Synthesis and application of reduced graphene oxide and molecularly imprinted polymers composite in chemo sensor for trichloroacetic acid detection in aqueous solution

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ABSTRACT

This work presents the fabrication of a simple, cheap and fast thin film chemo sensor for detection of trichloroacetic acid (TCAA) in aqueous solutions. Reduced graphene oxide (RGO) based molecular imprinted polymers (MIP) chemo-sensor has been developed. The recognition of TCAA was achieved by imprinted polymers synthesized by copolymerization of 4-vinylpyridine (4-VP) and a crosslinking monomer ethylene glycol dimethacrylate (EDGMA) in acetonitrile using bulk polymerization method. Adsorption studies to determine the rebinding properties of the MIP with the template were conducted using UV Visible spectrophotometer. The fabricated sensor exhibited high recognition ability and affinity for HAA in comparison with the non-imprinted one which was employed as a control, this indicated that the MIP could selectively rebind with TCAA. Reduced graphene oxide (RGO) was used to improve conductivity of the sensor; RGO was obtained from reduction of graphene oxide (GO) synthesized using modified Stauddmer and Hummers method. Polysulphone was used in solution blending of MIP and RGO to form a hybrid which was deposited between two gold plated electrodes by spin coating to form a thin film. The performance of the imprinted sensor was studied using a homemade circuit. The results demonstrate that the sensor based on TCAA-imprinted polymer is fast, cheap and sensitive screening method of TCAA in drinking water.

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1. Introduction

The specific objective of this paper was to develop a low cost, simple and fast method for detection of trichloroacetic acid (TCAA) using molecularly imprinted polymers (MIP). MIPs are synthetic polymers possessing specific recognition sites to a target or imprint molecule. The recognition cavities are complementary in size, functional groups and shape to the template molecule present during the synthesis process (Fuchs et al., 2012; Pichon and Chapuis-Hugon, 2008). Molecular imprinting is a simple and cost effective process. MIPs are prepared by co-polymerization of a cross-linking agent with a complex formed between the template and polymerizable monomer(s) with good functionality. The monomers contain functional groups which interact specifically with the template through covalent or non-covalent bonds (Pichon and Chapuis-Hugon, 2008). Covalent approach gives bonds which are very stable and molecular recognition is enhanced while non-covalent gives electrostatic or hydrogen bonding interactions (Beltran et al., 2010). Non-covalent interactions are preferred because they are easy to prepare, extraction of the template is simply achieved by continuous washing and a great number of functionalities can be introduced to the recognition sites (He et al., 2007). The polymerization process in the MIP synthesis is initiated by thermal or UV light. After polymerization, the template is extracted from the polymer matrix leaving binding sites in the material specific to the template or similar molecules (Fuchs et al., 2012; Pichon and Chapuis-Hugon, 2008; Beltran et al., 2010; He et al., 2007). MIPs are employed in a broad range of domains such as in directed synthesis and catalysis, chemical sensing, controlled drug delivery, immunoassays, affinity separation, solid phase extraction (SPE) and as stationery phases for liquid chromatography (Fuchs et al., 2012; Beltran et al., 2010; Duan et al., 2013). Advantages of MIPs compared to biological

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recognition systems such as antibodies, cells and receptors include low cost of production, high storage stability, MIPs can be re-used without loss of selectivity, ease of preparation, high mechanical strength, high thermal and chemical stability (Cirillo et al.; Baggiani et al., 2007; Yang et al., 2014; Ulbricht, 2004). MIPs suffer from limitation associated with limited concentration of imprinted cavities when applied as recognition system in sensors, in addition to bulk volumes of the polymer matrice that requires long diffusion paths of the imprinted molecule. Moreover, when used as recognition elements, MIPs materials lack the signal response to analyte binding events (Guan et al., 2008). These limitations lead to inefficient sensing process. MIP nanomaterials are proposed as a solution for improving homogeneity and accessibility of binding sites (Cirillo et al.). Since graphene has demonstrated to have unique properties such as high mechanical strength, good electron transport and large surface area (Kim et al., 2010; Han et al., 2011; Artiles et al., 2011; Singh et al., 2011), graphene could serve as reinforcing component in fabrication of MIPs for sensor application and also enhance MIPs signal response. The integration of high surface area and conductivity of graphene with high recognition properties of MIPs to form graphene based hybrid MIP demonstrates useful innovative materials for analytical determination of target analytes (see Fig. 1).

Trichloroacetic acid (TCAA) is one of disinfection by products (DBPs) formed when free aqueous residual chlorine reacts with components of humic acid during disinfection of water (Suedee et al., 2004). Other sources of TCAA in water include release as an industrial waste and water disinfection in swimming pools. TCAA has been used as a pre-emergence herbicide, a peeling agent for sun-damaged and wrinkled skin and tattoos as well a common laboratory solvent (Kurd et al., 2013). Due to its high solubility in water, it is considered as very toxic even at low concentration to aquatic life, human, animals, plants and algae (Kurd et al., 2013). Therefore, the determination of TCAA in drinking water is of great importance. The world health organization has urgently appealed for development of rapid, reliable, and accurate analytical methods for the detection of TCCA (Kurd et al., 2013). Routine analysis of TCAA involves use of chromatographic methods such as gas chromatography, ion chromatography, and liquid chromatography with either electron capture or mass spectrometry detector (Kurd et al., 2013; Suedee et al., 2006). These methods require long sample preparation procedures and need for sample derivatization. In addition, the instruments are expensive to maintain with high power demand and require well trained personnel. The use of sensor technology seem to be the most promising method to give simple, fast, cheap and continuous measurements.

Fig. 1. Structure of functional monomer (4-VP), cross linker (EGDMA) and the template (TCAA).

2. Experimental

2.1. Materials and methods

4-Vinyl pyridine (4-VP), ethylene glycol dimethacrylate (EDMA), dichloroethane (DCM), 2,2′azobis-valeronitrile, hydrogen peroxide (H_2O_2), sulfuric acid (H_2SO_4), hydrochloric acid (HCl), HPLC grade acetonitrile, formic acid were purchased from Sigma Aldrich chemical company, South Africa. Regulated trichloroacetic acid was studied in this work and was obtained from Darmstadt, Germany. Graphite used for the synthesis of RGO was obtained from Sigma Aldrich chemical company, South Africa. All standards were of analytical grade. Working standard solution was prepared daily. Stock solutions were stores at 4 °C.

2.2. Instrumentation

Brunauer Emmett Teller (BET) Micrometrics ASAP 2020 was employed for pore size and surface area analysis of the MIPs during optimization. X-ray diffractometer (Rigagu Ultima IV) was used in characterization of graphene/MIP hybrid. PerkinElmer FT-IR (Spectrum 100) was used to characterize the MIP, non-MIP, GO and RGO. Optical absorption spectra were recorded using Shimadzu UV–Visible spectrophotometer (UV-2450). A homemade circuit was used to study the sensor response to TCAA.

2.3. Preparation of TCAAs molecularly imprinted polymer

2.3.1. Bulk polymerization

Synthesis of MIP was done by bulk polymerization. It involved dissolving known moles of TCAA in acetonitrile followed by addition of 4-VP and EGDMA, the mixture was sonicated for 5 min. 90 mg of the initiator was added. The mixture was purged with nitrogen for 10 min to create an inert atmosphere. The polymerization of the monomeric monomer was performed at 60 °C for 24 h. Various factors known to affect the response behavior of the MIPs and non-MIPs were optimized. The monomer to template ratio, solvent and the percentage crosslinker were optimized based on surface area of the obtained polymer. The obtained bulk MIP was dried under vacuum, crushed in a pestle mortar into fine powder and then sieved through 0.45 µm wire mesh giving particles of uniform size distribution. The MIP powder was stored in a desiccator until use. The Non-molecularly imprinted polymer (non-MIP) included in the study as the control was prepared using the same procedure with the exception of addition of the template. Both MIP and non-MIP were characterized using FT-IR. Adsorption and binding studies were carried out for MIP and non-MIP.

2.4. Synthesis of RGO

Reduced graphene oxide (RGO) was prepared from reduction of GO. GO was synthesized using modified Stauddmer and Hummers method (Premkumar and Geckeler, 2012) which involves oxidation of graphite. 200 mL 9:1 mixture of concentrated H_2SO_4/H_3PO_4 was aged to 1.5 g of graphite flakes followed by addition of 9 g of KMnO4. The reaction mixture was heated to 50 °C and stirred for 24 h. The obtained product was allowed to cool down to room temperature, 400 mL of a mixture of water and H_2O_2 (7:3) was added to the product to reduce unreacted KMnO4. 250 mL of dilute HCl was also added. The obtained graphite oxide was ultrasonicated to exfoliate graphite oxide to GO. Reduction of GO to RGO was achieved using ascorbic acid as a reducing agent. 50 mL of GO was weighed and added to 500 mL of water, 2 g of ascorbic acid was added. The mixture was maintained at 80 °C with stirring for 24 h. The mixture was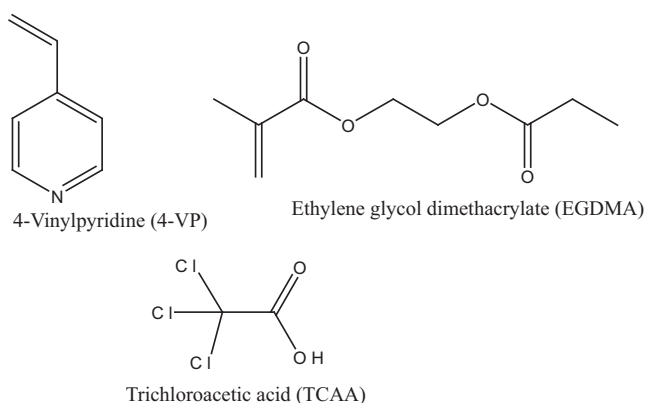 then filtered and washed continuously with