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Porous materials for the sorption of emerging organic pollutants from aqueous systems: The case for conjugated microporous polymers

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ABSTRACT

Emerging organic pollutants (EOPs) pose a challenge to water treatment facilities and are a potential hazard to the environment and human health. Potential ways of removing these pollutants in tertiary wastewater treatment processes to make it potable include the use of porous materials like biochar, zeolites, metal organic frameworks (MOFs), covalent organic frameworks (COFs), polymers of intrinsic microporosity (PIMs), zirconium based porous materials and, more recently, conjugated microporous polymers (CMPs). CMPs have attracted research attention owing to their porosity and π-conjugation which can easily be engineered for a wide range of applications. The synthesis of CMPs is relatively easily done through established pathways that include the Suzuki coupling, Sonogashira-Hagihara cross-coupling, Friedel-Crafts reactions, oxidative coupling, Ullmann reaction and the Yamamoto coupling. Post-synthetic functionalisation approaches have been used to obtain CMPs which have specific motifs suited for particular applications. Despite their potential, use of CMPs in removing EOPs from water has not received adequate research attention, and is therefore an area that needs research. This short communication highlights the challenges posed by EOPs, presents some of the possible porous materials that can be used for their removal, and proposes CMPs as suitable potential adsorbents. Basing on recent literature covering the period 2003–2016, the synthetic methods, properties and applications of these materials have been presented.

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1. Introduction

Water pollution is increasingly becoming a challenge due to anthropogenic pollutants from increased industrial and various other activities. Removal technologies are not efficient, especially against emerging organic pollutants (EOPs) like pesticides and pharmaceuticals [1–3]. Research on EOPs is only just beginning; this has been stimulated by, among other factors, the advancement in detection technology [4,5] and improvements in predictive modeling of physico-chemical properties of pollutants [6–8]. Recently, analytical technologies capable of trace pollutant detection, for example, electrospray ionization (ESI) devices that interface a high-performance liquid chromatography and a tandem mass spectrometer (LC/MSMS) have been developed and applied [9]. Consequently, awareness has been raised on pollutants that were previously unknown or were of little concern. The effect of EOPs on human health is still unknown, but it is believed they are deleterious to human health [6,10]. EOPs have been reported to affect the fertility of animals [11], and therefore could potentially harm humans. Because of their potential environmental and health effects, coupled with the limited knowledge about their behaviour and limited sampling and analytical techniques, action on EOPs is needed urgently [5].

Although earlier research has reported the removal of organics like atrazine using dairy manure derived biochar [12], phenol using zeolitic bagasse fly ash [13], pharmaceutical micropollutants using powdered activated carbon [2] and organic dyes using metal oxide-biochar nanocomposites [14] from aqueous systems, the large scale usage of these technologies is still unexplored. Recently, porous materials have been investigated for their ability to remove gases (e.g. CH_4, CO_2). These materials include activated carbons, zeolites, metal organic frameworks, carbon organic frameworks, polymers of intrinsic microporosity (PIMs), and conjugated microporous polymers (CMPs). Other materials that possess significant porosity could also be used for similar applications. For example zirconium based porous materials were reported to have excellent properties for removing nitrate [15] and fluoride [16] from water, while metal oxide based materials like polyacrylamide chromium

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oxide were reported for their ability to remove As(III) from environmental water samples [17]. CMPs encompass a wide range of polymeric materials which are conjugated and cannot easily pack together due to restricted rotation about the π-bond resulting in a microporous framework [18]. They can therefore host fugitive molecules like inorganics and organics and thus act as a molecular sponge that can be used for gas storage, molecular sieving, and for the removal of pollutants from environmental media. The porosity and pore geometry can be tailored to suit particular applications. The presence of unsaturation in the framework makes them suitable for other applications like light emission, light harvesting and electrical energy storage [19,7]. Although recent work has designed and fabricated membranes using a thiophene-based electropolymerisation process [20], applications of CMPs are generally limited by their insolubility in common solvents, rendering them unprocessable into membranes or films. As a result, most applications involve using the materials in powder form. This however, has an advantage in increased interaction surface area and therefore potentially enhances efficiency.

There is a dearth of literature on the removal of organics generally, and EOPs in particular using polymeric porous materials. Drawing from publications that span the period 2003–2016, we have sought to address the following objectives: (1) highlighting the problem of pollution due to EOPs, (2) synthesizing information on microporous materials for the sequestration of liquid and gaseous pollutants from water and air, and (3) proposing CMPs as a novel and effective way of removing EOPs from the aquatic environment.

2. Emerging organic pollutants

A significant number of reviews and research articles have been published on emerging pollutants (e.g., [21,5,22]. Although the definition of these is still problematic [6], it can generally be agreed that EOPs are either emerging in their chemical nature, their impact on the environment, or they have recently gained prominence largely due to improved detection technology [23]. The removal of these pollutants from aqueous media is problematic. This could mainly be because very little is known about their physico-chemical properties and, as such, wastewater treatment technologies in use have not been designed to remove them [2]. Because the existence of EOPs is a time dependant phenomenon, there will always be pollutants that are emerging at any one particular time. Sources of EOPs include industrial effluents, agricultural chemicals (e.g. pesticides and herbicides), household waste, and pharmaceutical and personal care products (PPCPs) [10]. For example, pharmaceutical residues are frequently detected in treated wastewater, surface water, and groundwater worldwide [24,22,23]. The pathways through which these pollutants find their way into surface and ground water are summarized in Fig. 1. From the surface and groundwater they go up the food chain to humans through the consumption of contaminated fish, or directly through consuming contaminated water.

The removal of these EOPs can be effected through the use microporous materials. These materials have the advantage of not only being porous, but have the potential to be engineered by incorporating functional groups to improve their efficiency and selectivity towards targeted pollutants.

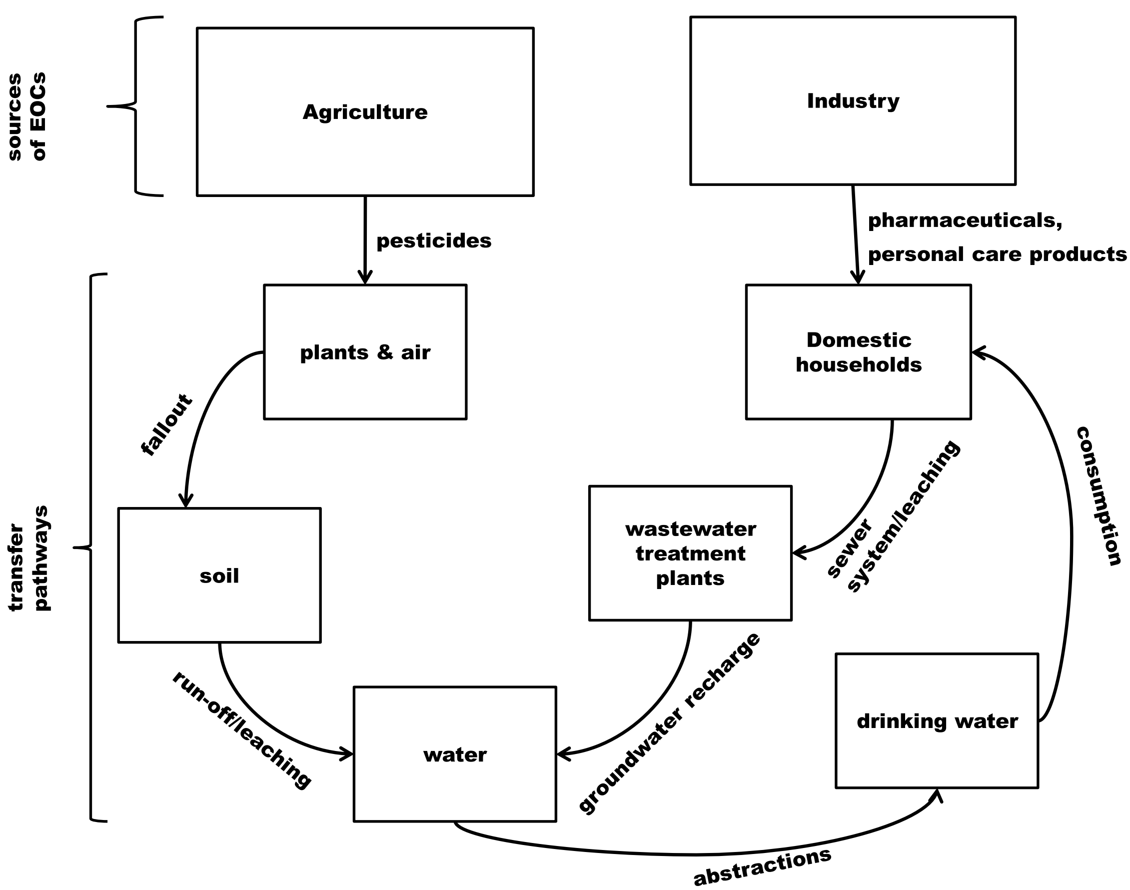

Fig. 1. Pathways for surface and groundwater pollution by emerging pollutants.

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