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Development of Molecularly Imprinted Polymers – from Environmental Sensors to Biotechnology Applications

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Many researchers have concentrated on the development of new methods for rapid determination of endocrine disrupting chemicals (EDCs) that are widely detected in environmental waters. Exposure to EDCs is associated with an earlier onset of puberty, decreased fecundity or fertility, altered sexual behavior, and increased incidence of abnormalities or cancers of the reproductive tract in humans [1]. The findings of a new study suggest that some endocrine disruptors may play a role in the obesity epidemic [2]. Direct determination of EDCs in water remains a challenging problem due to their low concentrations (ng/L to μg/L), which is further complicated by the presence of numerous other compounds (pharmaceuticals, personal care products, detergents and natural organic matter). Such matrix effects are formidable even when sophisticated instrumental techniques are used [3,4].

Considerable efforts have been focused on the synthesis of molecularly imprinted polymer (MIP) particles that specifically recognized estrogenic compounds. MIPs represent a class of smart materials that have artificially created receptor cavities to mimic biological antibodies. Researchers can imprint a plastic material to create molecularly sized and shaped cavities with specific interactions to bind the target analyte [5]. MIPs show outstanding affinity towards the analyte in aqueous solution, with a binding capacity as high as 300 mg/g. They can be used as sorbent materials in solid-phase extraction (SPE) for the quantitative enrichment of analytes in environmental water samples prior to determination by an instrumental method. Removal of interfering matrix constituents frequently extends the detection limit and improves the accuracy of trace analysis. The structural dimension of MIPs can influence partition kinetics, as both submicro- and nano-particle sizes have demonstrated improvements in analyte recovery. MIPs can be synthesized for several natural and synthetic EDCs such as estrone (E1), 17α-estradiol (α-E2), 17β-estradiol (β-E2), estriol (E3), 17α-ethynylestradiol (EE2) and bisphenol A (BPA), among which β-E2 exhibits the strongest estrogenic potency (EC50 0.015 ± 0.002 nM) [6]. They have been applied in different kinds of electrochemical sensors [7-11] and optical sensors [12,13].

Currently there is no commercial availability of online sensors that are suitable for monitoring EDCs rapidly and cost-effectively. Neither in-line immunosensor nor chromatography would be ideal as they have high costs and maintenance requirements. EDCs at ultra-trace levels in environmental water can be determined by selective pre-concentration using the molecular recognition property of MIP particles. After preconcentration, the extract can be quantitatively analyzed by spectrofluorometry, capillary electrophoresis and liquid chromatography-tandem mass spectrometry [14]. However, efforts will be required to optimize various parameters such as washing solvent, elution solvent and breakthrough volume to reduce non-specific interactions during the selective preconcentration of EDCs from water samples. A novel sensing scheme based on fluorescence quenching of 17β-estradiol (E2) was recently reported. Fluorescence emission from E2 non-specifically bound onto the MIP was first quenched by gold nanoparticles. Next nitrite anions penetrated the porous MIP structure to quench the fluorescence emission from E2 molecules specifically bound inside imprinted cavities. The difference between these two emission intensities varied with the initial E2 concentration in water from 0.1 to10 ng/mL [15]. One major advantage of this method is the high selectivity of MIP particles for E2 [16] over dissimilar structures [17]. Rapid screening of E2 in water takes only 10 min.

In field studies, ultra-trace EDCs can be more efficiently pre-concentrated by flowing 100-1000 mL of water through an optical cell packed with MIP particles. Flow injection analysis (without coupling to a HPLC system) is possible by automated sequential injections of AuNPs and sodium nitrite to make the fluorescence quenching measurements. A detection limit of 15 ng/L will attest to its suitability for rapid field analysis. Although MIP particles tend to suffer from biofouling, they are so simple in design and so cost effective in synthesis to be disposable after a single use. As these optical sensors have operational characteristics similar to a pH sensor in terms of durability, selectivity and concentration range, they will be suitable for autonomous, real-time data acquisition in a closed loop system at low maintenance costs. For EDCs which are not inherently fluorescent, quenching of the fluorescence from an indicator probe would be a feasible modification of the above measurement principle. These two options potentially will allow a suite of EDC sensors to be developed for benzophenone, dichlorodiphenyldichloroethylene, dienestrol, diethylstilbestrol, di-tert-butyl-benzoquinone, hexachlorobenzene, hexachlorocyclohexane, mestranol, nonylphenol, nonylphenol monoethoxylate carboxylate, oxychlordane phenanthrene, progesterone and triclosan.

The selectivity of a new MIP for 3-nitro-l-tyrosine, an oxidative stress marker associated with neuro-degenerative disorders, was demonstrated in human urine analysis [18]. Another MIP was developed for the SPE of irinotecan from human serum [19]. The fingerprint analysis concept, which distinctively identifies a pool of peptides composing a protein, was recently developed for the rational preparation of MIPs for protein recognition [20]. From environmental sensors to biotechnology applications, the diversity of areas and complexity of systems are both indicating numerous opportunities in the near future.

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