

Worner Research Lecture 2000

Soils: Our Interface
with the Environment

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Biography



Associate Professor Bruce Johnson grew up in Adelaide and Perth, attending the University of Western Australia, University of Adelaide and Flinders University. On completing his PhD he joined the staff of Bendigo Institute of Technology in 1970. He served as Dean / Head of School of Science and Engineering from 1989 to 1994, and is currently Deputy Head of School (Teaching) in Management, Technology and Environment. In addition he has spent significant periods as a Visiting Scientist at the University of Bristol, and at both Umeå University and Luleå University in Sweden. His research over the past 30 years has been diverse, with scientific publications in fields ranging from the chemistry of Antarctic ice, to the effect of geomorphology on aluminium concentrations in soils from Central Victoria. However, in recent years much of his research has been directed towards improving our understanding of the binding of trace and toxic elements to soil minerals.

Soils: Our Interface with the Environment

The Concise Oxford Dictionary (1976) defines a soil as “the ground, upper layer of earth in which plants grow, consisting of disintegrated rock with an admixture of organic remains, mould”. While that is an accurate definition, I suspect that if you were to ask a series of different people the question “What is a soil?” they would provide a wide variety of answers. For example:

- to a farmer, soil is a medium in which crops grow;
- to a hydrologist, it is a storage reservoir which affects the water balance in a catchment region;
- to a civil engineer, it is a material which must provide adequate support for building foundations and roads, and can sometimes be used to construct a dam;
- to a geologist, it is finely divided rock material; and
- to an ecologist, it is the material that influences the growth and distribution of different plant species.

All of these interpretations of the word ‘soil’ are valid; together they illustrate the remarkable range of roles fulfilled by soils.

From the viewpoint of a chemist, soils are frighteningly complex systems. To make matters worse, their chemistry varies widely from place to place, often changing in significant ways between areas just a few meters apart. Each soil contains a wide range of minerals derived from break-down of parent rock material, variously classified as phyllosilicates, oxides, hydroxides, carbonates, sulfates, halides, etc, and an even wider range of organic material derived from plants and animals. Clearly details of the chemical nature of each soil depend not only on the geology of the region but also on the plants and animals living there.

This lecture will present a view of soils through the eyes of a chemist who seeks to understand some of the fundamental processes that occur in soils. It will not be a general soil chemistry lecture as my principal task is to tell you about some of the research that has been completed by members of the Colloid and Environmental Chemistry group at La Trobe University, Bendigo over the past fifteen years or so. The material that will be presented represents an eclectic selection of research done largely by post-graduate students from Colloid and Environmental Chemistry.

We could study the chemistry of whole soils, investigating the chemical reactions that occur, and documenting our work. However, because soil properties vary so much, results obtained on a soil sample from a calcareous region, like the Wimmera, would bear no resemblance to those for an acid soil from the Axe Creek catchment.

As a consequence, we would need to repeat our experiments for each different soil – and remember that there are often significant differences in soil properties even within a given paddock. While such research may be beneficial, it is only really relevant and useful to the particular soil sample studied.

Let me try to illustrate the difficulty of conducting research on whole soil samples with the following example.

Metals are often present in soil solution as positively charged species called cations (e.g. zinc as Zn^{2+} , and potassium as K^+). Adequate amounts of essential cations such as calcium, potassium and zinc must be present in soils if plants are to thrive. The soil property that provides a measure of the ability of a soil to store metal cations in a way that allows them to be available to plants is called the Cation Exchange Capacity (CEC). The CEC is an important characteristic which helps to determine the fertility of a soil system. So, how can we measure it?

Four years ago an Honours student, Joe Kelly, looked at this problem. He found that many measurement methods had been suggested over the years, and from those available chose four that were in common use. These were tested on eight soils collected from various parts of North-Central Victoria. The results are shown in Figure 1.

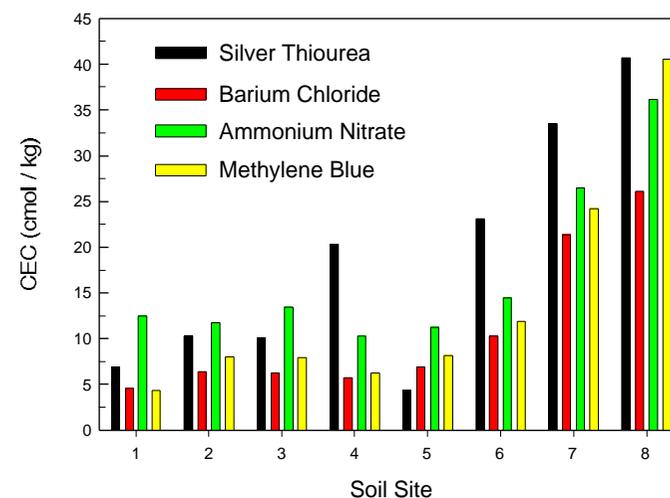


Figure 1. Cation Exchange Capacity (CEC) of eight soils from north-central Victoria measured by four different methods (Kelly, 1996)

Not only do the different methods give different results for a given site (e.g. site 4 has values ranging from 5.7 to 20.3 cmol/kg), but, if we attempt to list sites in terms of CEC, the order changes depending on the method chosen. For instance, for the methylene blue method the order in order is:

site 1 < site 4 < site 3 < site 2 < site 5 < site 6 < site 7 < site 8,

while for the silver thiourea method it changes to

site 5 < site 1 < site 3 < site 2 < site 4 < site 6 < site 7 < site 8.

Remember that all of these soils were collected from sites in North-Central Victoria: imagine the differences that would occur had we chosen to include samples from Gippsland and the Western District! Clearly, working with whole soils is very difficult, especially if you seek to understand soil processes at a molecular level, because whole soil properties change enormously from one location to another.

The alternative approach is to investigate very simple systems where a single soil component is selected and its adsorption characteristics investigated in detail. By studying several important soil minerals under a range of different conditions we might hope to build up a general picture that would allow us to predict the likely chemical behaviour of a soil from a knowledge of its chemical components.

Much of our research has sought to understand the fundamental reactions between trace and heavy metals and soil particles. This research should allow us to predict the extent to which these metals are available for uptake by plants, and help us to understand how the availability of metal nutrients and toxins can be manipulated. Some metals, like copper, zinc and cobalt, are essential for plant growth and need to be available in soil solution in sufficient concentrations to ensure crop growth. Others, like cadmium and lead, are toxic to humans and other animals; ideally the concentrations of these toxic elements in the soil solution should be minimised so that they are not available for plant uptake.

The binding of metal ions to surfaces occurs by a series of processes that are called 'adsorption' processes. We will define adsorption as the binding of elements and compounds to the surfaces of soil particles. These adsorption processes occur at the interface between soil particles and soil water (or, more correctly, soil solution).

In the past ten years or so we have investigated the adsorption of several important trace elements, including copper, zinc and cobalt, and have also studied the adsorption of toxic metals such as lead and cadmium. For the rest of this lecture we will look at some of our results and attempt to discover a little about the chemistry that drives these processes.

First, let's consider how adsorption properties depend on the type of mineral by investigating the adsorption of cadmium onto three common soil minerals. We have studied cadmium extensively because it has been inadvertently added to Australian soils as an impurity in superphosphate over the past 50 years or so. Cadmium is a highly toxic element, being a confirmed human carcinogen, with demonstrated experimental teratogenic and mutagenic properties (Lewis, 1991). Rayment (1995) estimates that 5,245 tonnes of cadmium have entered Australian soils as an impurity in phosphate fertilisers since the Second World War. Cadmium also has relatively simple solution chemistry which makes it a particularly useful element for modelling adsorption processes.

Figure 2 shows the per cent of a 100 μ M cadmium solution that is adsorbed by three mineral substrates. These are, kaolinite, an important clay mineral whose properties we will discuss later, goethite, a common iron oxide in soil systems, and alumina, another common soil oxide. The following trends are evident. Firstly, for all three minerals, the amount of cadmium adsorbed increases as the pH of the system is increased. In fact, under acidic conditions (below pH 4) cadmium adsorbs to none of the substrates, while under alkaline conditions (pH > 10) each substrate adsorbs all of the cadmium. There is an obvious difference between the adsorption behaviour of kaolinite and the other two substrates. At pH 6, more than 30 % of the cadmium is adsorbed by kaolinite while almost none adsorbs to goethite and alumina. The results also show that the adsorption behaviour of goethite and alumina is similar. This is encouraging as they are both oxides and therefore have some similarities in their chemistry. Note that the adsorption curves of these two substrates show a smooth increase in per cent adsorbed once a critical pH is reached.

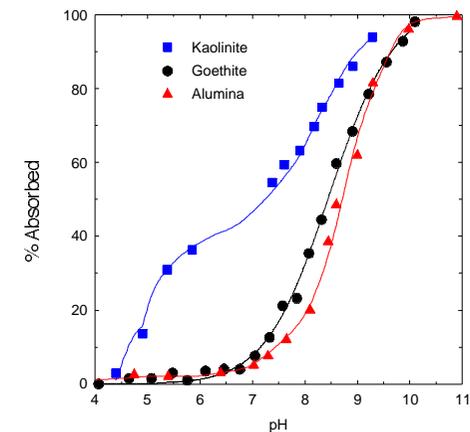


Figure 2. Adsorption of 100 μ M cadmium onto different substrates (Spark et al. 1996a,b)

Before trying to understand the results in Figure 2 in detail, let's look at another set of experiments. This time we will use the same substrate (goethite) and investigate the adsorption of four metal ions, copper, zinc, cobalt and cadmium. The results of this study are shown in Figure 3.

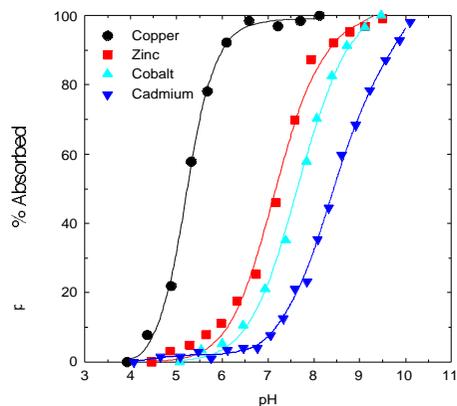


Figure 3. Adsorption of 100 μM solutions of various metals onto goethite (McLelland, 1986)

Here all adsorption curves have a similar shape, but each has a distinct pH range over which adsorption occurs. When we study adsorption of the same set of metal ions on different oxides we find the adsorption curves have a similar shape and also adsorb in essentially the same order. For instance, if alumina is chosen we find that copper adsorbs at a lower pH than zinc, which in turn adsorbs at a lower pH than cobalt, with cadmium requiring the highest pH for adsorption. That is, while the exact pH range over which adsorption occurs differs from one oxide to another, the pH order of adsorption remains the same.

Can we determine why metal ions adsorb in this order? Let's consider the chemistry of these metals in solution. Here they undergo a series of reactions with water that also depend on pH. These reactions are called hydrolysis reactions and can be written



etc.

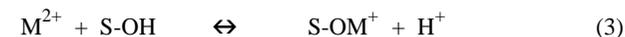
The extent to which these reactions occur is characterised by constants called equilibrium constants, K , which are related to the concentrations of the species in solution. If we look at the values of the equilibrium constants for the formation of MOH^+ , and compare them with the pH at which 50 % of the metal is adsorbed, we get the following results. (Note: the equilibrium constants are expressed as $-\log_{10} K$, or pK , for comparison with pH which is $-\log_{10} [H^+]$.)

Metal	$pK(MOH^+)$	$pH_{50\% \text{ ads}}$
Cu^{2+}	7.22 ^a	5.3
Zn^{2+}	8.96 ^b	7.1
Co^{2+}	9.65 ^b	7.65
Cd^{2+}	10.08 ^b	8.4

a Odani *et al.* (1992)

b Baes and Mesmer (1976)

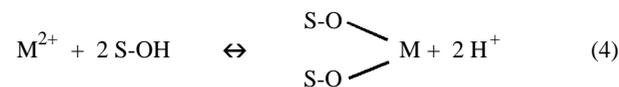
While the numbers are not identical, the trend is in the same direction and the steps between adjacent metals are of similar size which suggests that the adsorption reaction may have a similar form to reaction (1). Now, oxides like goethite are known to have chemical groups on the surface with the general form S-OH, so we believe, by analogy, that the surface adsorption reaction has the form



For adsorption of cadmium by goethite the reaction would be



This reaction predicts that H⁺ ions are expelled from the surface as metal ions adsorb: we should be able to detect them, and to determine the number expelled per metal ion adsorbed. When such measurements are made, as expected, H⁺ ions are produced on adsorption, but the number expelled per metal ion adsorbed is usually greater than 1 and depends, to some extent, on the identity of the metal and the mineral. Values greater than 1 can occur due to the following reaction:



Here the metal ion is bound to two surface sites, a process called bidentate bonding. Values for the number of H⁺ ions expelled of between 1 and 2 can result from the simultaneous operation of both reactions (3) and (4).

While reaction of metal ions with surface hydroxyl (S-OH) groups can explain the results for adsorption of metal ions on oxides, it cannot explain the very different curve shape found for adsorption on kaolinite. Again let's study the adsorption of the same set of metal ions on kaolinite to see if common features emerge. The results of this investigation are shown in Figure 4.

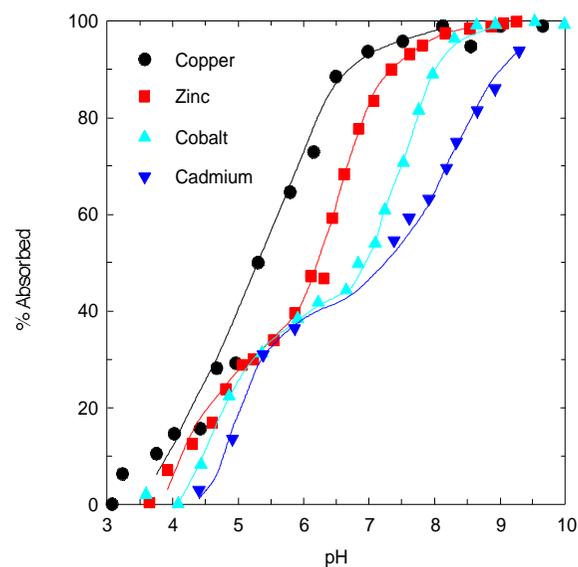
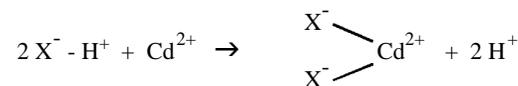


Figure 4. Adsorption from 100 μM solutions of metal ions onto kaolinite (Ikhsan et al. 1999; Spark et al. 1995b)

There are significant differences between these results and those shown previously for adsorption of these metal ions onto goethite. Firstly, adsorption begins for zinc, cobalt and cadmium at a similar pH to that for copper (about pH 4). Remember that for goethite, adsorption of copper began at pH 4 but the other metals showed little adsorption until much higher pH values (e.g. pH 7 for cadmium). The adsorption curves for zinc, cobalt and cadmium are quite similar between pH 4 and 6, with all showing a plateau at about 35% adsorption. While similarities are evident at lower pH, the adsorption curves are quite different at higher pH; in fact the shapes and positions of the curves are similar to those found on goethite in the higher pH range.

The curves for zinc, cobalt and cadmium suggest that adsorption of these metals to kaolinite involves two separate and different adsorption processes. The second, at higher pH, corresponds to adsorption on S-OH sites as the curve shapes and positions are similar to those found for adsorption on oxides. The adsorption process at lower pH, however, has quite different characteristics.

What can we deduce about the additional adsorption process that operates at low pH on kaolinite? The fact that the adsorption curves for zinc, cobalt and cadmium at low pH are so similar suggests that it may be largely independent of the nature of the metal ions. As the three metals are all present as doubly charged M²⁺ ions over this pH range, the characteristics of this adsorption stage can be explained by use of a simple charge replacement or 'ion-exchange' mechanism. This would only be a reasonable mechanism if kaolinite contained negatively charged surface sites. Now, through other experiments we can show that kaolinite crystals do carry a permanent negative charge on one face. Let's call these sites X⁻. Normally in solution these negatively charged sites attract positively charged ions from solution; in our experiments these may be H⁺ or Na⁺ ions. The 'ion-exchange' reaction can therefore be written for, say, cadmium as



Now, the pH of the solution is a measure of the concentration of H⁺ ions with higher pH values corresponding to lower H⁺ concentrations. Hence, as we increase the pH of the system there are less H⁺ ions present to bind to the X⁻ surface sites which favours adsorption of other positively charged ions in solution. While both Na⁺ and Cd²⁺ ions are present in our example, the Cd²⁺ ions will adsorb preferentially as they have a larger charge.

Since adsorption through this mechanism depends largely on the charge of the ion, we would expect adsorption to begin at a similar pH for ions with the same charge. In addition, the number of negatively charged sites on the surface should determine the maximum amount of adsorption of this type. Hence the 'plateau' should occur at the same % adsorbed for ions with the same charge; these features can be seen in Figure 4.

While this process appears, at first sight, to be absent for copper adsorption, that need not be the case. Since the adsorption of copper on S-OH sites occurs at lower pH than for the other metals (Figure 3), the two adsorption processes may occur simultaneously, thereby effectively masking the additional adsorption mechanism on kaolinite.

What further experiment could be undertaken to confirm our proposed adsorption mechanism? We could introduce increasing amounts of another positively charged ion to the system and determine its effect on adsorption of metal ions. If the 'ion-exchange' mechanism is correct, high concentrations of Na^+ ions should displace other metal ions from the surface. Figure 5 shows the effect of increasing NaCl (or salt) concentrations on the adsorption of cadmium. NaCl contains Na^+ which can compete with Cd^{2+} ions for X^- sites. Even 10 mM NaCl displaces a significant amount of Cd^{2+} , while 100 mM NaCl removes almost all of the cadmium from the surface at pH values below 7.5. Similar results have been found for every ion we have studied (Spark *et al.* 1996b).

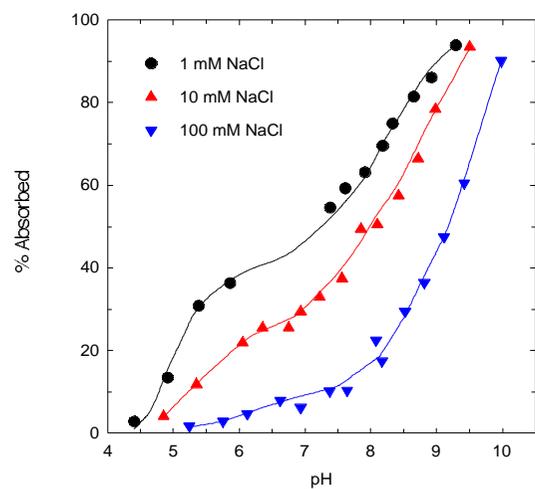


Figure 5. Adsorption of 100 μM cadmium onto kaolinite in the presence of NaCl

When the curves for adsorption in the presence of 100 mM NaCl are compared with those for adsorption onto oxides the results are almost identical. Hence, while increasing the salt concentration can suppress adsorption onto ion-exchange sites, it has little effect on metal ion adsorption to S-OH sites. Not only do these results provide strong support for our proposed adsorption mechanism onto kaolinite, but they also have relevance for our understanding of the consequences of salinity on soils with high clay content. For clay soils in the normal pH range (pH 5 to 7.5) increasing salinity will tend to displace trace and heavy metals from the ion-exchange sites found on all clay minerals. Hence, in addition to destroying soil structure, high salinity levels can also be expected to lead to trace element deficiencies in soils with relatively high clay content.

So far we have considered adsorption onto a range of pure soil minerals. Soils contain not only a range of mineral particles but also a variety of organic materials. If we are to understand the adsorption of metal ions by soils we need to know the effect of organic matter on the adsorption process, and hence on trace element availability to plants. Once again, when we consider organic material we are faced with very complex systems. A typical organic molecule found in soils is shown in Figure 6. Clearly it is very difficult to determine, with any precision, the chemistry of reactions that involve very complex species such as this. Again our solution is to study, in detail, relatively simple molecules that have some of the characteristics of these complex structures. Figure 6 shows that these soil organic molecules, called humic substances, contain several important chemical components. The most common of these are $-\text{COOH}$ and $-\text{OH}$ groups attached to aromatic ring structures. From solution chemistry we know that $-\text{COOH}$ groups bind readily to metal ions, so they are likely to play a significant role in determining the fate of metal ions in soil systems.

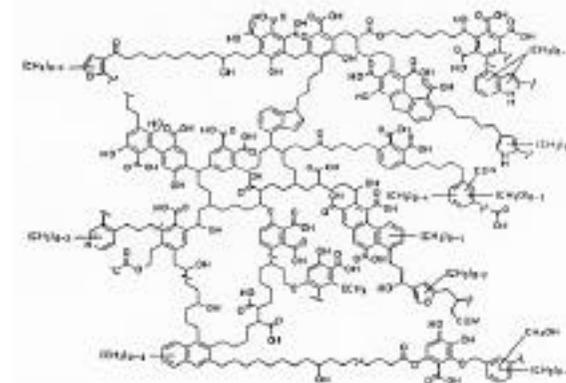
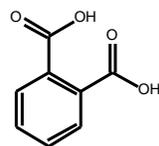


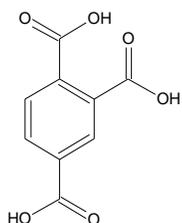
Figure 6. Model of a 'typical' humic substance (Schulten and Schnitzer 1993). Reproduced by permission of Springer-Verlag.

We have studied the adsorption of metal ions onto goethite in the presence of several different benzene carboxylates (i.e. benzene rings with different numbers of $-\text{COOH}$ groups attached).

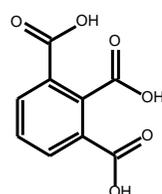
From these studies we find that the effect of these species on metal ion adsorption depends on the number of $-\text{COOH}$ groups attached to the benzene ring, and on the way in which the groups are arranged around the ring. To illustrate this, let's consider the effect of the following four benzene carboxylates on cadmium adsorption to goethite.



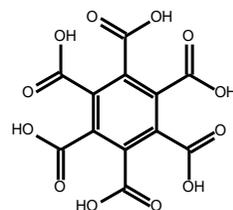
phthalic acid



trimellitic acid



hemimellitic acid



mellitic acid

The results in Figure 7 show that phthalic acid (having just two $-\text{COOH}$ groups) has a relatively small effect on cadmium adsorption, while mellitic acid, with six $-\text{COOH}$ groups, substantially enhances adsorption at low pH. The two species with three $-\text{COOH}$ groups both enhance adsorption, but to significantly different extents, reflecting the importance of the positioning of the groups around the benzene molecule.

It is clear from Figure 7 that the largest effect of these organic ligands is found from pH 3.5 to 6, pH values that are commonly found in acid soils. Figure 7 shows that at pH 4.5, about 7% of cadmium is adsorbed in the absence of the organic species. Addition of phthalic acid causes little change in the amount adsorbed, but hemi- and tri-mellitic acids cause an increase in adsorption to 18 and 23% respectively. The major change occurs when mellitic acid is used, with the amount of cadmium adsorbed at pH 4.5 increasing to 55%.

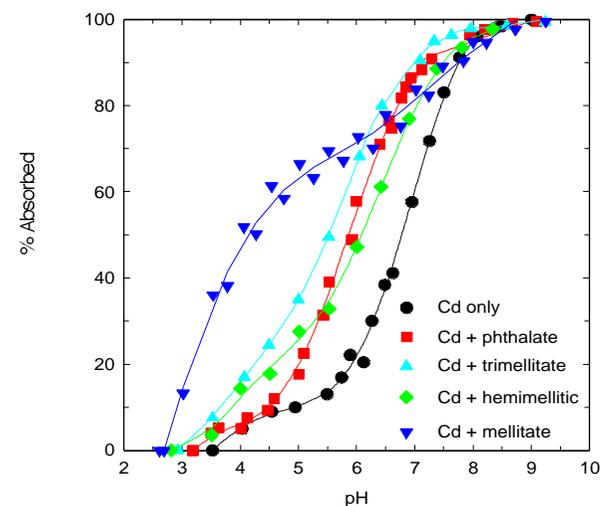


Figure 7. Adsorption of $50 \mu\text{M}$ cadmium on goethite in the presence of $1000 \mu\text{M}$ of various benzene carboxylic acids

In order to further investigate these effects, let's choose mellitic acid and study the effect of the concentration of organic ligand on cadmium adsorption. The results are shown in Figure 8. Even low concentrations of mellitic acid ($50 \mu\text{M}$) have a dramatic effect on the amount of cadmium adsorbed at low pH. When we increase the mellitic acid concentration to $100 \mu\text{M}$ even more cadmium adsorbs. The results at pH 4.5 show the effect of mellitic acid concentration on adsorption clearly. In the absence of mellitic acid less than 10% of the cadmium is adsorbed, but when the concentration of mellitic acid is increased to $100 \mu\text{M}$, about 80% adsorbs.

Surprisingly, a further increase in the concentration of the organic acid does not result in more cadmium adsorption. In fact, in the presence of $1000 \mu\text{M}$ mellitic acid the amount of cadmium adsorbed is reduced to 55% while at pH values above 7, this high concentration of mellitic acid actually appears to cause a slight suppression of cadmium adsorption.

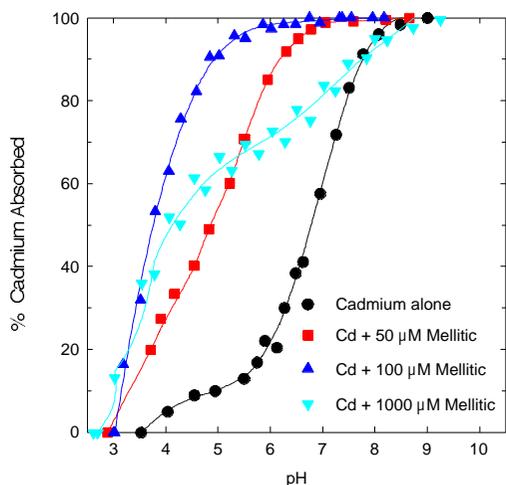


Figure 8. Adsorption of 50 μM cadmium on goethite in the presence of various concentrations of mellitic acid. (Angove 1999)

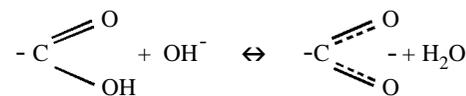
How can these results be explained?

Since we have both a metal ion (cadmium) and an organic ligand (mellitic acid) in our system we need to understand the nature of their interaction not only with the substrate surface but also in solution. When the solution interaction between mellitic acid and cadmium is studied in detail we find that they complex strongly. Now, when we have a high concentration of mellitic acid in the system only a small fraction of it adsorbs to the surface as there are insufficient surface sites to adsorb more than 10% of 1000 μM mellitic acid. This leaves the vast majority of the mellitic acid molecules in solution where they react strongly with cadmium. Hence, high concentrations of mellitic acid tend to hold cadmium in solution through simple competition with the species on the surface that can bind cadmium. This competition can result in suppression of cadmium adsorption at higher pH values. Through careful experimental measurements followed by mathematical and chemical modelling of the results we can develop a picture of the actual chemical processes occurring at the surface and in solution.

Our understanding of the chemistry can be further enhanced in other ways. For instance, recent advances in infrared spectroscopy now allow us to take the spectrum of adsorbed species. Now, infrared (IR) spectra result from the interaction of light in the infrared part of the electromagnetic spectrum with bonds between atoms in molecules. Every molecule has a different set of bonds, and hence a different interaction

profile, or spectrum. Hence an IR spectrum provides a fingerprint of the molecule investigated. If we change the bonds through chemical interaction between the adsorbing molecule and the surface, we would expect to see changes in the IR spectrum.

Let's see how this works by investigating the IR spectrum of mellitic acid both in solution and when adsorbed onto a goethite surface. We begin by measuring at the spectrum of mellitic acid in solution. Now, we expect the spectrum to change as the pH of the solution is increased because mellitic acid, being an acid, reacts with OH⁻ ions as pH increases causing changes in the bonds. That reaction can be represented:



The expected changes are clearly visible in the solution spectra (Figure 9).

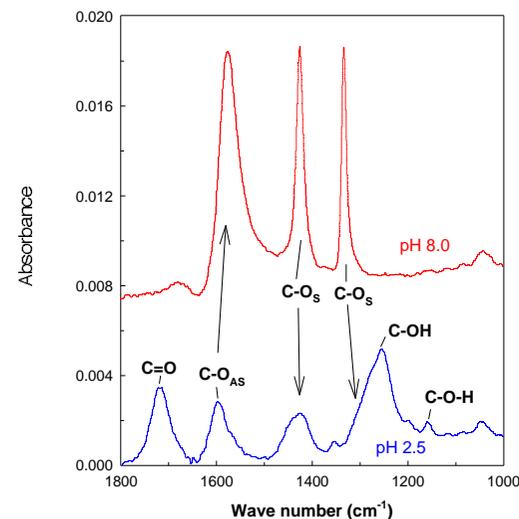


Figure 9. ATR-FTIR spectra of mellitic acid solutions.

At low pH, where there is a high concentration of H₃O⁺, peaks due to C=O and C-OH bonds are obvious, while at higher pH, where significant concentrations of OH⁻ can be found, only peaks due to C-O bonds are seen.

Let's see what happens to the spectrum when the mellitic acid is adsorbed to goethite. In the spectrum shown in Figure 10 we have subtracted any signal from mellitic acid solution species so we can be sure that we see only adsorbed mellitic acid.

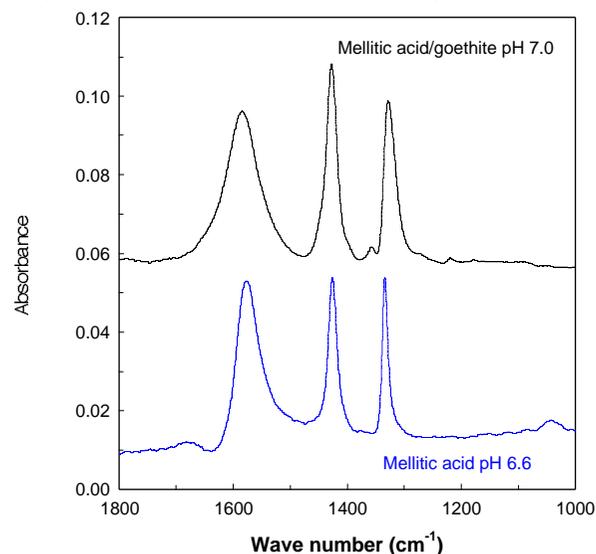


Figure 10. ATR-FTIR spectrum of mellitic acid adsorbed to goethite.

Two things are immediately apparent from Figure 10. Firstly we can get an excellent spectrum from adsorbed species, and secondly, the spectrum for adsorbed mellitic acid is almost identical to the spectrum of mellitic acid in solution. There are small changes in the width of the peaks and in the relative peak heights, but there are no new peaks and there are no significant changes in the positions of the peaks.

We stated earlier that if the bonds within molecules changed on adsorption then the spectrum should change; the magnitude of the differences expected is much greater than those found here. The lack of change in the spectrum for adsorbed mellitic acid indicates that it is adsorbed to goethite without the formation of bonds with the surface. This is only possible if the molecules are attracted to the surface by physical forces (for example by electrostatic attraction) rather than by chemical bonding. Electrostatic attraction is likely in this case because the goethite surface has a positive charge at pH values below 8.6, while mellitic acid, being partially or fully ionised, will be negatively charged over the whole pH range studied. The resulting attraction between the negatively charged ions and the positively charged surface binds the mellitic acid to the surface.

However, we saw earlier in Figure 8 that mellitic acid dramatically increased the adsorption of cadmium to goethite at low pH. If the mellitic acid is held to the surface by electrostatic forces, how can it enhance cadmium adsorption? Again, IR spectroscopy offers us insights into the process. Were the cadmium to be bound to the surface through chemical bonding to adsorbed mellitic acid we should see a change in the spectrum of the adsorbed mellitic acid. Figure 11 shows the spectrum of mellitic acid adsorbed to goethite from a solution containing equal concentrations of cadmium and mellitic acid at pH 4.5. We saw earlier that there was strong enhancement of cadmium adsorption under these conditions. Again the spectrum shows no significant change, indicating that the extra cadmium on the surface is not bound to adsorbed mellitic acid.

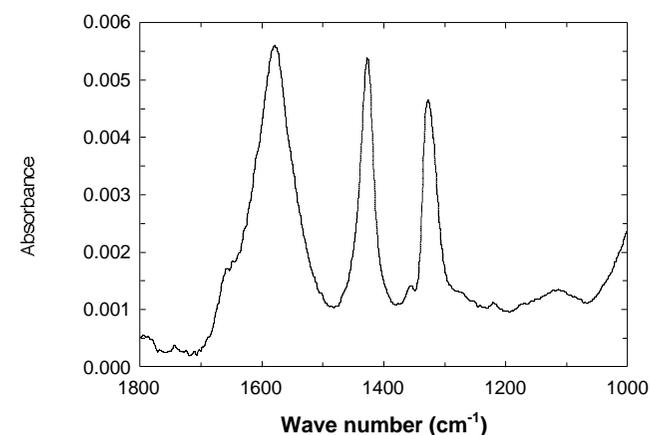


Figure 11. ATR-FTIR spectrum of the cadmium-mellitic acid-goethite system at pH 4.5.

How can the observed enhancement of cadmium adsorption by mellitic acid be explained? In the absence of mellitic acid, the positive charge on the goethite surface at pH 4.5 strongly repels Cd^{2+} ions, preventing them from coming close enough to the surface to chemically react with S-OH groups. When mellitic acid is added we have seen that it is attracted to the surface through electrostatic forces. Its large negative charge changes the net charge on the surface from positive to negative. Positively charged cadmium ions are then attracted, and able to get close enough to interact directly with S-OH sites on the goethite surface. Hence the enhanced adsorption in the presence of mellitic acid occurs indirectly through modification of the surface charge. This conclusion would not have been obvious without the additional information offered by the FTIR spectra.

Conclusion

Soils are remarkably complex systems with properties and characteristics that are dependent on their mineral and organic matter composition. Information on the detailed chemistry of processes within soil systems can best be obtained through a study of simpler systems involving single soil components. Modern spectroscopic methods provide invaluable additional information in this quest to understand the chemistry of surface reactions in soil systems. The information gained through these studies, together with a detailed knowledge of the composition of a soil, provides our best chance of understanding processes occurring within particular soil systems. Armed with this understanding we may hope to be able to predict how, for instance, the trace metal status of a given soil will change as the chemical and physical environment of the soil is modified because of modifications in farming practice.

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The Worner Research Lecture Series

The annual Worner Research Lecture forms a series of public lectures at La Trobe University, Bendigo. The aim of the series is to publicise research carried out at La Trobe University, Bendigo.

The University is proud to be associated with the Worner brothers, Howard, Neil and Hill, who were students at Bendigo School of Mines, a forerunner of La Trobe University, Bendigo. The three brothers were raised on a farm in the Mallee. In the early 1930s, they studied at Bendigo School of Mines: Howard and Hill for a Diploma of Industrial Chemistry and Neil for a Diploma of Civil Engineering. All three brothers later won prestigious scholarships to The University of Melbourne.

Howard Worner's distinguished career in academia and industry led him to his present honorary professorship at the University of Wollongong, where he has been Director of the Microwave Applications Institute since 1989. In 1994, La Trobe University conferred on him the degree of Doctor of Science (honoris causa).

Neil Worner pursued a career in civil engineering, including the position of Chief Civil Engineer with the Snowy Mountains Hydro-Electric Authority. His career continued in senior and advisory capacities in Australia and overseas on projects such as the design and construction of major dams.

Hill Worner's career included several years on the Executive of the CSIRO and 22 years as Professor of Metallurgy and three as Dean of Engineering at The University of Melbourne, where he is now Professor Emeritus in Engineering.

Lecturers in the series so far have been the following:

- 1995 R. J. Seviour, Micro-organisms: the Good, the Bad and the Ugly
- 1996 T. M. Mills, Join the Dots and See the World
- 1997 Howard K. Worner and R. Findlay Johnston,
Bendigo Gold: Past Present and Future
- 1998 John Humphreys, Rural Health and the Health
of Rural Communities
- 1999 Vaughan Prain, Learning in School through New Technologies
- 2000 Bruce Johnson, Soils: Our Interface with the Environment