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Synthesis of novel monolithic cartridges with specific recognition sites for extraction of melamine

Evin Mine Dursun, Recep Üzek, Nilay Bereli, Serap Şenel *, Adil Denizli

Hacettepe Universty, Faculty of Science, Department of Chemistry, Ankara, Turkey

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ABSTRACT

Synthesis of melamine (ME) imprinted polymeric sorbent for use as solid phase extraction adsorbent was targeted and the benefits of the synthesis in the monolith format were combined with imprinting technology advantages. Melamine as template and 2-vinylimidazole-Cu^{2+} as complexing agent were used as the first time for pre-complex formation, followed by the preparation of monolith by bulk polymerization method in the presence of ethyleneglycol dimethacrylate as crosslinker, azobisisobutyronitrile as initiator, and ethyl alcohol as solvent for a duration of 4 h at 80 °C. 1.0 M NaOH solution was used as a desorption agent to remove template. Non-imprinted monolith (NIP) were synthesized as a control without template in same receipt. The monolith samples were characterized by Fourier Transformed Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM), elementary analysis, and Branauer- Emmett- Teller (BET) studies. Melamine adsorption from aqueous solution was studied in continuous mode, and some parameters such as pH, temperature, concentration and flow-rate were optimized for melamine adsorption. The maximum adsorption capacities were determined as 147.9 mg/g for imprinted polymer (MIP), 82.0 mg/g for non-imprinted polymer (NIP) and 4.0 mg/g for polymer without pre-complex (E) at 25 °C, and pH 5.0 with 500 ppm melamine initial concentration for 1.0 mL/min flow-rate. In addition to interaction characterized by metal coordination bond formation, non- covalent interactions were responsible for melamine adsorption. No significant change in adsorption performance was recorded after 10 consecutive adsorption-desorption cycles.

Kinetic analysis indicated compliance with pseudo-second order kinetics. The Freundlich isotherm was found suitable for description of the process. Cyanuric acid (CY), aniline (AN), and phenol (PH) were used as competing agents in selectivity studies, and relative selectivity coefficients were calculated ($k'_{CY} = 4.45$; $k'_{AN} = 7.08$; $k'_{PH} = 3.98$).

The performance of melamine imprinted polymeric monolith (MIP) as solid-phase extraction adsorbent for extraction of melamine from milk samples was investigated and the recovery of melamine in spiked milk samples was 97.6% with the relative standard deviation (RSD) (8.1%).

1. Introduction

Solid-phase extraction (SPE)-a method used to isolate or to preconcentrate an analyte from liquid phase by a solid adsorbent has several advantages such as simplicity, ease in automatization, minimal consumption of organic solvents, and economical equipment [1,2]. Conventional sorbents are porous or graphitized carbon, chemically modified silica and polymers [3–5]. But these sorbents usually perform nonselective isolation of analyte resulting in coextraction of components having similar physicochemical properties [6]. This disadvantage has been overcome by selective sorbents- molecularly imprinted polymers (MIPs) and immunosorbents [7]. It is more convenient to use MIPs due to the advantages of physical and chemical stabilities, binding affinities comparable to bioreceptors, long shelf lives, and high selectivities for templates [8–11]. The template leakage or incomplete removal of template from polymeric structure is the most important risk in MIP synthesis. To overcome this difficulty is to use a structural analog of template [12].

Melamine [2,4,6-triamino- 1,3,5-triazine] is an industrial chemical compound used mainly in the production of plastics. The concentration of melamine in food may result from use of pesticides, industrial processing, plastic packaging and is typically less than 1 mg/kg and does not pose a food safety risk. Illegal addition of melamine to some dairy products and powdered milk to make them appear rich in protein due to its high nitrogen content paused a crisis (China crisis, 2008) all over the world. At high levels and in combination with cyanuric acid, melamine can form insoluble crystals, leading to the formation of kidney stones, and even deaths due to its nephrotoxic effect [13–15]. The

* Corresponding author at: Hacettepe University, Department of Chemistry, Beytepe-Ankara, Turkey.
E-mail address: senel@hacettepe.edu.tr (S. Şenel).

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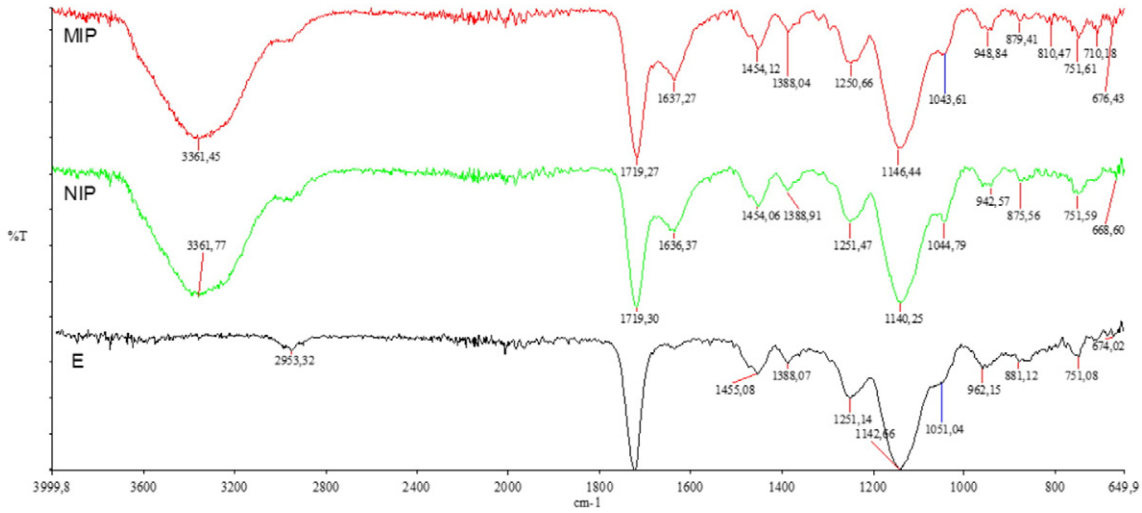

Fig. 1. The FTIR spectra of monolithic cartridges.

daily tolerable limit for melamine specified by WHO is 0.2 mg per kg of body mass [16].

Melamine detection was usually performed by LC, GC, LC-MS, SERS, MALDI/TOF, ELISA tests, and electrochemical or potentiometric sensors [17–21]. Several studies were performed for melamine isolation and detection. Surface imprinted silicagel, magnetic particulate MIPs using melamine or cryomazine as template, methacrylic acid or 9-vinylcarbazole as functional monomers were tried as sorbents for melamine removal by precipitation or dispersion polymerization methods [22–26]. In another study, Cu (II) methacrylate (chosen as functional monomer) was polymerized with melamine on vinyl modified silica particles [27]. Following the removal of melamine with phosphate buffer, the resulting MIP was able to remove 87–92% melamine from milk and powdered milk samples.

Fe_3O_4 nanoparticles or multiwalled carbon nanoparticles or magnetic graphene oxide covered by MIP layer (methacrylic acid: functional monomer; melamine: template) were also tried as alternative sorbents [28–30]. Matrix-template interaction was supplied with hydrogen bonds and electrostatic interactions when acrylic acid covered polypropylene fibers were crosslinked with ethylene glycol diglycydyl ether in presence of melamine [31].

In this study, 2-vinyl imidazole-Cu (II)-melamine precomplex was used for the first time to prepare melamine (ME) imprinted polymeric cartridges as a solid phase extraction sorbent. The complex was polymerized using EGDMA as crosslinker, AIBN as initiator in ethyl alcohol. Following the removal of template, MIP was prepared, characterized, and analyzed for its melamine removal performance and compared with NIP. Selectivity and reusability studies were also performed. Kinetics and isothermal models for adsorption were studied as well.

2. Experimental

2.1. Materials

Melamine, 2-vinylimidazole (VIM) and ethylene glycol dimethacrylate (EGDMA) were purchased from Sigma (St. Louis, USA).

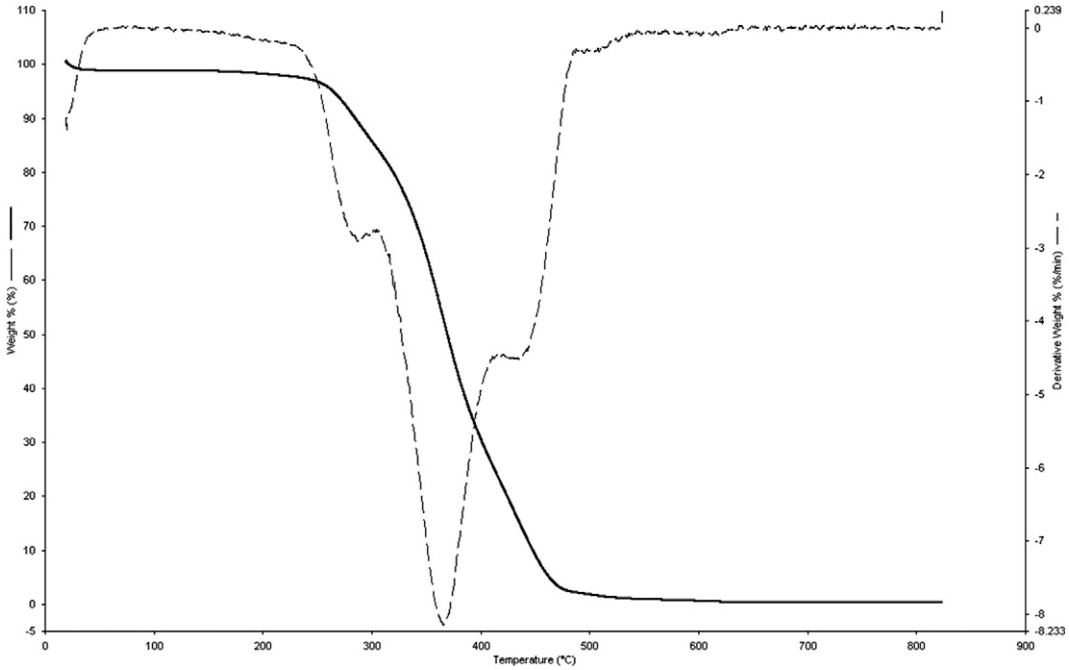

Fig. 2. TGA curve of E monolithic cartridge.