in the increase in CEC with pH, 2) the greater dispersion of the HA at the higher pH, and 3) the reduced quantity of H^+ ions that would otherwise compete for adsorption sites. Properties of the metals which could be effecting metal uptake are 1) the size of their hydrated radii and 2) their speciation.

At the lower metal concentrations, uptake of Pb is greater than uptake of Cd. Metal speciation analysis using critical stability constants from Martell and Smith (1974) reveals that at low concentrations, divalent metal cations are dominant. For metal retention by ion exchange, the greater uptake of the Pb^{2+} ion compared to that of the Cd^{2+}ion (hydrated radius ≈0.45 versus ≈0.50 nm, respectively) (Dean, 1985) could be due to their relative sizes. At low pH the metals are doubly protonated so chemical bonding might be discouraged (Bowden et al., 1980), but the HA is capable of sequestering metals within its voids, so this is another potential retention mechanism (Schulten and Schnitzer, 1995).

For the HA that was initially adjusted to pH 4, and for metal concentrations above 7 mmol/L, Cd uptake is constant while Pb uptake is increasing. The reasons for this seem to be that 1) Cd, more than Pb is governed by electrostatic forces (Gerritse and Van Driel, 1984), and 2) the HA is more flocculated and compact at the lower pH meaning that steric effects may be preventing further bonding.

Retention of Pb and Cd becomes more equal at increasing metal concentrations, and more so for the higher pH HA where steric effects might be less important. As the metal salt concentrations increase, the formation of $CdCl^+$ species exceeds the formation of $PbCl^+$ species. With more of the monovalent species being able to balance the negative charge on the HA, a greater uptake of Cd is possible, and the small hydrated radius of $CdCl^+$ (≈0.40 nm) (Dean, 1985) could also be facilitating its bonding with the HA.

For the HA that was initially adjusted to pH 6, data points for metal concentrations of 0.241 mmol/L Pb, 0.482 mmol/L Pb, 0.445 mmol/L Cd and 0.890 mmol/L Cd are missing because these samples could not be centrifuged. The repulsive forces on the HA surfaces at the higher pH were not sufficiently balanced by the low concentrations of acidic cations added so the suspensions remained dispersed.

The final suspension pH values for the batch tests with HA are plotted as a function of the initial Pb and Cd concentrations in Fig. 2c and d respectively. These figures show a reduction in pH according to the extent of metal uptake and displacement of H^+ ions from the HA surfaces.

Metal uptakes by the HA, mackinawite and kaolinite and the final pHs as a function of the initial metal concentration are shown in Fig. 3a and b respectively. The mackinawite is increasing the pH of the mixture (Coles, 1998), but the inconsistent trend in pH for the Pb contaminated suspension may be due to the presence of the HA. There is a further drop in pH at the highest Pb concentrations and it coincides with a dramatic increase in Pb retention at the maximum metal concentration. It appears that when the pH of the HA, mackinawite and kaolinite was raised by the mackinawite, some of the HA was dissolved. Then as more Pb was retained by the mackinawite and kaolinite, the pH dropped and some of the dissolved HA re-solidified and provided more sites for subsequent Pb uptake from solution. This may not have been observed for Cd because both the metal uptake and the drop in pH were less.

There is an advantage to raising the pH of HA so that metal retention can be increased. Too great a rise in pH, however, causes dissolution of the HA and although the metals may react with the HA by forming soluble metal humate species, the metals will not be precipitated out of solution. So this is one aspect that needs to be considered in treating metal contaminated wastewater.

The approximate maximum metal uptake by the HA and by the HA, mackinawite and kaolinite is 4 and 0.08 mmol/g, respectively. These values suggest that interactions between the three sediment components in the mixture are occurring and producing a structure with fewer sites available for metal uptake, and so the total metal uptake by the three components together is less than the sum of the metal uptake by the three components separately. Barancikova et al. (1997) found that HA that is part of the soil had less affinity for metal ions than HA isolated from the same soil. When the HA is isolated it can be more effective at scavenging metals and it appears that the hydrated HA could be an even better adsorbent than the dry powdered HA.

The pH 4 CEC of the HA would be approximately 190 meq/100 g, meaning the HA could retain 1.90 mmol/g of monovalent cations or 0.95 mmol/g of divalent cations. The maximum Pb and Cd uptakes when the final pH is ≈4 are 2.19 and 3.71 mmol/g respectively. This is greater than predicted by the CEC but within the same order of magnitude. In this case the CEC is providing a conservative estimate of metal uptake.

4. Conclusions

Organic matter within the soil matrix is responsible for significant bonding of heavy metals, but metal retention by HA may increase when HA is isolated, and even greater metal uptake by HA may be possible when the HA is not dried but kept in its hydrated state. This was illustrated by the CEC of the hydrated HA on an ash free basis as it was slightly higher than typical values. Since hydrated HA is not widely recognized as an important phase for reaction with contaminants, further research into metal uptake by this phase should be considered.

Another important feature of this research is that it indicated that HA could be effective at removing metals at as low as pH 0.5. Metal removal from solution by HA increases as the pH increases as long as the pH increase is not enough to dissolve the HA.

The quantities of functional groups present in the HA may provide information about the origin of the HA in terms of whether it is derived form a soil or a sediment, the degree of humification of the HA, and the presence of less decomposed fractions.

The CEC of the HA may provide a conservative estimate of the potential metal uptake. One of the retention mechanisms proposed for the pH 4 and 6 HA over the short term of 24 h is cation exchange and this could be influenced by the sizes of the hydrated radii and the concentrations of divalent and monovalent cations of Pb and Cd. Sequestering of Pb and to a lesser extent Cd may also be occurring.

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