ADSORPTION OF ARSENIC AND PHOSPHATE ONTO THE SURFACE OF CALCITE AS REVEALED BY BATCH EXPERIMENTS AND SURFACE COMPLEXATION MODELLING

Ashfaque Alam, Mr.Abhishek Kr Upadayay (Asst.Professor)

M.Tech , Environmental Engineering Department, Mewar University Chittorgarh, Rajasthan

ABSTRACT

The adsorption of phosphate, arsenate (As(V)) and arsenite (As(III)) onto synthetic calcite was studied in a series of batch experiments. The adsorption of the three ions was studied separately followed by studies of the competition between arsenate and phosphate. The experimental data was utilized to set up models for sorption of arsenate and phosphate onto calcite. This was done to enhance the understanding of the governing processes controlling adsorption as well as to develop a tool to predict the fate of arsenate and phosphate in a calcareous environment. The adsorption was studied in eleven different calcite-equilibrated solutions that varied in pH, PCO2, ionic strength and activity of Ca2+, CO3 2- and HCO3 -. To avoid the precipitation of phosphate or arsenic-containing minerals the experiments were conducted using a short reaction time (generally 3 h) and a low concentration of phosphate (≤ 50 µM) and arsenic (≤ 33 µM).The results show that little or no arsenite adsorbs onto calcite within 24 h at initial arsenite concentration of 0.67 µM. In contrast, both arsenate and phosphate adsorbs readily and quickly onto calcite, with arsenate adsorbing faster than phosphate (adsorption is complete after 1 and 2-3 hours, respectively). Also desorption is fast and complete for both ions within 0.5 h. The reversibility of the sorption process indicates that neither arsenate nor phosphate is readily incorporated into the calcite crystal lattice under our experimental conditions.

The phosphate adsorption affinity for calcite is greater as compared to arsenate and the phosphate sorption isotherms are more strongly curved. However, the amount of both arsenate and phosphate adsorbed varied with the solution composition in the same manner. In particular, adsorption increased as the CO3 activity decreased (at constant pH) and as pH increased (at constant CO3 activity). The dependency on the carbonate activity indicates competition for sorption sites between carbonate and arsenate/phosphate, whereas the pH dependency is likely a response to changes in arsenate and phosphate speciation.

.Introduction

The two elements arsenic (As) and phosphorous (P) are both found in the aquatic environment, arsenic primarily in the form of arsenite (As(III)) and arsenate (As(V)) and phosphorus in the form of phosphate (PO_4). Where phosphorus is essential to all living things, arsenic is highly poisonous and a known carcinogenic (Kohn et al., 2002; Smith et al., 2009).

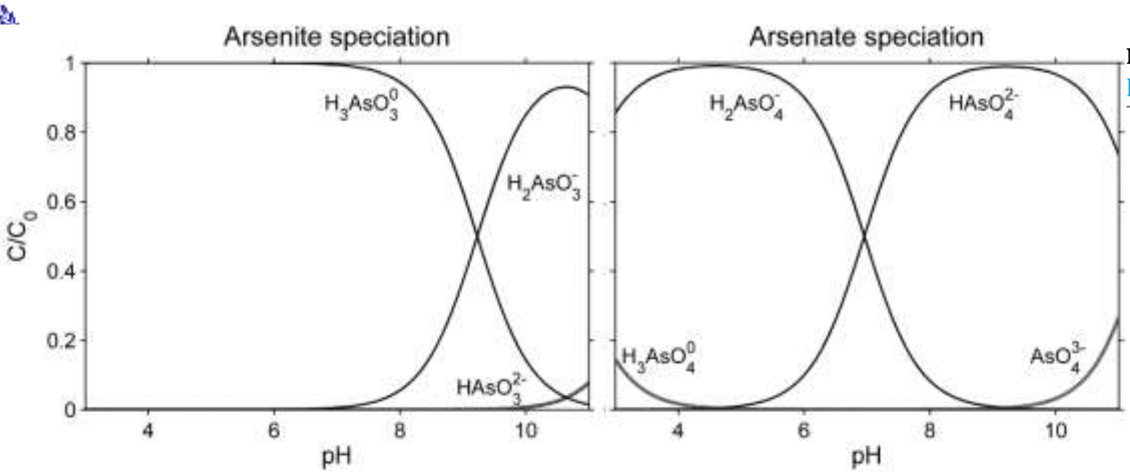
The primary exposure of humans to arsenic is through water, with the highest arsenic concentrations found in groundwater. Areas with high levels of arsenic in groundwater include Argentina, Bangladesh, Chile, China, Hungary, India, Mexico, Romania, Taiwan, USA, and Vietnam (Smedley and Kinniburgh, 2002), with the South East Asian deltas being the most severely arsenic affected regions worldwide (Smedley, 2007). High concentrations of arsenic in groundwater are considered to be one of the world's most challenging inorganic drinking water contaminants (Smedley andKinniburgh,2002)and understanding the mobility of arsenic in groundwater aquifers is of high importance.

Phosphorus plays a central role in biological systems, in soils and aquatic sediments. It is an important element in plant nutrition and is often the limiting growth factor and is therefore added to agricultural fields as a fertilizer on a large scale.In combination with soil erosion and there lease of waste waters enriched in phosphorus this has lead to an increase in the phosphate concentration in freshwater aquatic environments as well as in the oceans (Filippelli, 2008). The result has been the eutrophication of freshwaters and the coastal marine environment with a subsequent degradation of water quality and toxic algae blooms. The disturbance of the terrestrial phosphorous cycle by human activity (Filippelli, 2008) requires a proper understanding of the chemical processes regulating the aqueous phosphate concentration in order to predict the effects of our actions and measures.

One of the mechanisms controlling the bioavailability and mobility of both arsenic and phosphorus is their uptake and release by soils and sediments. The uptake of arsenic and phosphate by minerals may proceed via adsorption (the coordination of the ion to the mineral surface), co-precipitation (the ion substitutes for lattice ions and is thus incorporated into the mineral structure) and precipitation of arsenates or phosphates (Elzinga et al., 2006). Often arsenic and phosphate are present in concentrations so low that precipitation of arsenates or phosphates does not occur.

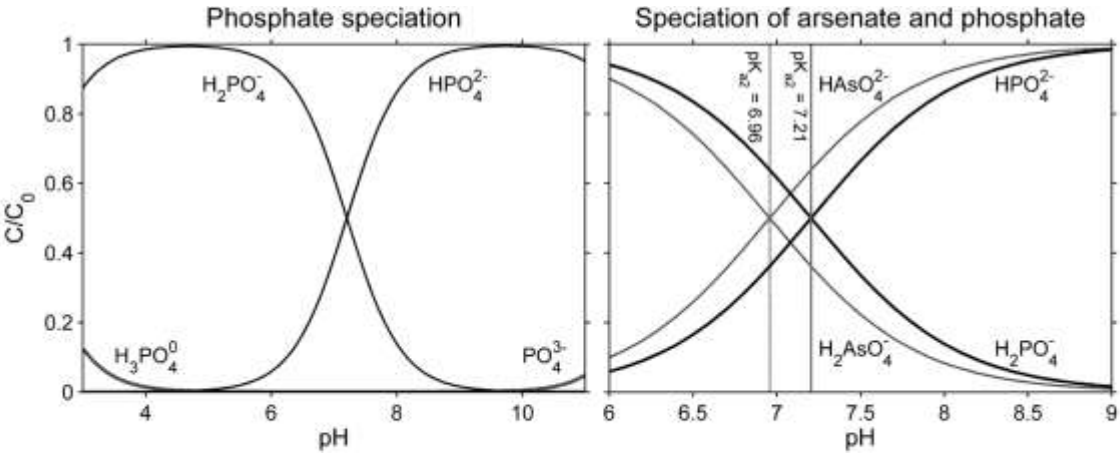
Geochemistry of arsenic

Arsenic is found in four oxidation states, -3(arsine), 0 (arsenic)+3 (arsenite) and +5 (arsenate), and in the aquatic environment both the organic and in organic form is found. Several bacterial species and fungi can methylate in organic arsenic by an initial reduction to arsenite and the addition of methyl groups. However, methylated arsenic is commonly below 1 µg/l and the pre dominant form of arsenic in natural aquatic systems is inorganic(Viraraghavanetal.,1999). The two dominant oxidation states for inorganic arsenic are the trivalent arsenite at moderately and strongly reduced conditions and the pentavalent arsenate in the aerobic environment. Cherry et al. (1979) suggested that the speciation of arsenic could be used to determine the dominant redox conditions if periods of years or longer are available for equilibration. However, more recent studies do not support this, as the redox kinetics are slow and the redox potential tends to be controlled by the major elements (O, C, N, S and Fe) (Welch et al., 1988; Masscheleyn et al., 1991; Smedley and Kinniburgh, 2002; Postma et al., 2007). Due to the slow redox kinetics, both arsenate and arsenite are found in most arsenic bearing ground waters.



Phosphorous (P) belongs to group 5A in the periodic table and is classified as a non-metal. Phosphorous is essential to all biological activity in its dissolved form and phosphate minerals are a major structural component in vertebrates, with the phosphate mineral apatite being the main mineral in the human body (Kohn et al., 2002).

Phosphorous is widespread throughout the Earth's crust and found in many different geological environments; in igneous, metamorphic, and sedimentary rocks, as well as in low temperature sedimentary environments and as a precipitate from hydrothermal solutions. The most abundant phosphate minerals are in the apatite group, with fluorapatite and hydroxylapatite being the most common in nature. The apatite minerals all consist of phosphate (PO_4) coordinated to Ca in a hexagonal structure, but with different elements at the corners of the hexagonal cell depending on the specific apatite mineral, e.g. F in fluorapatite ($Ca_5(PO_4)_3F$), OH in hydroxylapatite ($Ca_5(PO_4)_3(OH)$) and Cl in chlorapatite ($Ca_5(PO_4)_3Cl$) (Kohn et al., 2002).



Calcite

Calcite ($CaCO_3$) is one of the most common minerals in the environment. It is predominant in the sedimentary environment and is primarily formed at relatively shallow depth and forms rocks in both shallow and deep water settings. It is an important mineral in the aquatic environment due to its important role in regulating the pH and alkalinity (Morse and Mackenzie, 1990). Calcite is used for a wide range of industrial purposes, e.g.

paper production, building materials, agriculture, paints, plastics, ceramics, glasses, pharmaceuticals and cosmetics (Baltrusaitis and Grassian, 2009; Villegas-Jiménez et al., 2009).

Three different polymorphs of $CaCO_3$ are found in sediments and organisms: calcite, aragonite and vaterite. As they are polymorphs, they have differentcrystal structures and symmetry: calcite is trigonal-rhombohedral, aragonite is orthorhombic and vaterite is hexagonal. Calcite is the most abundant and ubiquitous form of the $CaCO_3$ polymorphs. It is the most stable polymorph at most temperatures and pressures encountered in the environment and aragonite and vaterite will therefore, over time, transform to calcite. Aragonite is also an abundant mineral, though not as common as calcite, whereas vaterite is rarely found in natural systems ,and always under conditions where it is meta stable with respect to calcite and aragonite (Morse and Mackenzie, 1990).

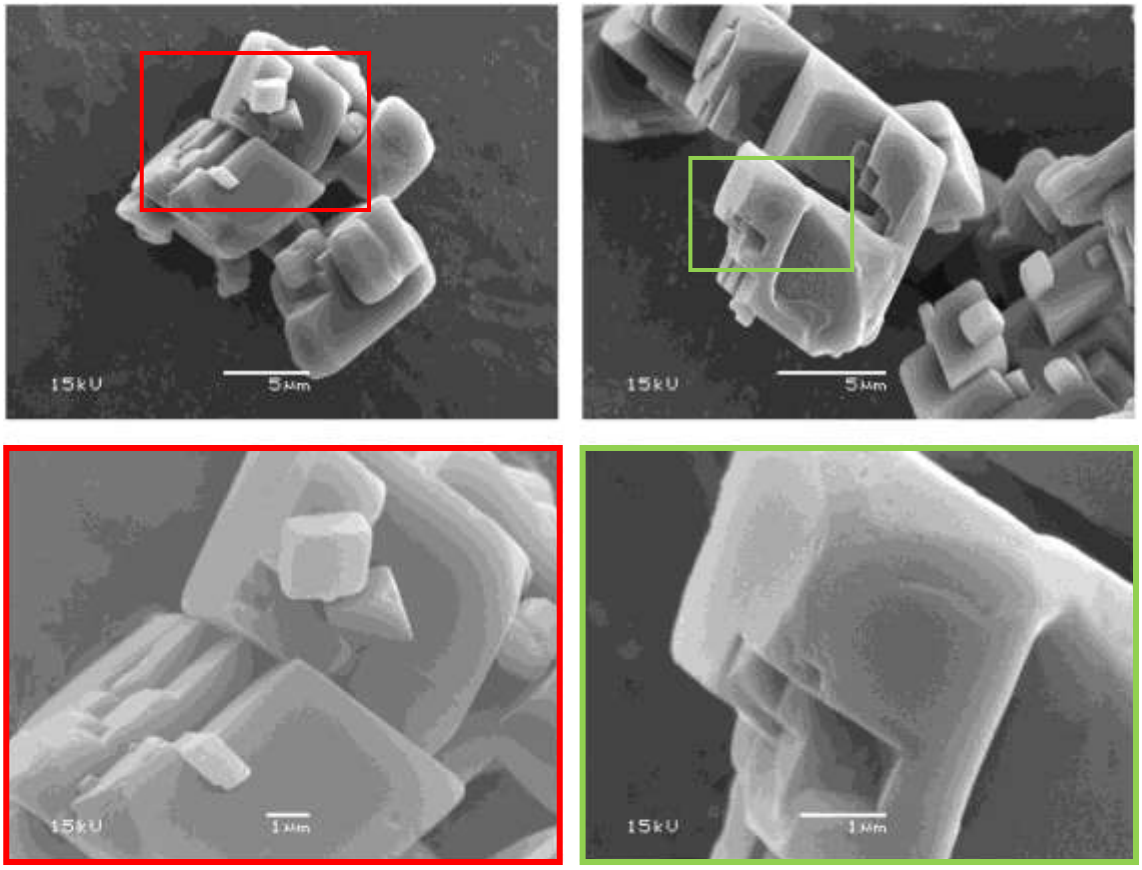
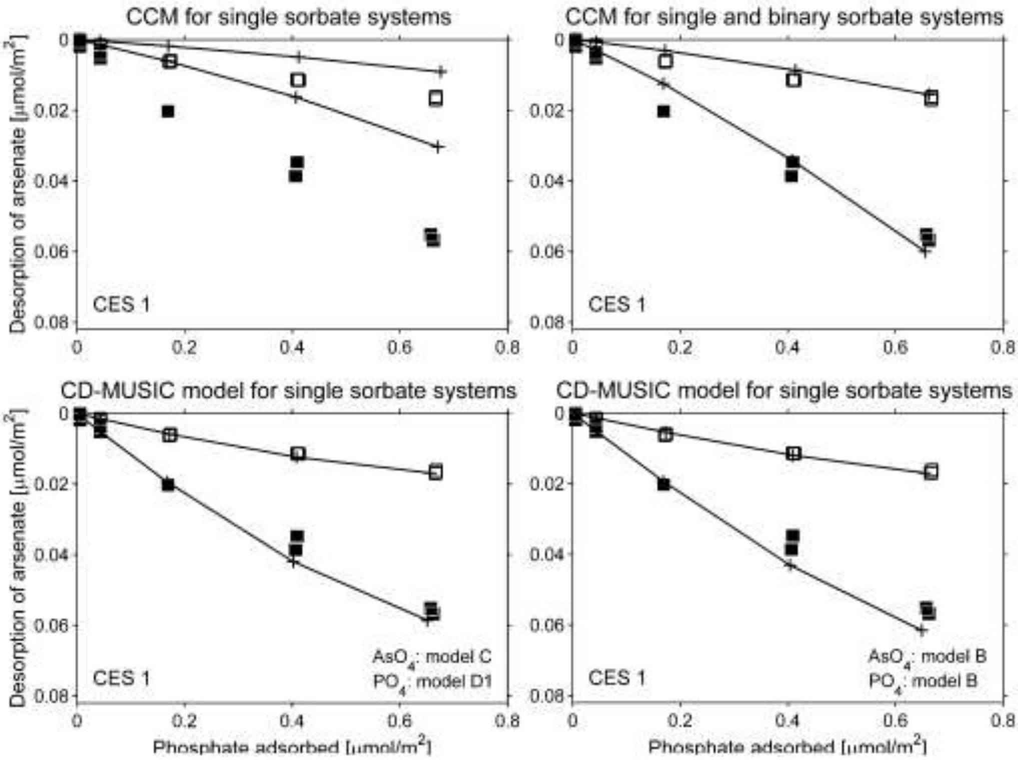


Fig. Scanning Electron Microscopy (SEM) of the calcite

Modelling competitive adsorption

The literature on competitive adsorption onto calcite is limited and modelling studies of competitive adsorption onto calciteare even more sparse . Cowanetal. (1990) successfully modelled the competition between phosphate and selenite onto calcite with the ion exchange model. However, the model for phosphate was based on data from the binary sorbate system and was not verified for the single sorbate system.



I. Conclusions

Arsenite does not adsorb significantly onto calcite within 24 h. In contrast, the extent of uptake of both arsenate and phosphate on the surface of calcite is high, fast and completed within 2-3 hours. Because the process is easily reversed by lowering the aqueous arsenate and phosphate concentration, the process is characterized as adsorption rather than surface precipitation.

The degree of phosphate adsorption is higher than for arsenate and the sorption isotherms for phosphate are more strongly curved. The adsorption of both arsenate and phosphate onto calcite depends on solution composition in the same way: adsorption increases as the activity of CO_3^{2-} decreases (at constant pH) and as pH increases (at constant CO_3activity). Changes in ionic strength also influence the degree of adsorption. For phosphate this can generally be accounted for by the concomitant changes in the activity of aqueous phosphate species, whereas there is an additional (electrostatic) effect on arsenate.

The adsorption of arsenate onto calcite is strongly reduced by the presence of phosphate, whereas phosphate adsorption is only slightly reduced by arsenate addition. The observed reduction is independent of the sequence of addition,even when the ions are introduced into the system three hours apart. The reduction in sorption of both arsenate and phosphate is most likely due to competition for the same sorption sites, considering the similarity in sorption edges, pKa's and geometry of the two anions.

The experimental results of the single sorbate systems were successfully modelled using either the constant capacitance model (CCM) or the CD-MUSIC model. The changes in adsorption as a function of the solution composition are well captured by both models. However, introducing two types of sorption sites was necessary in the CCM for the model to reproduce the convex shape of the experimental sorption isotherms, with the distribution between the two types of sites being different for the model of arsenate and phosphate. The competitive effect of arsenate and phosphate could also be modelled satisfactorily with the CD-MUSIC model. In contrast, the CCM under-predicted the competition based on individually fitted models. This shows the importance of competitive studies in validating multi-component adsorption models.

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