Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 153 (2016) 637–644

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Synthesis and application of ion-imprinted polymer for extraction and pre-concentration of iron ions in environmental water and food samples

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ARTICLE INFO

Article history:
Received 11 April 2015
Received in revised form 9 August 2015
Accepted 27 September 2015
Available online 9 October 2015

Keywords:
Ion imprinted polymer
Fe(III)
Pre-concentration
Food samples

ABSTRACT

In this work, a novel Fe(III) ion imprinted polymer as a sorbent for extraction of iron ions from different samples was synthesized. Precipitation of thermal copolymerization was used for preparation of polymeric sorbent. In this technique, methacrylic acid, ethylene glycoldimethacrylate, 2,2′-azobisisobutyronitrile and $(DHBPT)_2$ {$(DHBPT)_2$ = 3,6-bis (3,5-dimethyl-1-H-pyrzol-1-yl)-1,2-dihydro-1,2,4,5-tetrazine)} were used as monomer, cross-linker, initiator and ligand, respectively, in the presence of Fe(III) ions and ethanol as a porogenic solvent. Moreover, control polymer (NIP) particles were similarly prepared without the Fe(III) ions. XRD, FT-IR, SEM and nitrogen adsorption–desorption techniques have been used to characterization of these prepared polymeric samples. Iron ion imprinted polymer particles, abbreviated as Fe(III)–IIP, were leached with 50 mL of HCl (50% (v/v)). Absorption capacity for ion imprinted polymer was calculated about 40.41 $mg \cdot g^{-1}$. Per-concentration of iron ion was investigated as a function of pH, weight of IIP, adsorption and desorption times, and volumes of sample. FAAS technique was used to determination of Fe(III) ion in the foods and waters samples.

1. Introduction

Iron is an essential trace element of great importance for humans, animals and plants. Iron is a vital element in most biological systems like photosynthetic and respiratory electron transport, nitrate reduction, chlorophyll synthesis and detoxification of reactive oxygen species in plants and plays a key role in the transport of oxygen in the body. Most iron-containing proteins contain ferric ions, at least transiently. Well studied examples include iron–sulfur clusters, oxyhemoglobin, ferritin, and the cytochromes. Excess amounts of iron can be toxic. Oxidation ability of iron is a leading cause of poisoning in human body. Gulp of large amounts of iron salt causes vomiting and intestinal bleeding [1–7]. High iron concentration within water pipelines promotes undesirable bacterial growth (iron bacteria), resulting in the deposition of a slimy coating on the pipelines [8]. For these reasons, separation of iron ions is important and separation techniques for metal ions have been developed in recent years.

Imprinting polymer is used as a technique for preparing polymers that can be remarkably detected in different molecules in the presence of other species with high selectivity. Molecular imprinted polymers (MIPs) have a molecular "memory" that can provide selectivity for molecules [9].

Ion imprinted polymers (IIPs) are similar to molecular imprinted polymers (MIPs), But in IIPs after the imprinting process, the metal ions are detected [9–12]. Easy preparation and high selectivity of IIPs have developed using of the ion imprinted technology. IIPs are widely used as a selective absorbent for extraction of metal ions. Ions can put on the sites that created ion imprinted polymer [13].

Various methods employed using a solid absorbent for the extraction of ion in solution such as ion exchange precipitation and co-precipitation solvent extraction chemical and biosorption cloud-point extraction, solid phase extraction and on-line flow injection. In these methods, pre-concentration of ions carried out on a sorbent as solid phase.

Chang et al. reported a remarkable adsorptive performance for Fe(III) adsorption with Fe(III)-imprinted amino-functionalized silica gel that the maximum adsorption capacity of the ion-imprinted polymer obtained 25.21 $mg \cdot g^{-1}$ [14]. A Fe(III)–IIP prepared by Muharrem Karabork et al. that methacrylamidoantipyrine (MAAP) and ethyleneglycol dimethacrylate (EGDMA) used as the functional metal complexing monomer and crosslinking monomer, respectively. The adsorption capacity reported 29.32 $mg \cdot g^{-1}$ [3].

Singh and Misra reported a Fe(III)–IIP with adsorption capacity about 62.4 $mg \cdot g^{-1}$ that synthesized from acrylic acid (functional monomer) in cyclohexanol and copolymerization with styrene (monomer) and divinylbenzene (cross-linked) in the presence of 2,2′-azobisisobutyronitrile as initiator [15,16].

In this paper, pre-concentration of iron ions from aqueous solution has been studied over highly porous and novel nanostructure Fe(III)–IIP that was constructed using methacrylic acid (functional monomer, MMA),

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http://dx.doi.org/10.1016/j.saa.2015.09.029
1386-1425/

ethyleneglycoldimethacrylate (cross-linking monomer, EGDMA) and 1,6-bis(3,5-dimethyl-1H-pyrazol-1-yl)-1,2-dihydro-1,2,4,5-tetrazine (ligand) in the presence of 2,2′-azobisisobutyronitrile (initiator, AIBN) and acetonitrile that synthesized by the thermal copolymerization, in view of the effect of several parameters such as pH, adsorption and desorption time, type, concentration and volume of eluent, the weight of the polymer material, aqueous phase and desorption volumes on pre-concentration of Fe(III) from aqueous media at ambient temperature. Application of flame atomic absorption spectroscopy has been developed to detect iron ions which was then absorbed on IIP in various food and environmental samples. In this work, FAAS as main technique is used for determination of iron ions. The characterization of the synthesized material was confirmed by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), X-ray diffraction (XRD) and BET-N_2 sorption method.

In the past half-century, flame atomic absorption spectroscopy (FAAS) engaged as a common and operative analytical technique for detection and quantification of metal ions that usually determined the metal ion concentration at the ppm ($mg \cdot L^{-1}$) level, showing some advantages such as selectivity and reproducibility, considering the enormous range of atomic absorption spectrometers available on the market. However, FAAS techniques are limited by less sensitivity and depending on the level of analyte to be determined [17,18].

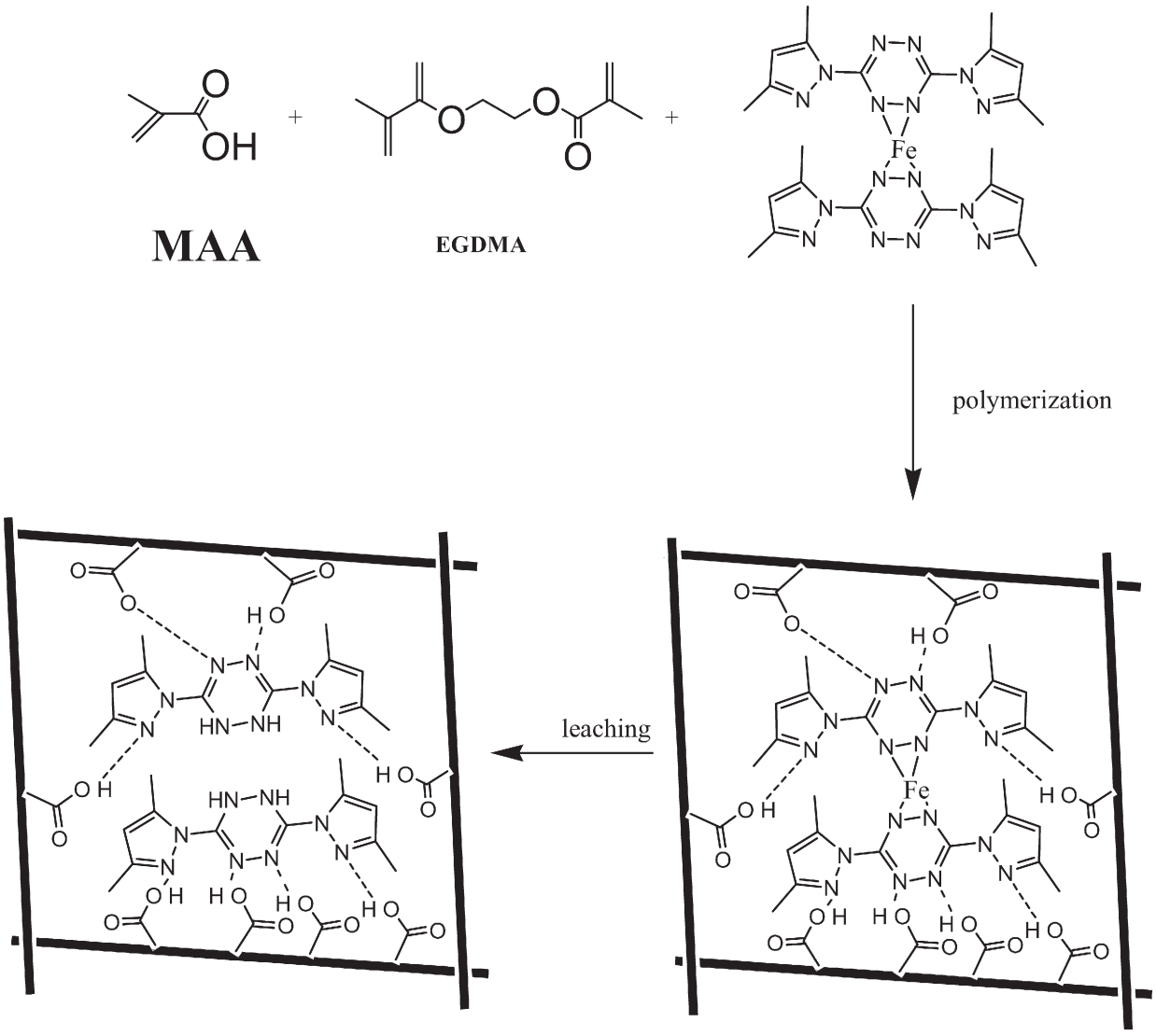
2. Experimental

2.1. Materials

Ethyleneglycoldimethacrylate (EGDMA), 2,2′-azobisisobutyronitrile (AIBN), Methacrylic acid (MAA), ethanol and $Fe(NO_3)_3 \cdot 9H_2O$ and nitrate or chloride salts of other cations were purchased from Merck chemical company and used as received. 3,6-bis(3,5-dimethyl-1H-pyrzol-1-yl)-1,2-dihydro-1,2,4,5-tetrazine) used as received. N,N′-*o*-phenylene bis (salicylideneimine) was synthesized by ultrapure water, that was prepared using a Milli-Q system from Millipore (Bedford, MA, USA) and used for the preparation of metal solutions.

2.2. Apparatus

An Analytik Jena model novAA400 flame atomic absorption spectrometer employed to determination of Fe(III) ions and other metallic cations from solutions. In order to pH measurement, a 780 digital pH Meter (Metrohm), equipped with a combined Ag/AgCl glass electrode was used for the pH adjustments at room temperature. Fourier transform infrared (FT-IR) spectroscopic analysis of the synthesized material was conducted using an infrared spectrometer (Bruker FT-IR Vertex 70) over the wavenumber range 400–4000 cm^{-1} in KBr. High angle X-ray



Scheme 1. Schematic representation for synthesis procedures for unleached and leached ion.