



Development of a novel dual-stage method for metaldehyde removal from water



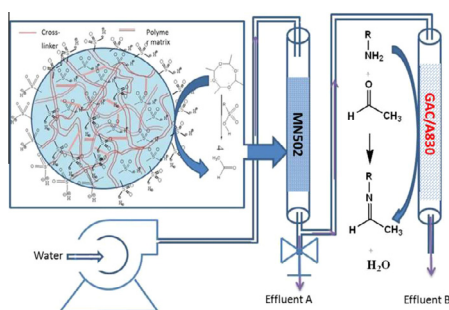
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HIGHLIGHTS

- Novel dual-stage method developed using optimized materials to remove metaldehyde.
- Properties of sulfonic acid functionalized Macronets were tuned and optimized.
- Metaldehyde was degraded and adsorbed by rationale-designed polymeric materials.
- Fabricated system showed consistent performance and practicality of actual application.
- Results are significant to development of metaldehyde remediation methods within UK.

GRAPHICAL ABSTRACT



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ABSTRACT

A dual-stage method was developed to first efficaciously degrade metaldehyde into acetaldehyde, before subsequent removal of acetaldehyde using an amine functionalized ion-exchange resin. A range of Macronets, with different surface areas, pore volumes, pore size distributions and extents of functionalization were evaluated for the depolymerisation of metaldehyde. Nuclear magnetic resonance spectroscopy was used to confirm the complete degradation of metaldehyde by the selected Macronets. Kinetic studies showed that the rates of catalytic degradation were primarily determined by the porous structure of the materials rather than the extent of surface functionalization, since high levels of acid surface groups were observed to decrease the porosity significantly. The rate constants obtained show excellent correlation with non-micro pore volumes, which are of import as the only pores that are accessible to hydrogen bonded metaldehyde molecules; Macronet MN502 exhibits the largest non-micro pore volume and, hence, demonstrated the best kinetic performance. The effect of competing ions on catalytic performance was also studied and the results demonstrate that competing ions compromise the performance of the proposed system to some extent, however, it is notable that a good level of performance is maintained even for competing ion concentrations as high as 100 times that of metaldehyde. Isothermal studies of acetaldehyde onto ion-exchange resin A830, including kinetic evaluation, showed that acetaldehyde could be chemically adsorbed by the resin. Consequently, a dual-column system was proposed, which was determined to effectively degrade metaldehyde (MN502) and remove the resulting by-product, acetaldehyde, via a second fixed bed adsorber (A830); this method could easily be adapted to existing facilities in water treatment works, making it very cost-effective and of great practical interest.

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1. Introduction

Recent reports of potable water contamination by metaldehyde [1] have drawn public attention to the matter; the maximum concentration of metaldehyde in U.K. drinking water is regulated, according to its role as a pesticide, at 0.1 µg/L (ppb) [2]. In 2010, several British water treatment works detected significant quantities of metaldehyde in their treated waters, reaching up to 1 ppb, i.e. ten times higher than the permitted level [3]. The detection of metaldehyde in drinking water supplies indicates that current methods utilized in the water treatment industry, i.e. Granular Activated Carbon (GAC) beds, are not working effectively and according to research conducted by the Water Research centre (WRc), a virgin GAC bed was exhausted after only 44 days of use, where metaldehyde breakthrough was detected [4]. Our previous research findings indicated that the rapid exhaustion of GAC is caused by the low adsorption capacity of metaldehyde onto GAC and a high leaching tendency [5]. An additional concern in the use of GAC beds is that, although it can lower the concentration of metaldehyde in water initially, GAC can only remove ~30–50% of the total metaldehyde within a water stream, meaning that water contaminated with metaldehyde at levels >0.15 ppb, even if treated, will still exceed the threshold of 0.1 ppb [4]. The poor performance of GAC for metaldehyde removal is a result of its low adsorption capacity, exacerbated by high leaching tendencies [5]. Recent work has shown an improvement to carbon based systems using the bespoke sorbent Nyex™, however, the process requires a number of cycles to reach high levels of remediation as well as electrochemical regeneration of the sorbent [6].

Investigations using Advanced Oxidation Processes (AOPs) for metaldehyde removal from drinking water have been undertaken by several researchers; AOPs comprise a category of destructive reaction processes, which have demonstrated promising performances for the removal of micro-pollutants. One sub-category of AOP is chemical activation via UV irradiation to generate highly reactive hydroxyl radicals (e.g. H₂O₂, TiO₂ and H₂O₂/Fe³⁺) [7–11]. Studies on the degradation of metaldehyde by AOPs using UV/H₂O₂ and UV/TiO₂ revealed that both methods had efficient degradation of metaldehyde with almost identical removal rates (~0.007 cm² mJ⁻¹) for synthetic laboratory water samples. However, when tested using real water samples, the degradation performance of UV/TiO₂ was completely limited due to the blockage of active sites by background organic substances. In the case of UV/H₂O₂ and real water samples, the rate of degradation was slowed from 0.007 to 0.002 cm² mJ⁻¹ by background organic matters [12]. Furthermore, more detailed investigations into the influence of competing organic substances on the performance of UV/H₂O₂ and UV/TiO₂ showed that hydrophobic matter had a greater inhibitory effect than hydrophilic matter [13]. Therefore, UV/H₂O₂ was deemed to be more effective than UV/TiO₂. However, in order to reach the desired metaldehyde removal performance, large quantities of H₂O₂ are required and high UV dosage needed, since irradiation at 254 nm (UV light) does not activate H₂O₂ effectively [12–14]. Although it is shown that AOP can remove metaldehyde from water, there are still key issues that need to be addressed before it may be employed in large-scale water treatment works, including the issues of by-product production and the prohibitively high infrastructure and running costs of the process [14].

Currently, as discussed above, existing methods for the removal of metaldehyde suffer certain limitations, therefore; alternative cost-effective and more practical methods are urgently required to address metaldehyde contamination within U.K. water supplies. Our previous research has shown that sulfonic acid functionalized silica materials efficiently remove metaldehyde from drinking water [15]; achieved by a mechanism involving the degradation

of metaldehyde into acetaldehyde, thereby, creating a secondary pollutant ameliorated using amine functionalized materials in a dual-stage process. Previous fabrication of a bench scale dual-stage system was attempted, however, some obstacles hindered the installation. Obstructions hindering the installation and evaluation of the previously proposed treatment system primary include (1) the large-scale production and commercialization of the prepared silica samples, which would require significant time to achieve particularly with regards obtaining regulatory permits for potable water; (2) the silica samples, as-synthesised, were in the form of very fine particles (<10 µm), which would cause tremendous pressure drops if used in fixed-bed columns. According to Darcy's law of describing flow in porous media [16], the pressure drop (Δp) of flow through porous material packed column can be calculated by the equation of $\Delta p = (Q \cdot \mu L) / (k \cdot A)$, where Q is flowrate, μ is viscosity of fluid, L denotes the length of bed, A is area of cross section and k is the permeability (or hydraulic conductivity) of the packed medium. Permeability of the packed material is affected by the particle size and porosity (e.g. pore size) of the material. As indicated by the characterization of silica samples [15], the particle size fell in the range of 1–50 µm and pores were micro and mesoporous, meaning the permeability of the silica packed column would be very small and the pressure drop would be tremendous. Therefore, alternative materials with bigger particle size and large pore sizes could solve these issues, hence, Macronets with sulfonic acid functionalisation, were, designed and supplied by Purolite® and, utilized in a dual-stage process. In comparison, the particle size of Macronets was in the range of 500–650 µm which is a common size in water purification applications. Also, the pore volume of Macronet MN502 is more than 0.3 mL/g. Therefore, the pressure drop associated with operation under standard operating parameters is in the normal range, allowing the proposed dual-stage method to be fabricated and tested. The Macronets used were selected on the outcomes of our previous study, which indicated sulfonic acid functionality showed good metaldehyde degrading performance [15], hence, a series of materials with controlled porosity (surface area, total pore volume, pore size distribution) and extent of sulfonic acid functionalization were synthesised to allow process optimization, via a highly efficacious dual-stage method for removal of metaldehyde from drinking water.

2. Experimental

Macronet samples were synthesised at Purolite® International, U.K., and are, subsequently, commercially available; six Macronet samples were prepared, in total, with varying porous textures and a range of acid capacities, allowing for optimization of desirable material characteristics. The materials can be divided into two sub-categories: Macronet (MN) and D code (DC) series. The MN series includes MN500, MN501 and MN502, while the DC series consists of DC564, DC565 and DC566. The key difference between MN and DC materials is the extent of sulfonation to the same parent matrix, which results in a significant variation in the porous textures of the materials. An ion-exchange resin A830, with complex amine functionality, used in the second stage of the method was also supplied by Purolite®. Textural characterization was performed via analysis of nitrogen sorption isotherms (ASAP 2420, Micrometrics) obtained at -196 °C [17], to provide specific surface areas and pore volumes. Pore size distributions were determined by mercury intrusion porosimetry, performed on a PoreMaster® PM-60 instrument (Quantachrome, UK) [18,19]. Quantification of extents of surface functionalization was performed using Boehm titration methods [20,21]. The concentration

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