Can we Quantify Trace Metals in an Adsorbent using Proton Induced   X-Ray Emission (PIXE)?

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Granular activated carbon (GAC) has been extensively used to remove trace metals from drinking water. We have used PIXE to quantify trace metals, in particular, arsenic in GAC. The results were compared with atomic absorption spectrophotometry (AAS). Some differences have been observed between these two measurements mainly due to the inhomogeneous structure of GAC.

1.   Introduction

Granular activated carbon (GAC) has been extensively used to remove trace metals from drinking water for a number of years because it is a highly cost effective treatment on a small scale. To date, there has been no published literature on non-destructive methods to quantify the actual amount of trace metals adsorbed by the GAC directly. Proton induced X-ray emission (PIXE) is an ideal analytical tool, which is suitable for simultaneously quantifying trace elements with sensitivity of at least parts per million (ppm).

Adsorption process is usually modelled by two types of isotherms, Freundlich and Langmuir isotherms. The Freundlich isotherm [1] is expressed as:

$$Q_e = K_f C_e^{1/n}$$

where, Q_e is the adsorption density (mg of adsorbate per g of adsorbent), C_e is the concentration of adsorbate in solution (mg/L), K_f and n are the empirical constants dependent on several environmental factors and n >1 [2].

The Langmuir isotherm [3] is often expressed as:

$$Q_e = \frac{X_m K C_e}{1 + K C_e}$$

where, Q_e is the adsorption density at the equilibrium solute concentration C_e (mg of adsorbate per g of adsorbent), C_e is the concentration of adsorbate in solution (mg/L), X_m is the maximum adsorption capacity corresponding to complete monolayer coverage (mg of solute adsorbed per g of adsorbent), K is the Langmuir constant related to energy of adsorption (l of adsorbent per mg of adsorbate)

In this work, GAC has been used as an adsorbent to remove arsenic from drinking water and the amount of arsenic adsorbed by GAC is being measured by means of PIXE. Various adsorption experiments were conducted to evaluate different aspects of adsorption mechanisms in GAC. The results were compared with the Atomic Absorption Spectroscopy (AAS) measurements.

2.   Experimental

We have carried out equilibrium and kinetic adsorption experiments to evaluate different aspects of adsorption mechanisms in GAC. In the equilibrium experiments, different amounts of GAC (between 0.1 and 10.0 g/l) was added to a solution with initial arsenic concentration

of 4.9 mg/*l* and then mixed on a platform mixer for a period of 72 hours. In the kinetic experiments, 5g/*l* of GAC was added to a solution with initial arsenic concentration of 5.3 mg/*l* and then agitated for between 5 minutes to 9 hours. After these treatments, the GAC was isolated from the solution and As concentration in GAC was measured directly using PIXE. PIXE measurements on these samples were carried out at William R. Wiley Environmental Molecular Sciences Laboratory (EMSL) accelerator facility. The details of the accelerator facility and the end stations are described elsewhere [4]. The proton beam with energy of 2.5 MeV and 1.0 mm in diameter was used for our PIXE measurements. Theoretical simulations of PIXE experimental data were performed to determine elemental composition using the computer program GUPIX [5]. These results were compared to the AAS measurements.

3. Results and Discussion

Figure 1 shows the results of equilibrium experiments. The concentration of the remaining As in the treated solution was measured using AAS. The amount of arsenic adsorbed by GAC was calculated by subtracting from the amount of arsenic present in the initial solution. Differences between these two measurements are clearly visible.
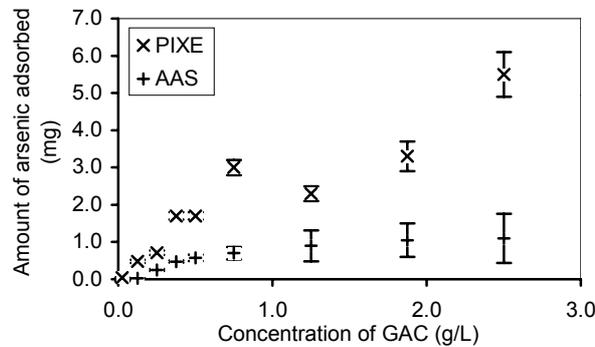

Fig.1. PIXE and AAS measurements of arsenic concentration in GAC after the equilibrium experiments.

PIXE and AAS data have been analysed using both the isotherms and the results are shown in Figure 2. Table 1 below summarises the constants associated with the isotherms.
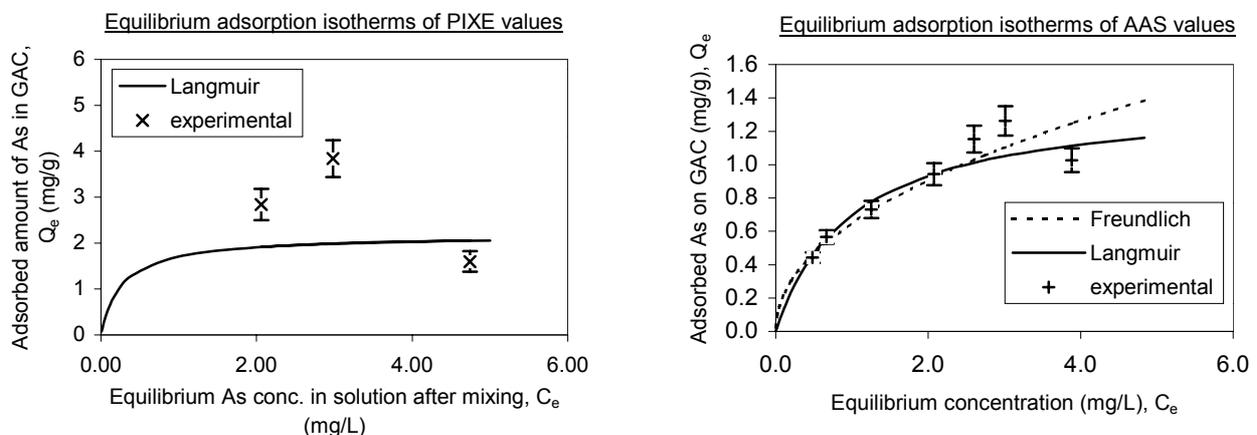

Fig. 2: Analysis of PIXE and AAS data using Langmuir and Freundlich isotherms.

Table 1: Constants associated with Langmuir and Freundlich isotherms.

	PIXE Data	AAS Data
Langmuir Constant X_m (Maximum adsorption capacity in mg/g of GAC)	2 ± 1	1.4 ± 0.5
Langmuir Constant k	4 ± 4	1.0 ± 0.5
Freundlich empirical constant K_f	6 ± 2	0.65 ± 0.01
Freundlich empirical constant n	-1.4 ± 0.8	0.5 ± 0.1

Figure 3 shows the results of the kinetic experiments. Significant differences are present between the two measurements. Again the PIXE values of arsenic concentration are higher than the AAS values. These differences are mainly due to the inhomogeneous structure of GAC, which includes the variable surface properties such as surface area and pore sizes in each particle. Micro-beam PIXE measurements carried out on a few granules of activated carbon clearly showed that different regions within each granule adsorb different amounts of arsenic.
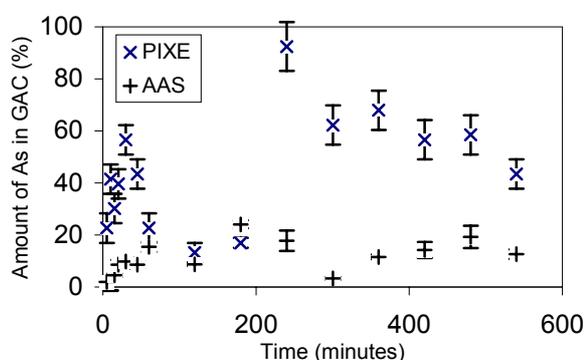

Fig. 3: PIXE and AAS measurements of arsenic concentration in GAC after the kinetic experiments.

The inhomogeneous nature of the target becomes more noticeable by the fact that there are "gaps" between the GAC grains being analysed by the beam. As a result, the area examined by the PIXE beam might not have been representative of the whole sample. Different sampling techniques need to be employed.

Acknowledgments

References
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