

ADSORPTION OF HEAVY METALS BY NATURAL CHARCOAL (BONE CHARCOAL): ITS POTENTIAL AS A WATER TREATMENT CLEANUP

Jonathan Wilson¹, Ian Pulford¹, Symon Thomas²,

1. Dept. of Environmental, Agricultural and Analytical Chemistry, University of Glasgow, Glasgow, G12 8QQ, Scotland, UK.
jonathaw@chem.gla.ac.uk

2. Tate and Lyle Process Technology (TLPT), 21 Dellingburn St, Greenock, PA15 4TP, Scotland, UK.

Abstract

The potential of natural* charcoal as an adsorbent of heavy metals in water was studied using batch tests on a variety of metal solutions. Its ability to adsorb aluminium, arsenic, copper, iron, lead and zinc was examined and the mechanisms involved in the process investigated. Natural charcoal has an alkaline pH ~9 following pyrolysis of the bone to make the charcoal and for many of its applications this needs to be reduced to pH7 by washing the charcoal before use. The difference in adsorption capacities of the washed and unwashed charcoal can also provide information on the mechanisms involved and on the conditions necessary for maximum adsorption.

Natural charcoal (mesh size 20-60) had a capacity of 37mg g⁻¹ Zn (washed) and 15mg g⁻¹ Zn (unwashed), 24mg g⁻¹ Al, 150mg g⁻¹ Pb and 23mg g⁻¹ Cu (washed). A smaller particle size (20-100mesh) caused a considerable increase in the adsorption capacity for some of the metals. For zinc the amount sorbed increased from 37mg g⁻¹ to 73mg g⁻¹. The effective removal of these metals from solution suggests that natural charcoal has a useful role in the water cleanup process.

Introduction

Heavy metal pollution in water from point and diffuse sources is a continuing problem with ever decreasing legislative limits. Natural charcoal has the ability to adsorb heavy metals from water and could provide a cost-effective cleanup procedure with many applications. (Dahbi et al., 1999), (Lewis 1995).

The ability of natural charcoal to adsorb Al, As, Cu, Fe, Pb and Zn was studied and the mechanisms involved in the process examined. Adsorption isotherms were plotted and Langmuir equations applied to the data. In addition, following metal adsorption, the pH and the amount of Ca and P released were measured. Natural charcoal has an alkaline pH of ~9 following pyrolysis of the bone, and before it can be used commercially this needs to be reduced to pH7 by washing. There are many factors that influence the adsorption of metals such as pH, contact time, and initial concentration (Xu et al. 1994), but with these conditions standardised the difference between unwashed, washed and fine charcoal was studied with a view to understanding the conditions necessary for optimum adsorption.

Experimental methods

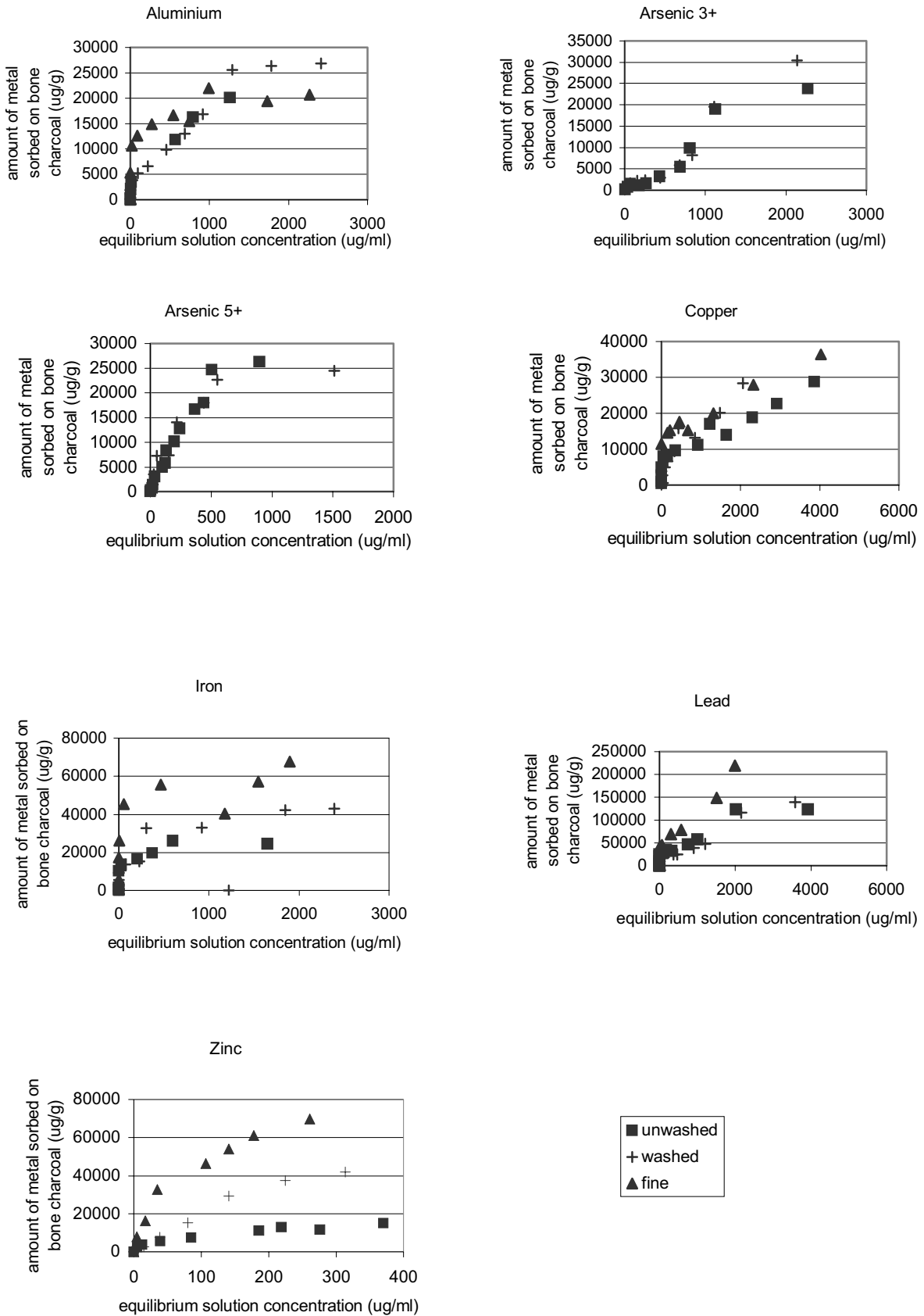
Materials – The natural charcoal used in this study was commercially manufactured Brimac 216 (TLPT).

Pyrolysis of the bone occurs at 700°C and the product is then ground and sieved to different mesh sizes. For most water purification applications 20-60 mesh size is used (850 – 250µm). For this work the natural charcoal was available in 3 different forms. Unwashed, washed and fine charcoal were used. Unwashed charcoal has only undergone pyrolysis and sieving, whereas washed charcoal has been washed with 17 bed volumes of water and fine charcoal has been further ground and sieved to mesh size 20-100. (850-150µm)

Deionised water was used throughout for making metal solutions and washing. The metal solutions were made from crystals of an appropriate salt >99.9% purity and all other chemicals were of reagent grade.

Sorption isotherms – A 1g sample of natural charcoal was shaken with 50ml of metal solution of varying concentration on an end-over-end shaker for 30minutes. The sample was immediately filtered through Whatmans No.2 filter paper into 60ml plastic bottles, where the solution was stored for future analysis. Flame atomic absorption spectrometry was used to quantify the total metal concentrations and the calcium concentration in solution. pH was also measured. PO₄ measurements were carried out on several of the filtrates using the molybdenum blue reaction or ICP-MS. However interference occurs when using the molybdenum reaction method especially when Cu or As are present in solution.

Figure 1. Sorption isotherms

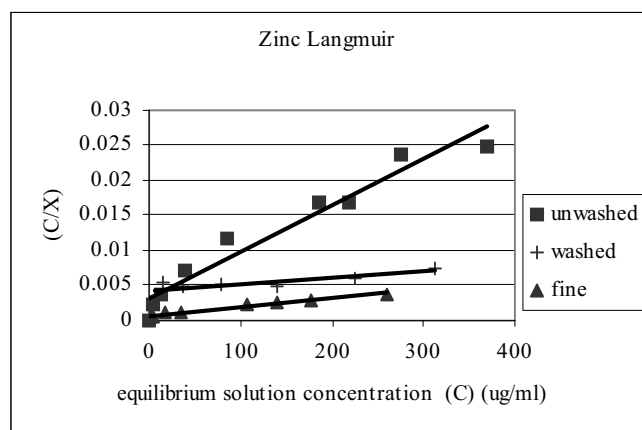


Results

Sorption isotherms were plotted for each of the metals (figure 1). Al, As⁵⁺, Cu, Fe, Pb, Zn all show similar shaped graphs with an initial steep rise in sorbed metal concentration before it levels out. There was no difference between unwashed and washed charcoal in the adsorption of Pb, As III or As V. For the other metals studied, the washed charcoal adsorbed more metal than the unwashed, with this effect being greatest for zinc. This difference, except for Zn, is small but increases at high metal concentrations. For Zn, Fe and Pb especially, and for Cu to a lesser extent, the fine charcoal adsorbed more metal than the coarser material. Using the Langmuir plot (figure 2) it is possible to obtain a value for the theoretical maximum capacity of the charcoal for each of the metals (X_{max}) See table 1. The fit of the data to the Langmuir for zinc is good with $r^2 > 0.95$. However for some of the other metals the fit is poorer. The As³⁺ data does not conform to the Langmuir plot at all.

The Ca released : metal sorbed ratio (table 1) shows there are three different interactions between the metals relative to the Ca ion release. For Al and As there appears to be little relationship between Ca and the amount of ion sorbed as seen by such small values for the ratio (table 1). For Cu, Fe, Pb and Zn there is a clear linear relationship between the amount of Ca released and the amount of metal sorbed. Approximately 1 mole of Ca is released for every 2 moles of Cu sorbed (ratio ~0.5), 1 mole of Ca is released for every 4 or 5 moles of Cu, Fe, Pb and Zn (metal ratio (~0.25-0.2)) There appears to be little difference between the types of charcoal and Ca release.

Figure 2. Langmuir isotherm for zinc



Discussion

Natural charcoal has a strong ability to adsorb heavy metal ions from water. It has a good capacity for lead in particular (150mg g⁻¹) and a capacity for over 20mg g⁻¹ for the other metals examined.

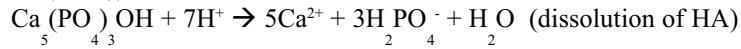
The washing of the natural charcoal prior to its use as a metal sorbent has clear advantages. The pH is lowered significantly (from pH9 to pH7). As well as this, the capacity of the charcoal for metal is increased. This would suggest that the mechanism by which metal ions are sorbed onto natural charcoal is more favourable at less alkaline pH or that in the washing process something is removed which allows more sites to be available for sorption. It is known (from XRD analysis) that on washing Na H(CO₃) .2H₂O, NaCl and KCl are removed. The sodium carbonate is responsible for the pH change while the salts may have been blocking some micro pore sites.

Ion-exchange appears to be a factor in the sorption of Cu, Fe, Pb and Zn due to the significant ratio of Ca release to metal ion sorbed. However it certainly is not the only mechanism at work as the ratios are not close enough to 1 to be a simple exchange of metal sorbing ion for a calcium ion. For Cu only 50% of the ions must undergo ion-exchange with calcium and an even smaller percentage for Fe, Pb and Zn. Unlike synthetic hydroxyapatite,

natural charcoal contains many other impurities especially Na, Fe and CO₂. In other work ion-exchange with both Na and Ca has been suggested (Takeuchi et al. 1990) and this may be occurring here. Complexation is likely to be a significant mechanism along with ion-exchange.

Certainly co-precipitation will be occurring as the metal is sorbed due to deprotonation of the charcoal. (The pH continues to drop as the metal is sorbed). The change in pH however may cause some dissolution releasing Ca. This is thought to be minimal though due to the blank values being small (even at lower pH). However, further work needs to be done on this. It is therefore difficult to conclude which mechanisms are at work for these metal ions. It is quite possible that several mechanisms are happening simultaneously with one process dominant at neutral pH and other mechanisms becoming more important as the pH falls.

Lead is known to undergo precipitation with hydroxyapatite(HA) to form hydroxypyromorphite(HP). (Ma Q.Y. et al. (1993)).



HP however was not identified by XRD and the relationship between pH v $-\log[\text{Pb}]$ was not conclusive to show a solid phase lead phosphate was the controlling phase in the solubility of the Pb. More work needs to be done on this.

The ratio of Ca:M⁺ for Al and As was negligible therefore ion-exchange is not going to be the mechanism by which they are sorbed. Precipitation appears to be the mechanism controlling Al as the pH v $-\log[\text{Al}]$ plot shows a typical Al solubility curve.

For arsenic it is interesting to note that both As⁵⁺ and the more toxic As³⁺ are sorbed. The two forms of arsenic (arsenate and arsenite) are both anions and the mechanism here was initially thought to be an ion-exchange with PO₄ however after solving some of the problems of PO₄ analysis and using ICP-MS the PO₄ concentration was found to be negligible. The possibility of ion-exchange with CO₃ is now being considered.

Natural charcoal has a good ability to adsorb heavy metal ions. Washing the charcoal improves this ability and the finer mesh size used in this work adsorbs even more, as would be expected due to increased surface area.

* bone charcoal is ISO accredited as natural charcoal and has been referred as such throughout

Table 1. Table of metal capacities and ratio of Ca released to metal sorbed

Metal	Charcoal	Capacity of charcoal X ^{max} (mg g ⁻¹)	Moles of Ca released: Moles of metal adsorbed
Al	U	19 ^{max}	0.021
	W	24	0.021
	F	21	0.023
As ³⁺	U	23	-0.004
	W	30	-0.023
As ⁵⁺	U	26	-0.001
	W	24	-0.001
Cu	U	22	0.44
	W	23	0.57
	F	31	0.29
Fe	U	25	0.26
	W	42	0.28
	F	55	0.25
Pb	U	108	0.18
	W	151	0.27
	F	207	0.20
Zn	U	15	0.23
	W	37	0.14
	F	73	0.17

References

- Dahbi S, Azzi M, delaGuardia M (1999), *Fresenius J. Anal. Chem.* 363(4): 404-407.
 Lewis J (1995), *J. Chartered Inst. Water and Env. Man.* 9(4): 385-395.
 Ma Q.Y, Traina S.J, Logan T.J (1993), *Environ. Sci. Technol.* 27:1803-1810.
 Takeuchi Y, Arai H (1990), *J. Chem. Eng. Jpn.* 23(1): 345-358.
 Xu Y, Schwartz F.W, Traina S.J (1994), *Environ. Sci. Technol.* 31: 2673-2678.