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Leaching column tests on arsenic-soil interactions

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Abstract: The leaching column test is a very useful and versatile tool that can be used to study the interactions between soils and various contaminants. This paper presents the results of leaching column tests conducted to examine the interactions of arsenic with soils. The migration of arsenic through compacted soil columns are monitored for both the sorption and desorption phases of the leaching column tests to study the arsenic-soil interactions during these phases.

The effects of varying amounts of organics in the soil on the sorption and desorption of arsenic are also investigated. While low contents of organics appear not to have too much effect on the sorption/desorption characteristics of the admixed soils, higher organics contents significantly affect these characteristics. Understanding the fundamental arsenic-soil interactions is a pre-requisite to solving the soil contamination and arsenic mobility problems and for any proposed clean- up or remediation measures.

Keywords: environmental geology, hazardous waste, laboratory tests, leachate, toxic materials

INTRODUCTION

Arsenic is a rather common contaminant of soils and groundwater. The case of groundwater contamination in Bangladesh and the Bengal Basin, due to the naturally high arsenic concentrations of the sediments, perhaps highlights the seriousness of this arsenic contamination problem, BGS and DPHE (2001). Locally in Malaysia, arsenic contamination of soils and groundwater is associated with mining or ex-mining land where arsenopyrite ($AsFeS_2$) often occurs with the other ore minerals or ore deposits. The interactions of arsenic with soils and groundwater are rather complex as they involve many physico-chemical processes. To better understand the complex interactions between arsenic and soils, a series of laboratory tests based on leaching columns were conducted recently at the Geo-environmental Research Centre in Cardiff University, Wales, United Kingdom. This paper presents the results of these laboratory investigations.

MATERIALS AND METHODOLOGY

Materials

An artificial or "surrogate" soil was used for the tests. The soil used was made from mixing a well-graded sand with milled shale from a South Wales colliery waste tip. The shale provides the clay content of the soil. This artificial or "surrogate" soil was developed to mimic soils from Bangladesh where arsenic contamination of ground water is a very serious on-going problem. The surrogate soil was thoroughly characterized for its physical, chemical and mineralogical properties before commencement of the leaching column tests. It has 66% sand, 26% silt and 8% clay and can thus be described as a clayey-silty-sand similar to alluvial deposits forming the groundwater aquifers in Bangladesh. Detailed physical, chemical and mineralogical characteristics of the surrogate soil can be obtained from the thesis by Shaw (2003).

The organic top-soil used for mixing with the surrogate soil, to study the effects of varying the amounts of natural organic matter (organics) in the soil on the adsorption/desorption behaviour of the soil, has an average organic content of 12.8%.

The permeant used for the leaching column tests consists of 250 ppm arsenate solutions prepared using reagent grade sodium arsenate (Na_2HAsO_4) in distilled, de-ionised water (DDW) of pH 7.

The leaching columns are made from acrylic tubing 150 mm long with an internal diameter of 75mm. Permeant is stored and delivered from Marriott tubes, which have the interesting feature of maintaining a constant pressure head over the soil column.

Methodology

The usefulness and versatility of leaching column tests have been highlighted in several previous publications, in particular with respect to studies on heavy metals in soils, for example Yong et al. (1994), Tan & Yong (1998), Tan (2001), Tan et al. (2003), etc. A series of leaching column tests were conducted employing four leaching columns (designated as columns A to D) run concurrently. In the series, the surrogate soil was mixed with various proportions of organic top-soil (2% to 10% by weight) and compacted at a constant 8.3% water content (optimum moisture content for the surrogate soil when compacted by the Standard Proctor method). The soil was compacted into the leaching columns in 6 layers, with each layer receiving 8 impacts of a 2.3 kg rammer dropped from a height of 200mm, Shaw (2003). The compacted soil columns were first saturated with 2 pore volumes (p.v.) of distilled, de-ionised water (DDW) with pH7 before leaching with the arsenate solution. Leaching of the soil columns with the arsenate solution was carried out up to about 8 pore volumes of permeation (representing the adsorption or arsenic loading phase of the leaching column test), after which leaching with DDW (pH 7) was conducted for another additional 5 p.v., representing the desorption phase of the leaching column test. Since the compacted soil columns have moderate permeabilities (10^{-7} m/s), the time taken for the permeation of ~ 13 pore volumes of permeants was about 1-2 weeks.

The content of arsenic in the effluent or leachate was monitored periodically, about every 0.5 p.v. of permeation, for both the sorption and desorption phases of the leaching column tests. This yields the breakthrough curves as well as the desorption or mobility curves of the arsenic. The amount of adsorbed arsenic in the soil solids at the end of the adsorption and desorption phases of the experiment was also measured by slicing the soil columns into 4 slices, and analyzing the arsenic content of each soil slice. This gives the migration profiles of the arsenic through the soil columns.

RESULTS AND DISCUSSIONS

Compaction and Permeability

Details for the compaction of the soil columns and initial permeabilities during the saturation stage (with DDW at pH7) are summarised in Table 1. For soil columns A – D, the computed pore volumes are ~ 200 cm^3 (ranges from 197 – 204 cm^3), and this value was used as the pore volume for all the soil columns for ease of monitoring the tests. The initial permeabilities during the saturation stage are of the order of 10^{-7} m/s for columns A – D, with only slight numerical variations from 1.1 x 10^{-7} to 3.6 x 10^{-7} m/s. Based on the test results for compaction and permeabilities, as presented in Table 1, there is a direct correlation between organics content and compacted densities as well as permeabilities. Increasing the organics content from 0% to 10% results in a slight decrease in compacted densities, as to be expected, and a corresponding increase in permeabilities (though the permeabilities are still of the same order of magnitude). This slight numerical increase in permeabilities may not be very significant. In another companion study (McDermott, 2003) involving a second series of tests with much higher organics contents, the permeability values show a significant decrease of one order of magnitude when the organic top soil content is increased from 10% to 20% and 30% (permeabilities of the order of 10^{-9} and 10^{-10} m/s). The compacted densities in that second series of tests also decrease slightly with increasing organics contents.

Table 1 : Compaction and permeability of the soil columns.

Column	% Topsoil	Dry Density (Mg/m^3)	P. V. (ml)	Permeability ($x10^{-7}$ m/s)
A	0	1.86	197	1.1
B	2	1.86	199	2.3
C	5	1.85	201	2.8
D	10	1.83	204	3.6

Breakthrough Curves

Figure 1 shows the complete bell-shaped leaching curves comprising two parts, namely an initial sorption or arsenic loading curve from 0 to ~ 8 p.v. leaching with the arsenate solution, followed by a second desorption or flushing curve from ~ 8 p.v. to ~ 13 p.v. with DDW pH7.

The initial sorption or arsenic loading curves from 0 to ~ 8 p.v., can also be regarded as the arsenic breakthrough curves. Breakthrough curves are useful in the understanding of the adsorption or retention characteristics of a soil with respect to a particular contaminant. In Figure 1, arsenic breakthrough, defined as when the relative concentration Ce/Co = 0.5, occurs at different times or different pore volumes for the different % organic top-soil. Ce=effluent arsenic concentration, while Co=original concentration of arsenic in the permeant, i.e. 250 ppm. Thus, in Figure 1, breakthrough of arsenic occurs when Ce = 125 mg/L. For the surrogate soil, breakthrough occurs at ~ 4.5 p.v. The 2% ORG curve also shows breakthrough at slightly over 4 p.v., ie. similar to that of the surrogate soil. While the 10% ORG curve shows a much delayed breakthrough at ~ 5.5 p.v., consistent with the greater adsorption of arsenic by the higher organic content of the soil. The 5% ORG curve shows an earlier, accelerated breakthrough at slightly less than 4 p.v., even earlier than the surrogate soil and the 2% ORG curve. The reasons for this “anomalous” behaviour of the 5% ORG curve are not totally clear. Perhaps since columns A, B and C have very similar compacted dry densities and permeabilities, the small differences in organic contents of these three soil columns are insignificant and hence do not cause any really significant change in arsenic adsorption, and hence all three curves show breakthrough of arsenic at ~ 4 – 4.5 p.v.. In contrast, the 10% ORG curve shows that, at this much higher organic content, the effect of organics is very significant and causes a distinct increase in arsenic retention by the soil and hence the much delayed breakthrough at ~ 5.5 p.v. Note that for the 10% ORG curve, the much delayed breakthrough occurs in spite of the fact that the 10% ORG soil column has the highest permeability value compared to the other three soil columns – hence, a clear-cut evidence of the overwhelming effect of soil organic material on arsenic retention.

Another possible interpretation of the breakthrough curves to explain the apparent “anomalies” is as follows. For the three curves comprising the surrogate soil (0% ORG), 2% ORG and 5% ORG curves, the breakthrough of arsenic is dependent solely on the permeabilities of the soil columns. Thus, the 5% ORG breakthrough occurs earliest since it has the highest permeability, while 0% ORG breakthrough occurs latest since it has the lowest permeability. The low organics contents from 0% to 5% do not affect the retention or breakthrough of arsenic significantly.

For the 10% ORG soil, the large increase or jump in organics contents is now the overwhelming controlling factor, hence the delayed breakthrough in spite of its highest permeability value.

Another interesting feature shown by Figure 1, is that the organics-enhanced soils attain higher peaks of > 200 mg/L compared to the surrogate soil which shows a peak of << 200 mg/L. Moreover, the peak values for the organics-enhanced soils are very similar. This would seem to indicate that at ~ 8 p.v., sorption or loading of the soil columns would be at about the maximum or saturation (with respect to arsenic sorption) for the three arsenic-enhanced soil columns.

Desorption of Arsenic

Desorption of arsenic from a soil contaminated with arsenic is an important aspect of study which has great relevance in the treatment or remediation of arsenic-contaminated grounds. The ease or otherwise of flushing or washing an arsenic-contaminated soil with a particular liquid or solvent will determine the success or failure of the method adopted. Desorption of arsenic is of course tied up with the mobility characteristics of the arsenic species vis-à-vis the soil type concerned. The chemical environment of the soil, such as pH, eH (redox potential), pore fluids chemistry, etc. all play a part in the mobility, sorption and desorption of the arsenic.

The second part of the leaching curves from ~8 p.v. to ~ 13 p.v. with DDW at pH7 in Figure 1, shows the desorption curves for columns A – D. The desorption phase of the leaching column tests was designed to see how well, or how difficult, it is to flush arsenic out of the arsenic-contaminated or arsenic-loaded soil columns. The "solvent" used to flush out the arsenic was distilled, de-ionised water (DDW) with pH 7. In an earlier companion study, it has been shown that the pH of the flushing liquid/solvent has a significant effect on the flushing or mobility of the arsenic, Shaw (2003), Shaw et al. (2004). Thus, it is important to maintain the same pH7 for the DDW solvent in this current study which is centered more on the effects of varying organics contents in the soil on the mobility of the adsorbed arsenic.

The results in Figure 1 show that with increasing pore volumes of DDW permeated, the arsenic concentrations in the leachate drop from ~ 200 mg/L to ~ 10 mg/L. The rate of desorption is particularly high at the initial 1-2 pore volumes of desorption, i.e. steep curves, and then flattens out after 2 pore volumes. The plots also show that desorption of arsenic from the soil with DDW is more difficult when organics are present in the soil – in other words, the organics result in greater retention of the arsenic. However, the relationship between the percentage of organics in the soil and the arsenic desorbed is not so clear. While the 2% ORG and 5% ORG curves both fall way below the Surrogate Soil (S.S.) curve, with the 5% ORG curve further down from the 2% ORG curve (consistent with the greater retention of arsenic with increasing organics content), the 10% ORG curve is only slightly below or nearer to the S.S. curve. The reason for this anomaly shown by the 10% ORG curve is not entirely clear – one possible explanation is that with the significantly greater amount of organics in the soil, reducing conditions were produced which reduced arsenate to arsenite, a more mobile form of arsenic. Unfortunately, measurements of redox potentials (Eh) in the leachate did not show low redox or reducing environments in the leachate. However, these Eh data do not necessarily reflect the Eh environments in the soil columns (limitation of the experiment).

Yet another interpretation to explain the discrepancies in the relative positions of the desorption curves is to invoke differences in soil permeabilities as before. The relative positions of the four desorption curves are similar to those of the sorption/breakthrough curves, and hence a similar interpretation in terms of permeability differences and/or significance of organics contents can be invoked.

Pore Volume vs Time Curves

The effects of differences in permeabilities and organics contents vis-à-vis the retention or mobility of arsenic can be further clarified by the plots of Pore Volumes versus Time, as seen in Figure 2. As shown in Figure 2, from 0 to ~ 8 p.v. representing the arsenic sorption or loading phase, the relative positions of the 0% to 5% ORG curves are dictated by differences in permeabilities. The relative position of the 10% ORG curve is dictated by the overwhelming control by high (10% ORG) organics even though the 10% ORG soil has the highest initial permeability. Due to the effect of high organics, the permeability of the 10% ORG soil column has been drastically reduced on permeation with the arsenate solution, in addition to the much higher arsenic retention as discussed above. Again, in Figure 2, the effects of permeability versus organics control are apparent from ~ 8 p.v. to ~ 13 p.v for the desorption or flushing with DDW phase.

Migration Profiles

Migration of arsenic through the compacted soil columns can be studied via analyzing the soil slices after permeation with arsenic or DDW. Figure 3 is a typical example. It shows the variation in arsenic concentration in the soil slices from the top to the bottom of the soil column after desorption with DDW.

Typically, for migration profiles plotted after the adsorption or loading phase, the results would show that there is great retention of the contaminant by the soil slices, especially at the uppermost portion of the soil columns. The migration profiles would then show a decreasing trend with depth down the column. The results in Figure 3, however, are for arsenic still retained by the soil columns after 5 p.v. of flushing/desorption with DDW. The results show that, in spite of 5 p.v. of flushing with DDW, much arsenic is still retained throughout the soil columns. The variation with depth is of course different from the typical migration profiles plotted for end of adsorption or loading phase. The 10% ORG curve shows the highest arsenic retention by the soil compared to the other three curves. These results are consistent with the role of organics in the retention of arsenic, i.e. the retention of arsenic increases with increasing organics contents. The variation or trend with depth shows differences among the four soil columns: the 0% and 2% ORG soils show increasing arsenic retention with depth (effect of movement and re-adsorption of arsenic due to flushing), while the 5% and 10% ORG soils show arsenic peaks at mid-columns, also signs of arsenic movement and re-adsorption due to flushing effect.

The Effects of pH and Eh

During the progress of the leaching column experiments, both pH and Eh were also measured for the effluent leachate to monitor their variations. For the adsorption phase where arsenate was used as the permeant, the effluent leachate shows increasing pH of ~ 8.5 – 9.1. Although a pH7 DDW was used as the permeant throughout the desorption phase of the leaching process, the effluent leachate during this desorption phase also shows higher pH values of ~9. It would appear that regardless of the % ORG used, high pH values were maintained by the sodium arsenate solution used.

Similar trends were shown by the Eh values for the effluent leachates, i.e increasing Eh from ~ 100 – 300 mV during the sorption phase with arsenate, then maintaining a high Eh value of ~ 250 mV during the desorption phase with DDW. All Eh values are high, showing oxic or non-reducing environments, regardless of the % ORG used in the soil.

A plot of pH versus Eh, Figure 4, also shows no apparent correlation between pH and Eh. Thus, the effects of pH and Eh vis-à-vis organics contents are not straight-forward, and perhaps reflect the underlying complexities of arsenic-soil interactions.

CONCLUSION

Arsenic-soil interactions can be studied via laboratory leaching column tests. While small amounts of natural organic matter do not significantly affect the adsorption and desorption of arsenic by the admixed soil, larger amounts of organics content will significantly increase the adsorption capability of the soil with respect to arsenic. Though pH and Eh are important factors in the adsorption/desorption behaviour of the soil, there is no straight forward correlation between these parameters vis-à-vis the organics content of the soil and arsenic retention.

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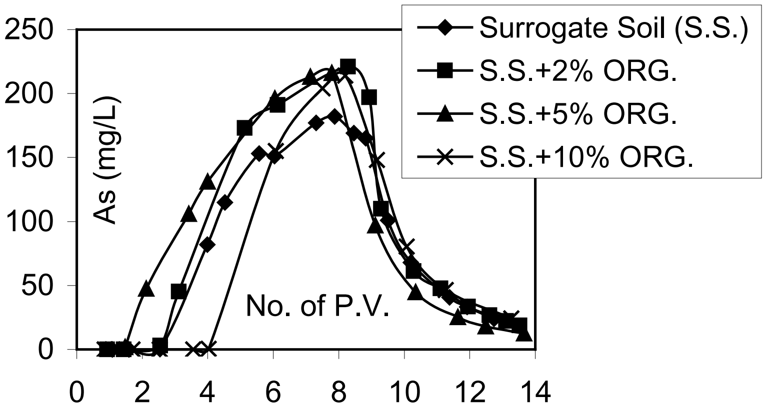

Figure 1. Sorption with As, followed by desorption with water. desorption after ~ 8 P.V.

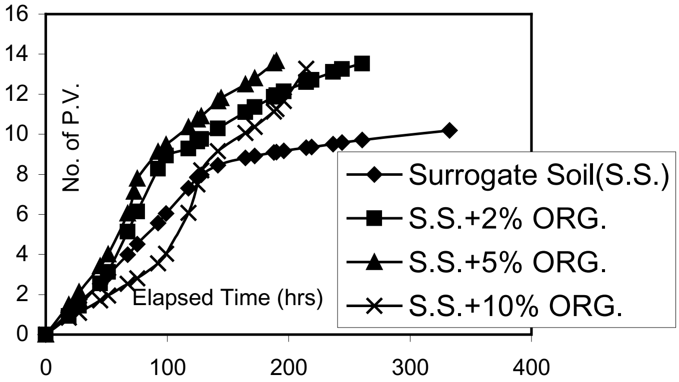

Figure 2. Sorption with arsenic followed by desorption with water(desorption from ~ 8 P.V.).

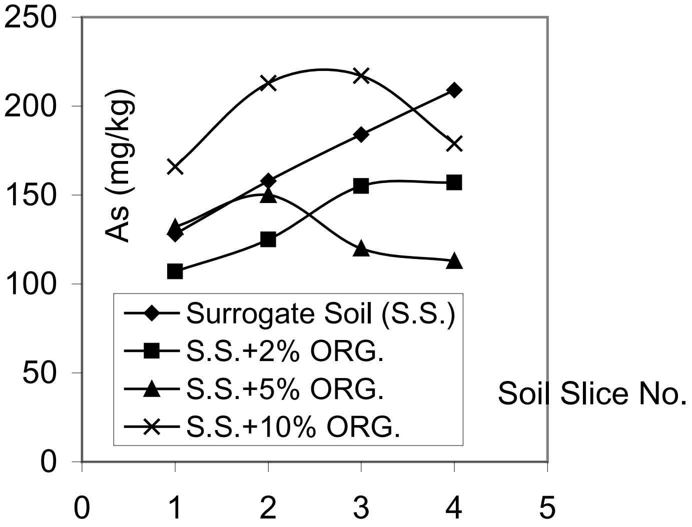

Figure 3. Arsenic distribution in soil columns at end of desorption. (slice 1=leachate entry, slice 4=exit)

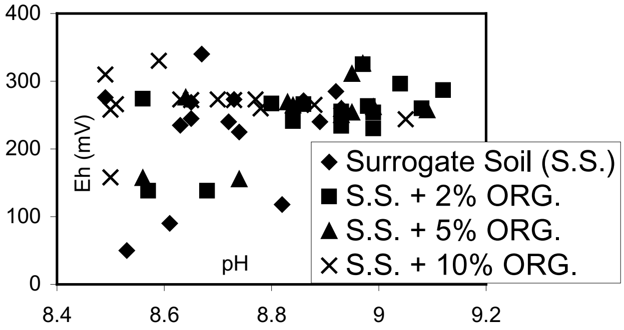

Figure 4. pH vs eh (mV), sorption with arsenic, followed by desorption with water (desorption from ~ 8 P.V.)