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Determination of iron, cobalt and nickel ions from aqueous media using the alkali modified miswak

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Abstract This paper describes a simple, rapid, inexpensive method for the preparation of a new biosorbent based on the modification of miswak fibers by NaOH (AT-Miswak-F). The synthesized AT-Miswak-F sorbent was utilized as an efficient sorbent for the extraction and preconcentration of iron group metal ions from various water samples. In this study, it was found that Fe(III), Co(II) and Ni(II) ions were completely extracted (100%) at pH range of 3–7 and flow rate of 0.3–2.0 mL min^{-1}. Also, the sorption capacity of AT-Miswak-F for Fe(III), Co(II) and Ni(II) are 0.54, 0.24 and 0.15 mmol g^{-1}, respectively. Equilibrium was best described by Freundlich isotherm model ($R^2 = 0.793$) and the initial rate constants were 0.077, 0.054 and 0.035 mmol g^{-1} min^{-1}, respectively. Under the optimized conditions, the method exhibited a detection limit of 1.4, 2.8 and 2.1 ng mL^{-1} for Fe(III), Co(II) and Ni(II) ions in water samples with relative standard deviations of 2.6% ($n = 4$). The method was successfully applied for the determination of Fe(III), Co(II) and Ni(II) ions in sea, ground and contaminated water samples.

1. Introduction

Iron has an essential role in life and a range of biochemical reactions in the living organisms. Iron–proteins are found in all living organisms, ranging from the evolutionarily primitive archaea to humans (Kassem and Amin, 2013; Pourjavid et al., 2014). Cobalt is also beneficial for humans since it is a metallo-cofactor in vitamin B12 (cobalamin); which contributes to the prevention of pernicious anemia and production of red blood cells and has a key role in the normal functioning of the brain and nervous system (Wen et al., 2013; Naushad et al., 2015a). Nickel is used in many industries such as stainless steel, nickel cast irons, alnico magnets, coinage, rechargeable batteries, electric guitar strings, and plating and as a green tint in glass (Gómez-Nieto et al., 2013).

Pollution from chemicals products is a real threat to the aquatic environment, air, and soil (El Haddad et al., 2012). Heavy metals are unpleasantly affecting our ecosystem due to their toxicological and physiological effects in environment (Naushad and AL-Othman, 2015). These metals, if present beyond certain concentration can be a serious health hazard which can lead to many disorders in normal functioning of human beings and animals (AL-Othman et al., 2012). Determi-

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nation of Fe, Co and Ni ions in water samples is to some extent problematic because of the high concentration of interfering matrix components. Preconcentration and separation procedures have been proposed to overcome this problem (Naushad et al., 2014; Awual et al., 2015; Naushad et al., 2015b). Methods employing biosorbents are recommended for the preconcentration and separation studies due to their simplicity and environmentally friendliness (He and Chen, 2014). Moreover, they offer improvements in the sensitivity and selectivity of spectrophotometric methods for the determination of many metal ions (Oguz and Ersoy, 2014). The root of *salvadora persica* tree (miswak) is used as a natural toothbrush (Aboul-Enein, 2014; Naeini et al., 2014) since it contains fluoride salts, detergents, antiseptics, and enzyme inhibitors (Alili et al., 2014). In previous studies, we used the miswak for the extraction of some organic dyes (Moawed and Abulkibash, 2012; Moawed, 2013). Though miswak is an excellent sorbent, the leaching of some of its components hinders its application. This problem necessitates the preparation of a chemically stable miswak for extraction purposes. To improve their properties, biosorbents were modified with different reagents including KOH, $ZnCl_2$ and/or C_6H_{12} (AL-Othman et al., 2012; Alshehri et al., 2014; Nadeem et al., 2014).

This paper describes a simple, rapid, inexpensive procedure with available versatile techniques for the preparation of a new biosorbent by the treatment of miswak fibers with an alkali (NaOH) to eliminate the problem of leached compounds. The AT-Miswak-F was characterized by IR and UV/Vis spectroscopy, SEM and elemental analysis. Parameters controlling the sorption of Fe(III), Co(II), and Ni(II) ions onto AT-Miswak-F, including pH, initial concentrations, shaking time and solution temperature were optimized.

2. Experimental

2.1. Instruments

Iron, cobalt and nickel ions were determined using a Shimadzu UV-1800 spectrophotometer (Shimadzu Corporation, Japan). A glass mini column 10 cm long and 1.0 cm in diameter was used for dynamic procedure. pH measurements were carried out by a Jenway pH meter model 3510, (U.K). Conductivity was performed using a Conductivity Meter (Jenway, model 4071, U.K).

2.2. Reagents and materials

Stock solutions of iron(III), cobalt(II) and nickel(II) (1 mg mL^{-1}) were prepared by dissolving appropriate amounts of iron(III) sulfate, cobalt(II) nitrate and nickel(II) nitrate salts (Fluka) in distilled water containing 1 mL of concentrated HNO_3 (Adwic, Egypt). *Salvadora persica* sticks (Miswak) were obtained from a plantation in El-Khtrichia, El-Qtif, Saudi Arabia.

2.3. General procedures

Alkali-treated miswak fibers (AT-Miswak-F) were prepared by blending miswak sticks (Miswak-F) in a food-processing blender, and then Miswak-F powder was soaked in 1 mol L^{-1} solution of NaOH for 24 h. AT-Miswak-F was filtered off then washed with distilled water, dried at 100 °C and sieved (particle size > 250 μm).

A portion of 0.05 g of the AT-Miswak-F was agitated with 25 mL solution of the tested metal ions for 60 min at 25 °C. The solutions were filtrated and the remaining Fe(III), Co(II) and Ni(II) concentrations was measured spectrophotometrically (Marczenko, 1986).

A 25 mL of the tested metal solutions (1 μg mL^{-1}) were passed through the AT-Miswak-F–containing columns at a flow rate of 1 mL min^{-1}. Metal ions were eluted from the AT-Miswak-F columns by 1 mol L^{-1} HCl. The eluates of metal ions were determined spectrophotometrically.

The tests of addition/recovery of different amounts of iron were performed for the underground water of Dammam city. A 0.1 g portion of the AT-Miswak-F was mixed with 25 mL of water sample which spiked with 20–125 μg of iron(III) then the batch procedure was applied.

To estimate the accuracy of the presented procedure for determination of iron in water; underground water of Nestle SA (Springer Water Factory Co Ltd), sea water of Arabian Gulf in Dammam city have been investigated using batch technique. Collection and determination of iron (III), cobalt (II) and nickel (II) ions in industrial wastewater of from the cooling pond of the casting iron company in Dammam city (spiked with 20 μg of metal ions) using dynamic technique has been investigated.

Density of AT-Miswak-F measurement was carried out in a 25 mL density bottle (pycnometer). The AT-Miswak-F was added to the density bottle with gentle tapping to ensure the settlement of the particles to the bottom; water was then added to the pycnometer in a way to fill all air spaces with water. Chemical composition of AT-Miswak-F, pH_{ZPC}, iodine number, density, electrical conductivity, acidic and basic sites were estimated according to procedure described elsewhere (Ververis et al., 2007; Moawed, 2013; Moawed et al., 2014).

3. Results and discussion

3.1. Characteristics of AT-Miswak-F

The densities of Miswak-F and AT-Miswak-F are 0.52 and 0.37 g cm^{-3}, respectively (Table 1). AT-Miswak-F (miswak after treatment by NaOH solution) is less dense than the normal one. This is due to hydrolysis of plant pigments, lipids and mineral salts and these fractions were leached out from the Miswak-F. Also, the hydrolysis process is leading to the increase in spaces, channels, and pores.

Table 1 Chemical and physical properties of miswak fibers and alkali treated miswak fibers.

Property	Miswak-F	AT-Miswak-F
Color	Yellow	Brown
Water solubility (g L^{-1})	3.27	0.56
Electrical conductivity (mS cm^{-1})	1.74	0.19
Bulk density (g cm^{-3})	0.52	0.37
pH_{ZPC}	5.20	4.62
Iodine number (mmol/g)	3.10	5.15