Sample Preparation Techniques in Trace Element Analysis of Adsorbents

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ABSTRACT

To date, the trace elemental analysis of solids with inhomogeneous internal structure has been limited particularly in the case of adsorbents. In this study, particle induced x-ray emission (PIXE) has been used to quantify arsenic in the adsorbent, activated carbon. Uncertainties resulting from the inhomogeneity of the sample were corrected using sample preparation methods and the results were compared against neutron activation analysis (NAA) and atomic absorption spectroscopy (AAS). The results indicate that sample preparation had limited success in resolving issues relating to the inhomogeneous internal structure of the solid.

Keywords: PIXE, sample preparation, activated carbon, adsorption, NAA, AAS

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1. INTRODUCTION

Inhomogeneous solids are frequently encountered in a wide range of sample types such as geological rocks, biological specimens and marine sediments. One other inhomogeneous solid commonly associated with water treatment analysis is adsorbents. Adsorbents are highly porous materials that use the process of adsorption to remove contaminants from wastewater. Contaminants such as trace metals are adsorbed to the surface of the pore walls, which are randomly distributed within an adsorbent. Determining the amount of trace metals adsorbed by adsorbents is vital to water utilities to gauge the effectiveness of particular types of adsorbents and also various treatment parameters. To date, bulk analysis techniques used to quantify the adsorbed metals in adsorbents have been restricted to wet chemical techniques and neutron activation analysis (NAA). Wet chemical techniques such as atomic absorption spectroscopy (AAS) require dissolution, decomposition or extraction when analysing solids, which is laborious and introduces the risk of contamination. NAA avoids virtually all this sample preparation but only offers the highest sensitivities with a very high neutron flux, achievable only in a nuclear reactor, and a large amount of sample [1]. A rapid, highly sensitive, non-destructive, quantitative, multi-elemental analytical method is best suited to investigate the issues associated with trace elements in solids. Particle induced x-ray emission (PIXE) is such an analytical tool and it is suitable for simultaneously quantifying trace elements with sensitivity of at least parts per million (ppm).

The inhomogeneously distributed pore walls that enable adsorbents to be highly effective in removing contaminants from water make the quantification of the elements attached to the pore walls highly complex. In PIXE analysis, significant errors can arise if there are multiple randomly oriented surfaces in the adsorbent. Uncertainties in the density play a major role in quantification of trace elements. These errors can be further magnified due to trace quantity of elements in the sample. Sample preparation has effectively been used in the past to attain homogeneous samples from inhomogeneous solids using a
variety of techniques including pellatising [2] and atmospheric aerosols [3] so that the errors could be minimized.

In this work, granular activated carbon (GAC) and powder activated carbon (PAC) were used as adsorbents to remove the trace metal arsenic from aqueous solutions. The amounts of arsenic removed were determined using PIXE, NAA and AAS. In the case of PIXE, two types of sample preparation procedures have been employed and the results are reported.

2. EXPERIMENTAL

The adsorbents, GAC and PAC were first exposed to an arsenic solution of known concentration for up to 9 hours. After this exposure, GAC and PAC samples were isolated from the solution and arsenic concentrations in the samples were measured using PIXE, NAA and AAS. Although the measurements using NAA and AAS did not require any special sample preparations, two different procedures were employed to prepare the samples for PIXE analysis.

In the first method, GAC and PAC were placed on carbon tapes that were mounted on sample holders. Although the GAC and PAC were tightly packed on the tapes, it was impossible to avoid small amount of voids in the samples. To further reduce the voids in the samples, in the second method, GAC (after grinding into a fine powder) and PAC were first mixed with polyvinyl alcohol to foam clay like texture. Then the fine powder was placed into small copper containers and pelletized using a hand held press (pressurized up to 400 psi). Before each operation, containers, press and all other parts were thoroughly cleaned with acetone, methanol and distilled water respectively to avoid cross contamination. After pelletising, these samples were air dried for up to 20 minutes and the dried pellets with the containers were directly mounted on the sample holders for the measurements.

The arsenic concentrations in GAC and PAC after the treatment were also measured directly using NAA. AAS was used to determine the amount of arsenic remaining in solution after the GAC and PAC were removed. The concentration of arsenic in GAC and PAC was determined from the difference between the initial amount of arsenic added to the solution before exposure ($C_0$) and the amount of remaining arsenic in solution after exposure ($C_t$).

3. RESULTS AND DISCUSSION

The GUPIX program was used to fit the experimental data [4]. The arsenic Kα line was used to determine the concentration of arsenic in the PIXE spectrum for each sample. These PIXE values were then compared to the results from NAA and AAS for PAC and GAC.
The arsenic concentration in the GAC samples is shown in Figure 1. Most techniques indicate that the amount of arsenic adsorbed by GAC increases as a function of mixing time. There is very close agreement between the NAA and AAS measurements but the PIXE values from samples prepared using both methods are much higher. Analysis of unmodified GAC using PIXE show that the results are not only highly variable but also produce much higher arsenic concentration values to what is given by both AAS and NAA. The shape of the curve from analysis done on pelletized GAC using PIXE is similar to the curves of AAS and NAA except for a region ranging from 100 minutes to 300 minutes. This region showed a steady increase in concentration from 100 minutes then a significant drop at 300 minutes. The anomaly in this region could be due to errors associated with experimental parameters during analysis of this particular batch samples. Excluding this region, the results from the GAC samples indicate that the inconsistent concentration values that result during PIXE analysis of inhomogeneous samples can be corrected for using pelletising as a sample preparation method prior to analysis.

The arsenic concentration results from the PAC samples varied much more than the GAC because their adsorption capacity was much lower thus more susceptible to slight inconsistencies in the adsorption experiments. This is evident from the significantly scattered results associated with AAS. However, NAA again provided consistent and expected results for arsenic concentration in PAC whilst the PIXE results resulted in low values for unmodified PAC and high concentrations for pelletized PAC. The shape of the curve from the pelletized PIXE values is very similar to that of the NAA. This shows that the difference in arsenic concentration in the NAA and pelletized PIXE samples is not due to sample inhomogeneity. The low values recorded for the unmodified PIXE samples can be due to small gaps in the sample that form in the sprinkling process.

The results show that pelletising GAC and PAC before PIXE analysis eliminates errors due to sample inhomogeneity. In addition, the measured concentrations appeared to be somewhat higher than those obtained using NAA, especially in the case of arsenic concentration below 200 ppm in PAC samples. This could be due to the PIXE detection limit along with errors associated with some other experimental parameters including the organic binder material used to make the pellets, slight density changes due to trapped gases in pellets and accurate measurement of charge during data collection [5, 6]. Further studies are required to understand the role associated with some of these parameters.

4. CONCLUSION

It was shown that sample preparation was successful in dealing with uncertainties that resulted in trace arsenic element quantification from sample inhomogeneity in PAC and GAC adsorbents. It was also discovered that the concentration values measured using PIXE, AAS and NAA significantly deviate from each other when the arsenic concentration is less than 200 ppm in PAC samples.

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