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Simultaneous determination of silver and other heavy metals in aquatic environment receiving wastewater from industrial area, applying an enrichment method

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Abstract   In the present study, silver (Ag), cadmium (Cd), nickel (Ni), cobalt (Co) and lead (Pb) were simultaneously determined in water samples of fresh water canal receiving untreated effluents from an industrial area, of Sindh Pakistan. The analytes in the water sample were determined by CPE using ammonium pyrrolidinedithiocarbamate (APDC) as a complexing agent and then entrapped in non-ionic surfactant, octylphenoxypolyethoxyethanol (Triton X-114). The surfactant rich phase was diluted with acidic ethanol prior to analysis by flame atomic absorption spectrometry. The variables affecting the complexation and extraction steps such as pH of sample solution, concentration of oxine and Triton X-114, equilibration temperature and time period for shaking were investigated in detail. The validation of the procedure was carried out by analysis of a certified reference sample of water (CRM1634e). Reliability of the proposed method was also checked by the standard addition method in a real sample at three concentration levels of all metals. Under the optimum conditions, the preconcentration of 10 mL sample solutions, allowed preconcentration

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factor of 20-fold. The lower limit of detection obtained for Ag, Cd, Ni, Co and Pb was 0.42, 0.48, 0.92, 0.62, and 1.42 $\mu g\,L^{-1}$, respectively. The proposed procedure was successfully applied to waste and fresh water samples for simultaneous determination of different metals. The concentration of Ag, Cd, Ni, Co and Pb has shown a decreased trend from 46.5–6.96, 23.0–8.92, 30.2–12.8, 14.2–4.45 and 15.3–5.32 $\mu g\,L^{-1}$, respectively from initial entrance of waste water along the downstream of canal.

1. Introduction

The contamination of surface water with high level of toxic metals is a matter of serious concern today (Tuzen and Soylak, 2006; Turkmen et al., 2008; Anazawa et al., 2004). Silver (Ag) is both vital and toxic for many biological systems, and its content in environmental samples is increased with the increasing use of its compounds as well as silver-containing products in industry and medicine (Yang and Rose, 2005). In many countries Ag impregnated filters are used for water purification and concentration of up to 50–200 mg L^{-1} of Ag (depending on country) is permitted to control antimicrobial activity with no risk to human health (Tunceli and Turker, 2000). Ag can enter into the environment via industrial waters and might pose a potential risk as water pollutant (Shamsipur et al., 2002).

Cobalt (Co) is known to be an essential micronutrient for metabolic processes in both plants and animals (Sasmaz and Yaman, 2006). It is mainly found in rocks, soil, water, plants, and animals. The determination of trace level of Co in natural waters is very important because Co is important for living species and it is part of Vitamin B12 (Soylak et al., 1997). Exposures to high level of Co lead to serious public health problems and are responsible for several diseases in humans such as, in the lung, heart and skin (Soylak et al., 2001).

Nickel (Ni) is widely used in modern industry. Its overexposure in human beings can provoke significant effects including the lung, cardiovascular and kidney diseases (Zeiner et al., 2007; Ghaedi et al., 2005; Carletto et al., 2009). More attention has been focused on the toxicity of Ni because it can cause allergic reactions and its certain compounds may be carcinogenic (Hirano et al., 2001). Ni with other heavy metals enters in water bodies through natural process from dissolution of rocks and soils, biological cycles, atmospheric fallout, especially from industrial processes and waste disposal production of Ni–Cd batteries and pigments, electronic products, electrodepositing and as catalyst in hydrogenation reactions, which might increase the exposure of this element (Nielsen et al., 1999; Templeton, 1990).

Cadmium (Cd) is highly toxic to human health and damages organs such as the kidneys, liver and lungs (Nordberg et al., 1988). A prolonged intake of Cd leads to a disturbance in the calcium metabolism in biological systems, which induces cell injury and death. It also inhibits the action of zinc enzymes by substitution. Cd is also a teratogenic and carcinogenic agent (Barrera et al., 1997; EPA, 1993).

Lead (Pb) is a toxic metal and it is a widely distributed pollutant in environment. It is an accumulative toxic metal, which produces several diseases, such as hematological disorder, brain damage, anemia, and kidney disorder (Shah et al., 2010). Humans and animals are exposed to Pb from natural as well as anthropogenic sources, e.g. drinking water, soils, industrial emissions, car exhaust, contaminated food and beverages.

A variety of techniques including flame atomic absorption spectrometry (Detcheva and Grobecker, 2008), electrothermal atomic absorption spectrometry (Kiptoo et al., 2008), inductively coupled plasma optical emission spectrometry (Zhu and Alexandratos, 2007), inductively coupled plasma mass spectroscopy (Huang and Hu, 2008) and stripping voltammetry (Zejli et al., 2007) have been extensively used for the determination of heavy metals in different environmental and biological samples. Direct determination of trace amounts of metal ions in samples by FAAS is difficult because of low sensitivity especially of FAAS. Thus, preconcentration procedures are often required (Lee et al., 1997; Ghaedi et al., 2013a,b,c). The cloud point phenomenon has been used in the separation science for extraction, purification and preconcentration of organic and inorganic analytes. This technique is based on the behavior of nonionic surfactants in aqueous solution, which exhibit phase separation by an increase in temperature or by addition of a salting-out agent (da Silva et al., 2001; Quina and Hinze, 1999). Ligands such as dithizone (Manzoori and Karim-Nezhad, 2004, 2003; Manzoori and Bavili-Tabrizi, 2003), 1-(2-pyridylazo)-2-naphthol (PAN) (Cerrato Oliveros et al., 1998; Pinto et al., 1996), ammonium pyrrolidinedithiocarbamate (APDC) (Dadfarnia et al., 2007; Giokas et al., 2001), 1-nitroso-2-naphthol (Manzoori and Bavili-Tabrizi, 2003; Manzoori and Karim-Nezhad, 2003), and 2-amino-cyclopentene-1-dithiocarboxylic acid (ACDA) (Safavi et al., 2004) have been employed for cloud point extraction in several procedures for understudy metals. These ligands are widely employed due to several advantages obtained, such as capacity to form complexes with a large variety of metals and low solubility in water. APDC is a classical reagent used for complexing purposes in preconcentration procedures for metals (Giokas et al., 2005).

There is much concern about metal contamination in fresh water bodies of developing countries including Pakistan. The present work is underway to better quantify the addition untreated industrial waste water contains number of contaminant including toxic elements to fresh water bodies. For this purpose the simultaneous preconcentration method was developed and established for preconcentration of trace quantity of Ag, Cd, Ni, Co, and Pb in stream of canal receiving industrial waste water at different distances to evaluate the dilution factor of these toxicants. For the proposed CPE method, ammonium pyrrolidinedithiocarbamate (APDC) was used as a chelating agent and Triton X-114 as non-ionic extractant. The effect of different variables, concentration of complexing reagent, Triton X-114, pH, equilibrium time and temperature were investigated and discussed in detail. The accuracy of the CPE method was evaluated by certified reference material