4. CONCLUSIONS

On-line analysis techniques allowing metal ion speciation have been investigated in this work. Interaction of metal ions with aquatic colloids and the size ranges of the colloids were investigated with asymmetric flow field-flow fractionation (AF^4) on-line with inductively couple plasma-mass spectrometry (ICP-MS) system. The colloid formation of the metals released from a contaminated soil in natural water was found by the AF^4-ICP-MS. The results showed that the leached metals from the coal-mining disposal soil could be associated with humic acid colloids, frequently found in surface water. Depending on the concentration ratio of metal ions to humic acid, pH, small colloidal or large particulate species are formed. It is assumed that larger aggregates are composed of inorganic FeOOH and/or AlOOH particles coagulated with humic acid. The sizes of the particles strongly influence the mobility of the metal ion containing colloids to the environment. It means those metal colloids could be either precipitated or transported to the environment depending on their size. The smaller the colloid size, the higher might be their mobility.

Systems with anodic stripping voltammetry (ASV) combined with flow injection analysis (FIA) and sequential injection analysis (SIA) for the determination of dissolved metal ions were developed. The performance of the FIA-ASV was tested to determine some metal ions in model samples, which contain less complicated matrices, namely drinking water and digested wastewater samples. The experience from developing the FIA-ASV system was adopted to assemble two SIA-ASV systems.

At the beginning of the development of the FIA- and SIA-ASV systems, on-line preparation of mercury film electrode (MFE), used as the working electrode in ASV, was studied (see section 3.1). The preplated MFE was successfully prepared on-line. It showed good performance when used with the developed FBA systems. Using the preplated MFE is safer for the operator than working with mercury drop electrodes, which may generate toxic mercuric vapor. The mercury waste containing solution from on-line preparing the MFE could be kept separately and are easy to be further managed.

A single line FIA-ASV system was assembled for the simultaneous determination of some metal ions (Zn(II), Cd(II), Pb(II) and Cu(II)) (see section 3.2). Effects of acetate buffer concentration as an electrolyte and a carrier solution, sample volume, reagent flow rate and mixing coil length were studied. The selected parameters provided satisfactory performance of the method. The developed FIA-ASV system was applied to determine some metal ions (Zn(II), Cd(II), Pb(II) and Cu(II)) in model samples. In the case of wastewater analysis, pretreatment such as UV digestion was needed to remove organic matter that interfere the analysis. A homemade UV digester was taken to remove the organic matter in the wastewater samples.

A cost-effective SIA system was assembled using a modified autotitrator as the liquid delivery unit. A controlled-software, based on LabVIEW®, was created for this purpose. The proposed on-line standard addition SIA-ASV system was successfully used for simultaneously determination of some metal ions (Cd(II), Pb(II) and Cu(II)) with good precision, low detection limits and satisfactory recoveries. The on-line single solution standard addition method applied to calibrate the SIA-ASV system was very practical and easy to operate.