

# Capture and Release Recyclable Dimethylaminomethyl-Calixarene Functional Cloths for Point-of-Use Removal of Highly Toxic Chromium Water Pollutants

Vera S. Bieber, Egemen Ozelik, Harrison J. Cox, Christopher J. Ottley, Jatinder K. Ratan, Mustafa Karaman, Mustafa Tabakci, Simon K. Beaumont, and Jas Pal S. Badyal\*



Cite This: <https://dx.doi.org/10.1021/acsami.0c14772>



Read Online

ACCESS |



Metrics & More

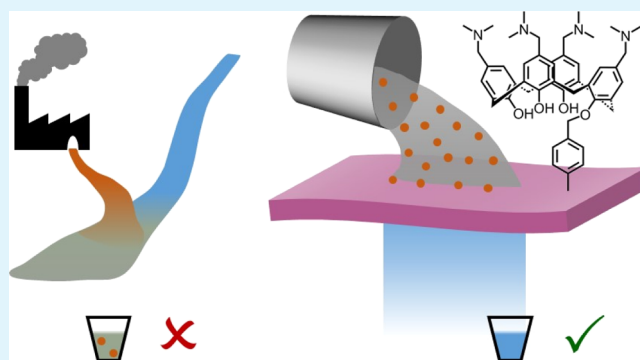


Article Recommendations



Supporting Information

**ABSTRACT:** Chromium(VI) contamination of drinking water arises from industrial activity wherever there is a lack of environmental legislation enforcement regarding the removal of such pollutants. Although it is possible to remove such harmful metal ions from drinking water through large-scale facilities, there currently exists no safe and simple way to filter chromium(VI) oxoanions at the point of use (which is potentially safer and necessary in remote locations or humanitarian scenarios). High-surface-area cloth substrates have been functionalized with calixarene molecules for the selective capture of aqueous chromium(VI) oxoanions in the presence of structurally similar anions. This is accomplished by pulsed plasmachemical deposition of a linker layer and subsequent functionalization with dimethylaminomethyl-calixarene (5,11,17,23-tetrakis[(dimethylamino)methyl]-25,26,27,28-tetrahydroxycalix[4]arene). Chromium(VI) oxoanions are captured by simply passing polluted water through the functionalized cloth, while other ions not harmful/beneficial to human health remain in the water. These cloth filters are simple to use, highly selective, and easily recyclable—thus making them attractive for point-of-use application in geographic regions lacking appropriate wastewater treatment plants or flawed environmental monitoring systems. Chromium(VI) pollutants have been successfully removed from real-world contaminated industrial wastewater streams using the dimethylaminomethyl-calixarene functionalized cloths.



**KEYWORDS:** chromium(VI) pollution, functional surface, calixarene, plasmachemical, water filtration, recyclable

## 1. INTRODUCTION

Water pollution is a major threat to human health around the world and is recognized as a key global sustainable development challenge, particularly, in some developing countries, where large amounts of industrial wastes can sometimes drain into rivers without there being adequate remediation—leading to contaminated human drinking supplies.<sup>1</sup> According to the United Nations, each year more people die from unsafe water than from all forms of violence put together (including war).<sup>2</sup> In contrast, for example, in the European Union, strict environmental regulations are enforced.<sup>3–5</sup>

Conventional large-scale removal of toxic heavy metal ion pollutants from drinking water relies on methods such as reverse osmosis, electrodialysis, ion-exchange resins, or ultrafiltration; these techniques can be expensive or require a constant energy supply and are therefore often not installed in countries with a low gross domestic product.<sup>6</sup> Point-of-use water purification systems offer a safer alternative in poorly regulated jurisdictions. Despite there being a wide range of techniques employing mechanisms such as heat,<sup>7</sup> UV light,<sup>8,9</sup>

antibacterial agents,<sup>10,11</sup> and ultrafiltration through small pores,<sup>12,13</sup> most of these methods only address bacterial contamination and are entirely ineffective against dissolved contaminants (such as toxic heavy metal ions).<sup>14</sup> Hence, there exists a need for the development of point-of-use methods targeting the removal of dissolved harmful contaminants from drinking water supplies.<sup>15–18</sup>

A common class of toxic heavy metal water pollutants are aqueous hexavalent chromium compounds based on Cr(VI) oxoanions (chromate ( $\text{CrO}_4^{2-}$ ), hydrogen chromate ( $\text{HCrO}_4^-$ ), and dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ )). These chemicals have been widely utilized by industry since the 19th century for pigments, leather tanning, metallurgy, chrome plating,

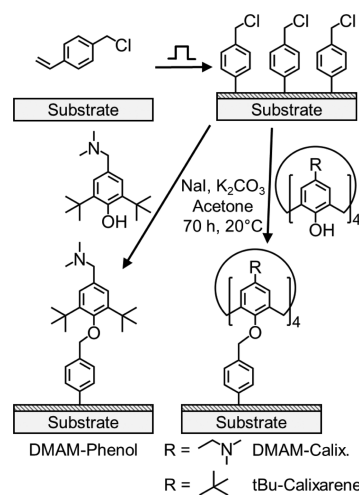
**Received:** August 16, 2020

**Accepted:** October 21, 2020

corrosion inhibitors, and numerous other applications.<sup>19–21</sup> However, there are significant dangers associated with their usage toward human health—skin contact leads to sores<sup>22</sup> and inhalation causes perforation of the nasal septum,<sup>23</sup> while animal testing has shown that injection and ingestion give rise to cancer.<sup>24–26</sup> Such high levels of toxicity associated with Cr(VI) oxoanions (such as chromate) are attributed to structural similarities with phosphate and sulfate anions—which are known to be easily transported into biological cells acting as nutrients (whereas chromate causes cell damage).<sup>27,28</sup> In vitro studies have shown that within a biological cell, hexavalent chromium species can be reduced to stable trivalent chromium compounds by ascorbate and different thiol-containing molecules (such as glutathione and the amino acid cysteine).<sup>29</sup> During this reduction of Cr(VI) oxoanions, oxygen radicals and intermediate chromium oxidation states are formed which react with and damage different parts of the biological cell—for example, cleavage of DNA strands.<sup>30</sup> The resultant trivalent chromium ions are able to form complexes with amino acids and the phosphate groups of DNA present within the cell.<sup>31</sup> These stable Cr(III) complexes are difficult to break up and therefore impair the functions of the cell—causing cancer and other health issues.<sup>28</sup> In contrast, trivalent chromium species found in the environment are relatively harmless because they are unable to easily permeate biological cell walls.<sup>27</sup> Given the aforementioned toxicity of hexavalent chromium (even when ingested at very low concentrations over an extended period of time), strict legal limits have been set by government regulatory bodies, limiting the maximum permitted chromium concentration in drinking water (for the European Union, the current legal limit of  $50 \mu\text{g L}^{-1}$  will shortly be lowered to  $25 \mu\text{g L}^{-1}$ —agreed by the European Commission in December 2019).<sup>3–5</sup> However, elevated concentrations of Cr(VI) oxoanions are often detected in ground and drinking water supplies across many other parts of the world.<sup>32–34</sup>

Point-of-use water purification systems for the chromium-(VI) oxoanion containing effluents potentially offer a cheaper and more targeted approach compared to larger scale upstream installations which are susceptible to mismanagement because of the lack of legal enforcement of safe pollutant drinking levels within some developing countries. Earlier attempts to use ion-exchange materials have offered limited practical use because of their requirement for low pH values in order to achieve effective pollutant capture.<sup>35,36</sup> To overcome the challenges outlined above, we have devised a system based on the attachment of a layer of highly selective calixarene molecules to commercially available cloths using a combination of plasmachemical surface functionalization and robust chemical coupling of calixarene molecules. In contrast to anion-exchange resins, calixarenes provide higher selectivity because of multidentate complex formation with aqueous chromium ion pollutant species. This has facilitated efficient removal of hexavalent chromium oxoanions from water at pollutant levels found in real-world scenarios. Specifically, pieces of a high-surface-area cloth functionalized with tertiary amine-terminated calixarene (5,11,17,23-tetrakis[(dimethylamino)methyl]-25,26,27,28-tetrahydroxycalix[4]arene, or DMAM-calixarene) have been shown to capture Cr(VI) oxoanions from polluted industrial wastewater, Scheme 1. This encompasses pulsed plasma deposition of poly(vinylbenzyl chloride) onto the cloth substrate to provide benzylchloride groups for reaction with the calixarene lower rim hydroxyl groups via a nucleophilic

**Scheme 1. Pulsed Plasma Poly(vinylbenzyl chloride) Deposition Onto a Cloth Substrate, Followed by Tethering of Calixarenes Containing Either Tertiary Amine Groups (DMAM-calixarene) or *tert*-Butyl Groups on the Upper Rim (5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrahydroxycalix[4]arene, *t*-Bu-calixarene), or Alternatively with a Phenol Derivative Containing a Tertiary Amine Group (2,6-Di-*tert*-butyl-4-(dimethylaminomethyl)phenol, DMAM-phenol)**



substitution mechanism.<sup>37</sup> DMAM-calixarene was chosen because of its promising capability to capture Cr(VI) oxoanions (although unknown selectivity).<sup>38</sup> Previous studies utilizing calixarenes for Cr(VI) oxoanion removal have utilized solution-phase separation which is impractical in terms of real-world applications given that the most practical approach for the end user is simply to pour water through a filtration medium. Nonwoven polypropylene is employed as the cloth substrate because it is readily available and less prone to fungal growth compared to natural materials (such as cotton).<sup>39</sup> Also, it is flexible enough to be easily inserted into cartridges of any size and geometry without leaving any gaps through which the water flow could circumvent the filtration media. Cr(VI) oxoanions are removed with high efficiency from water by simply filtering the pollutant solution through the functionalized cloth. It is shown that DMAM-calixarene-functionalized cloth completely removes hexavalent chromium oxoanions from water at pollutant levels comparable to real-world scenarios (up to  $100\text{--}260 \mu\text{g L}^{-1}$ ).<sup>33,40,41</sup> Furthermore, high ion selectivity toward Cr(VI) oxoanion capture is demonstrated for real-world polluted wastewater, as well as multiple-use recyclability.

## 2. EXPERIMENTAL SECTION

**2.1. Preparation of Functionalized Cloth.** Nonwoven polypropylene cloth was used as the high-surface-area substrate (taken from the middle layer of disposable surgical masks,  $80 \mu\text{m}$  thickness,  $5.0 \pm 1.5 \mu\text{m}$  fiber diameter, SD Medical Ltd.). The fabric was rinsed with ethanol and thoroughly dried in air prior to plasmachemical surface functionalization.

Pulsed plasma deposition using the vinylbenzyl chloride precursor (+97% mixture of 3- and 4-isomers, Sigma-Aldrich Ltd.) was conducted in a cylindrical glass chamber (5 cm diameter,  $470 \text{ cm}^3$  volume, base pressure less than  $3 \times 10^{-3}$  mbar, and a leak rate better than  $2 \times 10^{-9}$  mol s<sup>-1</sup>) enclosed in a Faraday cage.<sup>42,43</sup> The chamber was connected to a  $30 \text{ L min}^{-1}$  two-stage rotary pump (E2M2, Edwards Vacuum Ltd.) via a liquid nitrogen cold trap. An inductor–

capacitor impedance matching network was used to minimize the standing-wave ratio for power transmission from a 13.56 MHz radio frequency (rf) power generator to a copper coil (10 turns, spanning 8 cm) externally wound around the glass chamber. For pulsed plasma deposition, a signal generator (model TH503, Thurlby Thandar Instruments Ltd.) was used to trigger the rf power supply, and the corresponding pulse shape was monitored with an oscilloscope (model V-252, Hitachi Ltd.). Prior to each plasma deposition, the reactor was scrubbed with the detergent, rinsed with acetone, and oven-dried at 200 °C. Next, continuous wave air plasma was run at 0.2 mbar pressure and 50 W for a total of at least 30 min to remove any remaining contaminants from the chamber walls. Nonwoven polypropylene cloth sheets (120 mm × 150 mm) were rolled against the interior chamber walls avoiding any overlap. Following evacuation to the system base pressure, vinylbenzyl chloride monomer (purified using at least five freeze–pump–thaw cycles) vapor was admitted into the chamber at 0.15 mbar pressure for 15 min. Next, electrical discharge was ignited with a pulse duty cycle on-period of 100  $\mu$ s and off-period of 4 ms, in conjunction with 30 W peak power for a duration of 20 min. Upon extinction of the plasma, the chamber was purged with monomer vapor for an additional 15 min. Finally, the system was evacuated to base pressure and vented to the atmosphere. Following coating of one side of the nonwoven polypropylene cloth, it was removed from the chamber, flipped over, and placed into a clean chamber, and the process was repeated for uniform coating of the other side. Subsequently, the pulsed plasma poly(vinylbenzyl chloride) functionalized fabric was cut into four pieces each measuring about 60 mm × 70 mm for further surface functionalization, and the remaining 120 mm × 10 mm strip was used for analysis at this stage.

Each cloth piece was placed into a separate glass vial (28 mL volume) containing 15.2 mg of potassium carbonate (Sigma-Aldrich Ltd.). Subsequently, 27.5 mL of an 8 mmol L<sup>-1</sup> sodium iodide acetone solution (Fisher Scientific UK Ltd.) and either 0.4 mmol L<sup>-1</sup> of the desired calixarene or 1.6 mmol L<sup>-1</sup> 2,6-di-*tert*-butyl-4-(dimethylaminomethyl)phenol (DMAM-phenol; Tokyo Chemical Industry UK Ltd.) were added into each vial. The calixarenes used were either DMAM-calixarene (synthesized according to earlier literature<sup>38,44</sup>) or 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrahydroxycalix[4]arene (*t*Bu-calixarene; 99%, Acros Organics B.V.B.A.). The vials were sealed and rotated at 40 rpm for about 70 h. Subsequently, the functionalized cloth pieces were removed from the vials, rinsed with acetone, followed by water, and finally air-dried.

**2.2. Characterization.** Thickness of pulsed plasma poly(vinylbenzyl chloride) coatings deposited onto silicon wafers (Silicon Valley Microelectronics Inc.) placed at each end of the cloth was measured using a spectrophotometer (NKD-6000, Aquila Instruments Ltd.). Transmittance–reflectance curves (350–1000 nm wavelength) were acquired using a parallel p-polarized light source at 30° incident angle to the substrate. These curves were fitted to a Cauchy model for dielectric materials<sup>45</sup> using a modified Levenberg–Marquardt algorithm (version 2.2 Pro-Optix software, Aquila Instruments Ltd.).<sup>46</sup>

Infrared spectra of the functionalized cloth were recorded using an FT-IR spectrometer (model Frontier IR, PerkinElmer Inc.) equipped with a universal attenuated total reflectance (ATR) accessory (DiComp crystal with the diamond surface (refractive index 2.4) in direct contact with a zinc selenide focusing element, PerkinElmer Inc.), providing a penetration depth in the range of a few micrometers.<sup>47</sup> Samples were pressed against the ATR accessory crystal with a force of 110 N using the instrument software. Acquired spectra were averaged over 20 scans at 2 cm<sup>-1</sup> resolution across the 380–4000 cm<sup>-1</sup> wavenumber range.

X-ray photoelectron spectroscopy (XPS) was carried out using an electron spectrometer (ESCALAB II, VG Scientific Ltd.) fitted with an unmonochromatized Mg K $\alpha$  X-ray source (1253.6 eV) and a concentric hemispherical analyzer. Photoemitted electrons were collected at a take-off angle of 20° from the substrate normal with electron detection in the constant analyzer energy mode (CAE mode pass energy = 20 eV). Experimentally determined instrument

sensitivity (multiplication) factors were C (1s)/O (1s)/N (1s)/Cl (2p) = 1.00:0.35:0.70:0.37, respectively. A linear background was subtracted from core-level spectra and then fitted using Gaussian peak shapes with a constant full width at half-maximum.<sup>48</sup>

For scanning electron microscopy (SEM), nonwoven polypropylene cloth samples were mounted onto carbon disks supported on aluminum stubs and then coated with a thin gold layer (5–10 nm, Polaron SEM Coating Unit, Quorum Technologies Ltd.). Surface topography images were acquired using a scanning electron microscope (model Vega 3LMU, Tescan Orsay Holdings a.s.) operating in the secondary electron detection mode, in conjunction with an 8 kV accelerating voltage and a working distance of 8–11 mm.

Cr(VI) oxoanion aqueous solution concentrations and changes thereof were measured using a UV–Vis–NIR spectrophotometer (Cary 5000, Agilent Technologies Inc.) in conjunction with a quartz cell (10 mm light path length, Suprasil high precision quartz 300, Hellma Analytics GmbH & Co. KG).<sup>49</sup> The previously reported isosbestic point for the light absorbance of Cr(VI) oxoanion solutions at 339 nm was verified by acquiring UV–vis spectra of fixed concentration potassium dichromate solutions at six different pH values ranging between pH 2.25–10.11. Subsequently, a calibration curve was created by measuring the absorbance at 339 nm for 10 different potassium dichromate solutions spanning a hexavalent chromium concentration range of 3 orders of magnitude from 70  $\mu$ g L<sup>-1</sup> (70 ppb) to 70 mg L<sup>-1</sup> (70 ppm). For each solution, division of the measured absorbance at 339 nm by the respective Cr(VI) concentration and light path length (Beer–Lambert Law<sup>50</sup>) yielded the mean molar extinction coefficient value ( $\epsilon = (1.47 \pm 0.04) \times 10^3$  M<sup>-1</sup> cm<sup>-1</sup>—which is in agreement with the literature).<sup>49</sup> Unknown concentrations of Cr(VI) oxoanion solutions collected following water filtration experiments were subsequently calculated by measuring their absorbance at 339 nm in conjunction with the aforementioned experimentally determined molar extinction coefficient ( $\epsilon$ ).

**2.3. Chromium Solution Filtration.** Cr(VI) oxoanion solutions were prepared by dissolving potassium dichromate (>99.0%, Sigma-Aldrich Ltd.) in ultrahigh purity (UHP) water (18.2 M $\Omega$  cm, SELECT Neptune Analytical water polishing unit, Purite Ltd.) and subsequent dilution to the desired concentrations for water purification testing.

Static Cr(VI) oxoanion uptake measurements were made by immersing each of the four pieces of 30 mm × 35 mm DMAM-calixarene-functionalized cloth obtained from different batches (quarters of the initial 60 mm × 70 mm pieces) into 13 mL of aqueous potassium dichromate solution containing 20 mg L<sup>-1</sup> Cr(VI) concentration. The sealed vials were rotated at 40 rpm for 4 h. Subsequently, the Cr(VI) concentrations in the initial and set of four purified solutions were measured.

Flow-through water filtration testing entailed inserting 30 mm × 35 mm pieces of functionalized nonwoven polypropylene cloth into glass Pasteur pipettes (Fisherbrand, 15 cm length, inner diameter 5.6 mm, Fisher Scientific UK Ltd.). Potassium dichromate solutions and real-world water samples were passed through the cloth-loaded Pasteur pipette in the absence of any externally applied pressure (this filtration typically took about 8–15 min for 10 mL volumes of the liquid). By measuring the Cr(VI) concentration in each of the filtrates, the amount of chromium captured in the cloth following each filtration step could be calculated. All measurements were repeated at least twice.

For cloth recycling, the release of Cr(VI) oxoanions captured by DMAM-calixarene fabrics back into solution was carried out by deprotonation of the calixarene amine groups by adding the base in conjunction with displacement of the captured Cr(VI) oxoanions using high concentrations of sodium chloride (ion exchange).<sup>51</sup> A range of regeneration solutions were screened using sodium hydroxide (analytic reagent grade pellets, Fisher Scientific UK Ltd.), sodium bicarbonate (+99%, Acros Organics B.V.B.A.), and sodium chloride (+99.5%, Sigma Aldrich Ltd.). For each regeneration experiment, first 10 mL of a 6 mg L<sup>-1</sup> Cr(VI) oxoanion solution was filtered through

the DMAM-calixarene-functionalized cloth, then, 5 mL of deionized water was filtered through to rinse out any chromium(VI) solution trapped by capillary forces, followed by passing 5 mL of one of the prepared regeneration solutions through the hexavalent chromium oxoanion-loaded cloth. By measuring the Cr(VI) concentration released into each of the filtrates via UV-vis spectroscopy, the amount of Cr(VI) remaining in the cloth could be calculated. The quantity of chromium(VI) released during each solution regeneration was divided by the initial filtrate chromium(VI) uptake by the cloth to determine the release efficiency (percentage) for each recycle.

In order to test the selectivity of functionalized cloth for chromium(VI) oxoanion capture in the presence of competitive aqueous anions, model solutions were prepared using sodium chloride (+99.5%, Sigma-Aldrich Ltd.), monosodium phosphate (Sigma-Aldrich Ltd.), sodium sulfate (+99% anhydrous, Fisher Scientific UK Ltd.), and sodium nitrate (99%, Acros Organics B.V.B.A.).

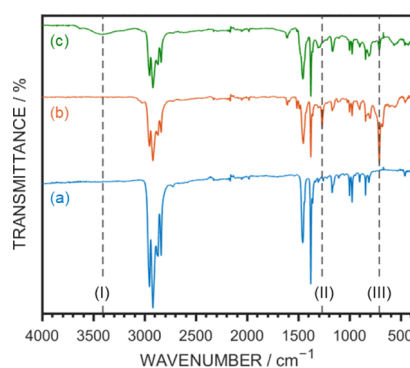
Water collected from a vegetated rainwater pond (Durham University, UK) was used to simulate real-world water containing a natural mixture of ions. The water was collected directly from the pond and filtered using a membrane filter (Whatman Polydisc GW In-Line polyamide filter with 0.45  $\mu\text{m}$  pore size, GE Healthcare Inc.) to remove particulate matter (as stipulated for dissolved chromium analysis by the United States Environmental Protection Agency<sup>52</sup>). Following removal of particulate matter, the pond water was spiked with potassium dichromate solution at known concentrations. Duplicate untreated pond water samples were analyzed to determine the concentration of common naturally occurring anions that may compete with chromate, namely, chloride, phosphate, sulfate, and nitrate (UKAS/ISO17025 accredited, ALS Environmental Ltd.), Supporting Information Table S1. All filtration experiments with pond water were conducted within 3 h of collection.

Real-world industrial wastewater samples were collected in polypropylene bottles (Azlon 30 mL round wide neck bottles, Scilab Ltd.) from two different locations (A and B) in an industrial zone near Jalandhar, India. Filtration experiments and analyses were performed within a week of water sample collection. Particulate matter was removed using a membrane filter (Whatman Polydisc GW In-Line polyamide filter with 0.45  $\mu\text{m}$  pore size, GE Healthcare Inc.) as stipulated for dissolved chromium analysis by the United States Environmental Protection Agency.<sup>52</sup> The total chromium content was measured using inductively coupled plasma optical emission spectroscopy (iCAP 6500, Thermo Fisher Scientific Inc.). Calibration standards were prepared by serial dilution of a 1000 mg L<sup>-1</sup> Cr(NO<sub>3</sub>)<sub>3</sub> reference solution (ROMIL Ltd.). Each sample analysis consisted of three replicate measurements for 13 characteristic chromium wavelengths to ensure that the complex environmental matrix was not causing spectral interferences.

### 3. RESULTS

**3.1. DMAM-calixarene-Functionalized Cloths.** The deposition rate for pulsed plasma poly(vinylbenzyl chloride) films coated onto silicon wafers was measured to be 43.6  $\pm$  3.6 nm min<sup>-1</sup>. All of the nonwoven cloth filters were uniformly coated.<sup>53</sup>

The ATR-infrared spectrum of the uncoated nonwoven polypropylene cloth displays features characteristic for polypropylene, such as broad and intense C-H stretches in the 2830–2970 cm<sup>-1</sup> region and two intense bands at 1454 and 1377 cm<sup>-1</sup> corresponding to the methylene CH<sub>2</sub> and methyl CH<sub>3</sub> bending vibrations, respectively.<sup>54,55</sup> Given the thin nature of the plasma-deposited coatings, spectral features from the underlying nonwoven polypropylene cloth were also within the ATR-Fourier transform infrared technique sampling depth (few  $\mu\text{m}$ ),<sup>47</sup> Figure 1. Fingerprint peaks of the pulsed plasma poly(vinylbenzyl chloride) layer present on the cloth include a characteristic C-Cl stretch absorbance at 708 cm<sup>-1</sup> (III) and a -CH<sub>2</sub>Cl group C-H wag absorbance at



**Figure 1.** ATR-infrared spectra of (a) uncoated nonwoven polypropylene cloth; (b) pulsed plasma poly(vinylbenzyl chloride)-coated cloth; and (c) following functionalization of (b) with DMAM-calixarene. Dashed lines indicate characteristic vibrations: (I) O-H stretch, (II) C-H wag of the -CH<sub>2</sub>Cl group, and (III) C-Cl stretch.

1263 cm<sup>-1</sup> (II).<sup>37,53,55,56</sup> These features became attenuated following reaction with DMAM-calixarene. The absorbance peak associated with the calixarene tertiary amine group C-N stretch (1020–1250 cm<sup>-1</sup>) is difficult to assign unambiguously because of overlap with the underlying polypropylene cloth spectral features.<sup>47,55</sup> However, a broad O-H stretch band at 3406 cm<sup>-1</sup> (I) associated with the unreacted hydroxyl groups on the lower rim of the DMAM-calixarene molecules is clearly visible.<sup>55</sup>

XPS analysis of the pulsed plasma poly(vinylbenzyl chloride)-functionalized cloth prior to reaction with DMAM-calixarene gave surface elemental compositions in good agreement with expected theoretical values, Table 1.<sup>43,53,56,57</sup> This confirms conformal coating of the nonwoven polypropylene fibers. A small amount of aerial oxidation was evident because of the reaction of trapped free radicals within the deposited plasma polymer film.<sup>58–60</sup>

XPS surface elemental composition following DMAM-calixarene functionalization is consistent with predicted theoretical values, Table 1. The detection of 2.4 at. % chloride following DMAM-calixarene reaction is either due to not all surface chloride groups of the pulsed plasma poly(vinylbenzyl chloride) undergoing reaction or the presence of unreacted subsurface chloride groups within the XPS technique sampling depth (0.2–5 nm).<sup>61,62</sup> This would also explain why the measured nitrogen content of the DMAM-calixarene-functionalized cloth is lower than the theoretically expected value for the model reaction mechanism corresponding to each vinylbenzyl chloride repeat unit reacting with one DMAM-calixarene molecule, Scheme 1.

SEM showed that there was no significant swelling of the pulsed plasma poly(vinylbenzyl chloride) films following DMAM-calixarene functionalization, Supporting Information Figure S1.

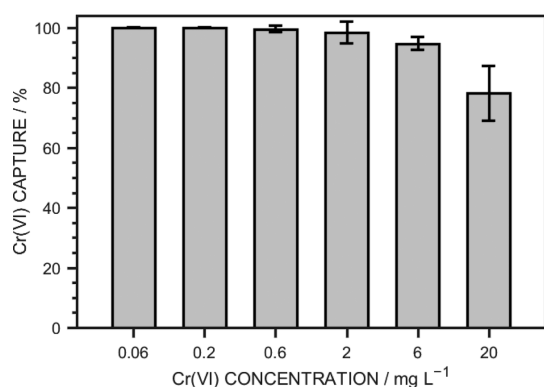
**3.2. Cr(VI) Oxoanion Pollutant Capture.** Static immersion of DMAM-calixarene-functionalized cloth pieces into 13 mL of 2 mg L<sup>-1</sup> Cr(VI) solution (approximately 10 times greater concentration compared to typical real-world pollution levels<sup>33,40,41</sup>) for 4 h removed at least 99% of chromium(VI) oxoanions from solution (concentration dropped to below the UV-vis instrument detection limit of 20  $\mu\text{g}$  L<sup>-1</sup>)—meaning any residual pollutant level met the forthcoming stricter European Union drinking water standards (<25  $\mu\text{g}$  L<sup>-1</sup>).<sup>3</sup> For an even higher starting chromium(VI)

**Table 1.** XPS Compositions for Vinylbenzyl Chloride (VBC, Theoretical); Pulsed Plasma Deposited Poly(vinylbenzyl chloride) (pp-VBC); One Unit of Vinylbenzyl Chloride Reacted with One DMAM-calixarene Molecule (Theoretical See Scheme 1); and Pulsed Plasma-Deposited Poly(vinylbenzyl Chloride) Subsequently Functionalized with DMAM-Calixarene

surface	composition/atom %			
	C	O	N	Cl
VBC (theoretical)	90.0	0.0	0.0	10.0
pp-VBC	89.4 ± 1.6	1.0 ± 1.1	0.0 ± 0.0	9.5 ± 0.4
VBC + DMAM-Calix (theoretical)	86.0	7.0	7.0	0.0
pp-VBC + DMAM-Calix	85.7 ± 1.0	8.3 ± 1.0	3.5 ± 0.4	2.4 ± 0.3

concentration of 20 mg L<sup>-1</sup>, 70 ± 4% of the chromium(VI) oxoanions (6.6 ± 0.4 mg<sub>Cr(VI)</sub> g<sub>cloth</sub><sup>-1</sup>) could be captured by the DMAM-calixarene cloth following an immersion time of 4 h, thereby demonstrating the high overall pollutant capture capacity.

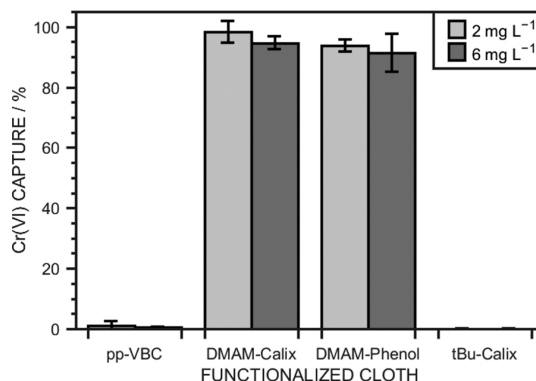
Dynamic flow-through filtration testing of DMAM-calixarene-functionalized cloths utilized a range of different concentration aqueous potassium dichromate solutions, Figure 2. Virtually, all chromium(VI) oxoanion contents were



**Figure 2.** Flow-through Cr(VI) oxoanion capture using DMAM-calixarene-functionalized nonwoven polypropylene cloth as a function of starting pollutant concentration. Potassium dichromate solution (5 mL of) was used for each filtration and repeated five times using fresh pieces of functional cloth. Three different batches of DMAM-calixarene-functionalized cloths were tested. Typical real-world pollution levels correspond to about 0.2 mg L<sup>-1</sup>.<sup>33,40,41</sup>

removed for starting Cr(VI) concentrations below 1 mg L<sup>-1</sup> (i.e., applicable to real-world scenario pollution concentrations which are reported to be up to 100–260 μg L<sup>-1</sup>.<sup>33,40,41</sup>). Even for significantly higher Cr(VI) concentrations (20 mg L<sup>-1</sup>), 78 ± 9% of the aqueous chromium(VI) oxoanion species could be captured in a single pass (corresponds to 2.7 ± 0.4 mg<sub>Cr(VI)</sub> g<sub>cloth</sub><sup>-1</sup>). Variation of the pulsed plasma poly(vinylbenzyl chloride) layer thickness was found to have a negligible effect on the chromium(VI) capture efficiency.

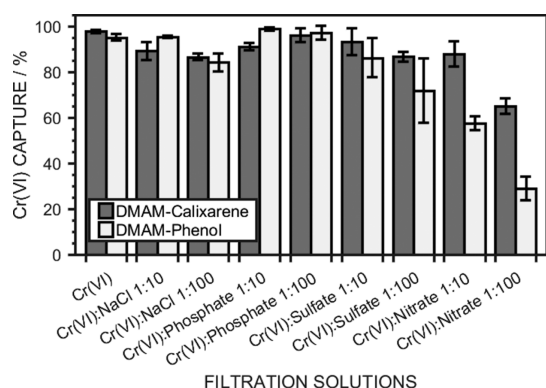
Control Cr(VI) oxoanion filtration experiments were conducted using pulsed plasma poly(vinylbenzyl chloride)-coated nonwoven polypropylene cloth, as well as following functionalization with either calixarene-containing *tert*-butyl groups instead of dimethylaminomethyl groups (*t*Bu-calixarene) or 2,6-di-*tert*-butyl-4-(dimethylaminomethyl)phenol (DMAM-phenol—equivalent to the repeat building block for DMAM-calixarene), Scheme 1 and Figure 3. Virtually, no chromium(VI) oxoanion capture was measured for *t*-Bu-calixarene cloth, whereas DMAM-phenol cloth showed similar levels of removal efficiency as found for DMAM-calixarene cloth—thereby confirming the role of dimethylaminomethyl



**Figure 3.** Flow-through Cr(VI) oxoanion capture efficiencies for pulsed plasma poly(vinylbenzyl chloride)-functionalized nonwoven polypropylene cloth pieces (pp-VBC) and following subsequent reaction with DMAM-calixarene, DMAM-phenol, or *tert*-butyl (*t*-Bu) calixarene, Scheme 1. Potassium dichromate solutions (5 mL) were used with starting Cr(VI) concentrations of 2 and 6 mg L<sup>-1</sup>.

groups for Cr(VI) oxoanion capture. Notable advantages of DMAM-calixarene- compared to DMAM-phenol-functionalized cloths were found with respect to better Cr(VI) oxoanion capture selectivity in the presence of other waterborne pollutants (as described later in Section 3.3).

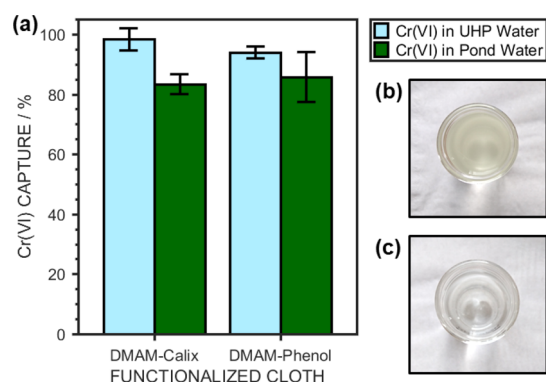
**3.3. Cr(VI) Oxoanion Filtration Selectivity.** Flow-through filtration tests were conducted with solutions containing commonly occurring real-world competitive aqueous anions in order to compare the selectivities between the DMAM-calixarene- versus DMAM-phenol-functionalized cloths for chromium(VI) oxoanion removal, Scheme 1. The competitive anions chosen were chloride (due to its ubiquitous presence in water), phosphate, sulfate, and nitrate (these three because of their structural similarity to chromate CrO<sub>4</sub><sup>2-</sup>). In order to allow for a direct comparison to be made against earlier reported studies,<sup>38</sup> solutions were prepared with similar molar chromium(VI) oxoanion to competitive anion ratios as those employed previously (1:10 and 1:100), Figure 4. The presence of chloride, phosphate, or sulfate ions did not have any significant impact on the chromium(VI) oxoanion removal efficiency for the DMAM-calixarene- and DMAM-phenol-functionalized cloths. However, the chromium(VI) pollutant removal efficiency in the presence of nitrate anions was reduced significantly more for the case of DMAM-phenol-compared to DMAM-calixarene-functionalized cloths. The Cr(VI) oxoanion pollutant capture efficiency of DMAM-calixarene cloth remains high (88 ± 5%) at a Cr(VI)/nitrate ratio of 1:10 (containing about 24 mg L<sup>-1</sup> nitrate—which is similar to 18–20 mg L<sup>-1</sup> nitrate concentration commonly found in real-world scenarios<sup>63</sup>). Hence, the multidentate calixarene macrocycle is key for Cr(VI) oxoanion capture in the presence of other water-borne anions.



**Figure 4.** Flow-through Cr(VI) oxoanion capture efficiencies for pulsed plasma poly(vinylbenzyl chloride)-coated nonwoven polypropylene cloth functionalized with DMAM-calixarene or DMAM-phenol. Solutions (10 mL) were used, each containing  $2 \text{ mg L}^{-1}$  Cr(VI) and either a 1:10 or 1:100 M ratio of competitive anions (chloride, phosphate, sulfate, or nitrate).

### 3.4. Model Real-World Contaminated Wastewater. In

order to further model chromium(VI) oxoanion removal for real-world applications, a water sample was collected from a vegetated rainwater pond. The slightly opaque and greenish pond water was filtered through a  $0.45 \mu\text{m}$  membrane filter to remove particulate matter. Chemical analysis gave the following anion concentrations: chloride =  $4.0 \text{ mg L}^{-1}$ , P (phosphate) <  $0.120 \text{ mg L}^{-1}$ , sulfate <  $4.4 \text{ mg L}^{-1}$ , and N (nitrate) <  $0.7 \text{ mg L}^{-1}$ , Supporting Information Table S1. The pond water was subsequently spiked with potassium dichromate to give a Cr(VI) concentration of  $2 \text{ mg L}^{-1}$ , Figure 5. Compared to the earlier flow-through filtration



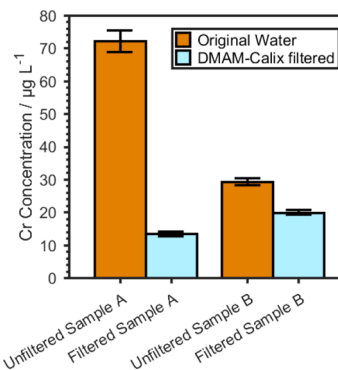
**Figure 5.** Flow-through filtration of  $2 \text{ mg L}^{-1}$  Cr(VI) solution using DMAM-calixarene- and DMAM-phenol-functionalized cloths. Cr(VI) oxoanion solutions were prepared using either UHP water or filtered pond water: (a) filtration efficiency; (b) untreated pond water appearing slightly colored and opaque; and (c) after filtration of particulate matter through the  $0.45 \mu\text{m}$  membrane filter showing clarity (prior to spiking with Cr(VI) oxoanion solution).

experiments performed with UHP water, both DMAM-calixarene- and DMAM-phenol-functionalized cloths captured slightly less Cr(VI) oxoanions from the spiked pond water. However, both functionalized cloth types still managed to remove more than 80% of the chromium(VI) oxoanions from pond water—highlighting the selectivity of the tertiary amine groups in real-world scenarios. The much lower measured real-world nitrate concentration ( $<0.7 \text{ mg L}^{-1}$  N) compared to the earlier modeling studies (Section 2.3) means that the DMAM-

phenol-functionalized cloths also display good Cr(VI) oxoanion capture efficiency, Figures 4 and 5.

### 3.5. Real-World Polluted Industrial Wastewater.

Drainage wastewater containing chromium pollutants was collected from an industrial zone in India. After removal of sludge by filtration through  $0.45 \mu\text{m}$  membrane filters, the water was passed through DMAM-calixarene-functionalized cloth and analyzed for total chromium content via inductively coupled plasma optical emission spectroscopy. Compared to the Cr(VI) oxoanion test solutions employed in the laboratory, the real-world wastewater samples had a fairly low chromium concentration, Figure 6. The chromium concentration for

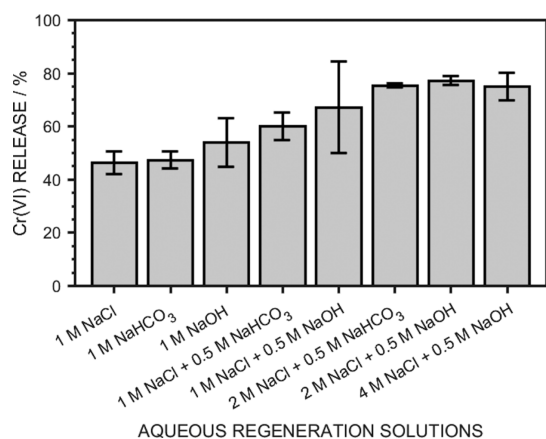


**Figure 6.** Chromium concentration of real-world water samples before and after filtration through DMAM-calixarene cloth for industrial zone locations A and B in India. Collected wastewater (10 mL) was used for each filtration.

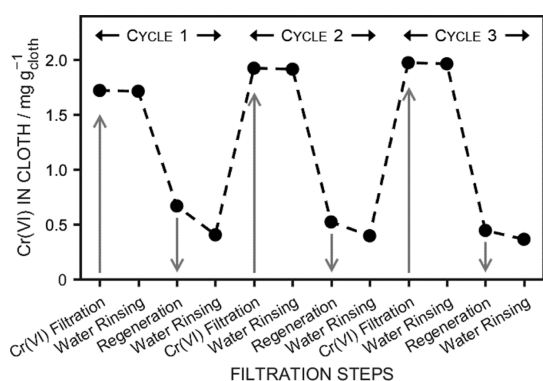
location A was however well above the World Health Organization (WHO) recommended limit of  $50 \mu\text{g L}^{-1}$ , and the concentration for location B was higher than the forthcoming EU limit of  $25 \mu\text{g L}^{-1}$  (provisionally agreed by the European Commission<sup>4</sup>). This indicates that water from both sources could be harmful to the population living nearby if they are exposed to it for a long time. Following passage through the DMAM-calixarene cloth, the chromium concentration in both elutes was lower than  $20 \mu\text{g L}^{-1}$ , confirming that sufficient chromium was successfully removed to make the water safe for human consumption (in compliance with EU regulations). Any remaining chromium following filtration for location B samples is most likely to be the much less toxic cationic Cr(III) species which can also be present in industrial wastewaters.<sup>64</sup>

**3.6. Cloth Recycling.** Cloth regeneration using different permutations of aqueous solutions ( $\text{NaCl}_{(\text{aq})}$  for anion exchange and either a weak base ( $\text{NaHCO}_{3(\text{aq})}$ ) or a strong base ( $\text{NaOH}_{(\text{aq})}$ ) for deprotonation of DMAM-calixarene amine groups) showed that combined salt and base mixtures are the most efficient, Figure 7. Almost 80% Cr(VI) oxoanion release from DMAM-calixarene cloths could be achieved for an aqueous regeneration solution comprising a mixture of 2 M NaCl and 0.5 M NaOH.

In order to demonstrate the scope for repeated usage (recycling) of DMAM-calixarene cloths, the 2 M NaCl and 0.5 M NaOH mixture regeneration solution was used following consecutive Cr(VI) oxoanion capture cycles, Figure 8. Multiple recycling of the functionalized cloth did not lead to any deterioration in Cr(VI) oxoanion capture capacity. In fact, the recycled cloth showed a slightly improved hexavalent



**Figure 7.** Cr(VI) release into solution (filtrate) from Cr(VI) oxoanion-loaded DMAM-calixarene cloth using 5 mL of different aqueous regeneration solutions. The cloths were preloaded using 10 mL of a 6 mg L<sup>-1</sup> Cr(VI) solution followed by rinsing with 5 mL of UHP water (to give an average cloth loading of 1.8 mg<sub>Cr(VI)</sub> g<sub>cloth</sub><sup>-1</sup>).



**Figure 8.** Recycling of DMAM-calixarene-functionalized cloth for Cr(VI) oxoanion capture by alternate passage through the cloth of 10 mL of 6 mg L<sup>-1</sup> Cr(VI) pollutant solution and 5 mL of 0.5 M NaOH + 2 M NaCl regeneration solution, interjected with 5 mL water rinsing steps.

chromium oxoanion uptake during the second and third cycles compared to the first cycle.

#### 4. DISCUSSION

For real-world scenarios, point-of-use filtration is a straightforward and instantaneous water purification technique. Nonwoven polypropylene cloth functionalized with DMAM-calixarene has been shown to effectively capture chromium(VI) oxoanion species from polluted water. Previously reported chromium pollutant capture studies using amine functionalized materials were predominantly performed at low pH values—conditions that are unrealistic in terms of real-world water purification applications and being unfit for human consumption.<sup>26,35,38,65</sup> Effectively, such low pH values promote the capture of Cr(VI) oxoanions through protonated (positively charged) amine groups.<sup>66,67</sup> Literature  $pK_a$  values for tertiary amine groups indicate that they remain charged because of protonation of the Brønsted acidic amine under all but the most alkaline conditions (and certainly under the near neutral conditions employed in the present investigation).<sup>68,69</sup> The efficient capture of chromium(VI) oxoanions by both DMAM-calixarene- and DMAM-phenol functionalized cloths indicates that there is sufficient positive charge on the amine

groups to facilitate the removal of pollutant Cr(VI) oxoanions by filtration without requiring any alteration to the water pH (through usage of chemical additives), Figure 2. Without any alteration of the pH, a very high capture efficiency is attained with up to 100% chromium removal. For a Cr(VI) concentration of 200  $\mu\text{g L}^{-1}$  (a value comparable to real-world chromium pollution levels<sup>33,40,41</sup>), the DMAM-calixarene cloth removes all of the chromium from solution (UV-vis instrument detection limit for quantification is about 20  $\mu\text{g L}^{-1}$ ), thus rendering the water safe to drink (European Union limit for chromium in drinking water is 50  $\mu\text{g L}^{-1}$ , to be lowered to 25  $\mu\text{g L}^{-1}$  in the near future<sup>4,5</sup>).

In order to obtain a lower estimate of Cr(VI) capture capacity, static immersion of DMAM-calixarene-functionalized pieces of cloth into 13 mL of much higher concentration Cr(VI) solutions (20 mg L<sup>-1</sup>) for 4 h gave rise to 70  $\pm$  4% removal of chromium(VI) oxoanion species (6.6  $\pm$  0.4 mg<sub>Cr(VI)</sub> g<sub>cloth</sub><sup>-1</sup>). Given that the actual chromium capture coatings supported onto the nonwoven polypropylene fibers are very thin, the inherent chromium capture capacity of the present system is very high compared to earlier studies.<sup>65</sup> For an upper limit, if one assumes that all of the DMAM-calixarene molecules present in solution during cloth functionalization become tethered to the pulsed plasma poly(vinylbenzyl chloride) coating, then the experimentally measured maximum Cr(VI) uptake value correlates to each calixarene molecule capturing 1.3  $\pm$  0.1 chromium atoms belonging to Cr(VI) oxoanions (Supporting Information calculation). Given that there exists a concentration- and pH-dependent equilibrium between Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, HCrO<sub>4</sub><sup>-</sup>, and CrO<sub>4</sub><sup>2-</sup> oxoanion species in solution, it is feasible to envisage the surface-tethered calixarene macrocycles capturing a combination of chromate and dichromate anions—thus accounting for the estimated chromium to calixarene ratio exceeding 1:1. On this premise, the use of higher surface area support cloths and larger densities of tethered calixarene could provide even greater Cr(VI) oxoanion removal capacities.

Although a variety of molecules containing amine groups are capable of capturing Cr(VI) oxoanions, the comparison between DMAM-calixarene- and DMAM-phenol-functionalized cloths illustrates that the macrocycle cavity shape of calixarenes underpins the higher chromium(VI) oxoanion capture selectivity in the presence of other water pollutants (particularly high concentrations of nitrate), Figure 4. In the European Union, the legal limit for nitrate in drinking water is 50 mg L<sup>-1</sup>.<sup>3</sup> Groundwaters in the European Union contained an average of about 18–20 mg L<sup>-1</sup> of nitrate in the years 1992–2012.<sup>63</sup> The Cr(VI)/nitrate 1:10 solution used in the present study corresponds to a nitrate concentration of about 24 mg L<sup>-1</sup>. At these nitrate concentrations, DMAM-calixarene-functionalized cloth readily captures 88% of Cr(VI) from solution in a single filtration pass (whereas the chromium capture efficiency for DMAM-phenol cloth is much lower at about 57%). This greater capture efficiency of DMAM-calixarene compared to DMAM-phenol can be explained by the concerted orientation of coordinating tertiary amine groups associated with each calixarene cup. The calixarene cavity shape enhances the chelating effect between the tertiary amine groups and the Cr(VI) oxoanions.<sup>44</sup> Experiments with spiked pond water and polluted industrial wastewater samples taken from India have shown that DMAM-calixarene cloth is effective at lowering the chromium concentration in real-world complex water mixtures to levels considered safe for

human consumption (in accordance with the forthcoming lower European Union drinking water standards  $<25 \mu\text{g L}^{-1}$ ).<sup>3</sup>

Recyclability for multiple usage is a crucial factor for real-world applications in relation to remote locations and environmental sustainability. DMAM-calixarene cloths can be used multiple times by rinsing with small quantities of an aqueous solution containing widely available salt (NaCl) for Cr(VI) oxoanion exchange and base (NaOH) for deprotonation of DMAM-calixarene amine groups, Figure 8. In earlier studies, the regeneration of amine groups employed for the capture of Cr(VI) oxoanions was often performed using pure base solutions (following the logic that higher pH values eliminate the protonation of the amine groups).<sup>51,70</sup> In the present investigation, the regeneration efficiency has been further improved by sodium chloride addition to the base solution. In addition to the base-assisted deprotonation of the surface-tethered DMAM-calixarene amine groups, the chloride anions displace Cr(VI) oxoanions being held by the positively charged amine coordination sites in the aqueous phase.<sup>71</sup> Such Cr(VI) oxoanion exchange is realistic, given the significantly higher concentration of chloride anions present in solution compared to chromium(VI) oxoanions during the functional cloth regeneration step.

## 5. CONCLUSIONS

DMAM-calixarene macrocycles can be tethered to pulsed plasma poly(vinylbenzyl chloride)-coated nonwoven polypropylene cloths. These functional cloths provide a high-surface-area filtration medium for flow-through water purification. Toxic chromium(VI) oxoanions can be captured from water with high efficiencies (up to 100% at typical real-world industrial pollution levels). Unlike most other Cr(VI) oxoanion filtration materials, there is complete Cr(VI) oxoanion removal from water (even at low pollutant concentrations) without the need to artificially decrease the pH value. Selectivity remains high in the presence of other common anions found in wastewater, including chloride and those that are structurally similar to chromates (phosphate, sulfate, and nitrate). Furthermore, the captured chromium(VI) oxoanion species can be easily released by rinsing the cloth with a small amount of a NaCl and NaOH mixture solution—thereby providing scope for multiple time reuse of the DMAM-calixarene-functionalized cloths. Removal of toxic chromium(VI) species from real-world polluted industrial wastewaters to meet safe drinking water standards has been demonstrated.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.0c14772>.

SEM images, pond anion concentrations, and chromium captured per tethered DMAM-calixarene calculation (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

Jas Pal S. Badyal — Chemistry Department, Durham University, Durham DH1 3LE, England, U.K.; [orcid.org/0000-0002-5086-5737](https://orcid.org/0000-0002-5086-5737); Email: [j.p.badyal@durham.ac.uk](mailto:j.p.badyal@durham.ac.uk)

## Authors

Vera S. Bieber — Chemistry Department, Durham University, Durham DH1 3LE, England, U.K.; [orcid.org/0000-0002-6952-3892](https://orcid.org/0000-0002-6952-3892)

Egemen Ozcelik — Chemical Engineering Department, Konya Technical University, Konya 42075, Turkey; [orcid.org/0000-0002-2604-4656](https://orcid.org/0000-0002-2604-4656)

Harrison J. Cox — Chemistry Department, Durham University, Durham DH1 3LE, England, U.K.; [orcid.org/0000-0001-5966-6083](https://orcid.org/0000-0001-5966-6083)

Christopher J. Ottley — Earth Sciences Department, Durham University, Durham DH1 3LE, England, U.K.; [orcid.org/0000-0003-1613-5551](https://orcid.org/0000-0003-1613-5551)

Jatinder K. Ratan — Chemical Engineering Department, Dr. B. R. Ambedkar National Institute of Technology, Jalandhar 144011, Punjab, India; [orcid.org/0000-0002-0804-816X](https://orcid.org/0000-0002-0804-816X)

Mustafa Karaman — Chemical Engineering Department, Konya Technical University, Konya 42075, Turkey; [orcid.org/0000-0001-8987-4246](https://orcid.org/0000-0001-8987-4246)

Mustafa Tabakci — Chemical Engineering Department, Konya Technical University, Konya 42075, Turkey; [orcid.org/0000-0003-2941-2191](https://orcid.org/0000-0003-2941-2191)

Simon K. Beaumont — Chemistry Department, Durham University, Durham DH1 3LE, England, U.K.; [orcid.org/0000-0002-1973-9783](https://orcid.org/0000-0002-1973-9783)

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acsami.0c14772>

## Author Contributions

J.P.S.B. and S.K.B. made equal contributions. J.P.S.B. devised the concept. V.S.B. carried out sample preparation. V.S.B., S.K.B., J.K.R., and C.J.O. undertook the water purification studies. H.J.C. performed X-ray photoelectron spectroscopy and scanning electron microscopy. E.O., M.K., and M.T. synthesized DMAM-calixarene. The manuscript was jointly drafted by J.P.S.B., S.K.B., and V.S.B. All authors gave final approval for publication.

## Author Contributions

Data created during this research can be accessed at: <https://collections.durham.ac.uk>.

## Funding

This work was supported by the Royal Society (International Collaboration Award reference IC160021).

## Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We thank T. Davey of the Electron Microscopy Research Services at Newcastle University for assistance with SEM analysis.

## ■ REFERENCES

- (1) Nunez, C. Water Pollution Is a Rising Global Crisis. Here's what You Need to Know. National Geographic 2010. <https://www.nationalgeographic.com/environment/freshwater/pollution/> (accessed Dec 3, 2018).
- (2) United Nations International Decade for Action "Water for Life" Website. <http://www.un.org/waterforlifedecade/quality.shtml> (accessed Dec 3, 2018).
- (3) Council Directive 98/83/EC; Official Journal of the European Commission, 1998. [http://ec.europa.eu/environment/water/water-drink/legislation\\_en.html](http://ec.europa.eu/environment/water/water-drink/legislation_en.html) (accessed March 12, 2018).



- (4) European Commission. Proposal for a Directive of the European Parliament and of the Council on the Quality of Water Intended for Human Consumption. COM(2017) 753 final. Brussels, 2018. [http://ec.europa.eu/environment/water/water-drink/review\\_en.html](http://ec.europa.eu/environment/water/water-drink/review_en.html) (accessed March 12, 2018).
- (5) European Commission Press Release. Commission Welcomes Provisional Agreement to Improve the Quality of Drinking Water and the Access to it. Brussels, 2019. [https://ec.europa.eu/commission/presscorner/detail/en/ip\\_19\\_6830](https://ec.europa.eu/commission/presscorner/detail/en/ip_19_6830) (accessed March 3, 2020).
- (6) Ahalya, N.; Ramachandra, T. V.; Kanamadi, R. D. Biosorption of Heavy Metals. *Res. J. Chem. Environ.* **2003**, *7*, 71–79.
- (7) Ericsson, C. D.; Steffen, R.; Backer, H. Water Disinfection for International and Wilderness Travelers. *Clin. Infect. Dis.* **2002**, *34*, 355–364.
- (8) McGuigan, K. G.; Joyce, T. M.; Conroy, R. M. Solar Disinfection: Use of Sunlight to Decontaminate Drinking Water in Developing Countries. *J. Med. Microbiol.* **1999**, *48*, 785–787.
- (9) Boyle, M.; Sichel, C.; Fernández-Ibáñez, P.; Arias-Quiroz, G. B.; Iriarte-Puña, M.; Mercado, A.; Ubomba-Jaswa, E.; McGuigan, K. G. Bactericidal Effect of Solar Water Disinfection under Real Sunlight Conditions. *Appl. Environ. Microbiol.* **2008**, *74*, 2997–3001.
- (10) Tata Uses Nano Technology for Water Purifier; Centre for Science and Environment. <https://www.cseindia.org/tata-uses-nano-technology-for-water-purifier-852> (accessed on March 20, 2019).
- (11) Dankovich, T. A.; Gray, D. G. Bactericidal Paper Impregnated with Silver Nanoparticles for Point-of-Use Water Treatment. *Environ. Sci. Technol.* **2011**, *45*, 1992–1998.
- (12) Elsanousi, S.; Abdelrahman, S.; Elshiekh, I.; Elhadi, M.; Mohamadani, A.; Habour, A.; ElAmin, S. E.; Elnoury, A.; Ahmed, E. A.; Hunter, P. R. A Study of the Use and Impacts of LifeStraw in a Settlement Camp in Southern Gezira, Sudan. *J. Water Health* **2009**, *7*, 478–483.
- (13) Frechen, F.-B.; Exler, H.; Romaker, J.; Schier, W. Long-term Behaviour of a Gravity-Driven Dead End Membrane Filtration Unit for Potable Water Supply in Cases of Disasters. *Water Sci. Technol.: Water Supply* **2011**, *11*, 39–44.
- (14) Shannon, M. A.; Bohn, P. W.; Elimelech, M.; Georgiadis, J. G.; Mariñas, B. J.; Mayes, A. M. Science and Technology for Water Purification in the Coming Decades. *Nature* **2008**, *452*, 301–310.
- (15) Babel, S.; Kurniawan, T. A. Low-Cost Adsorbents for Heavy Metals Uptake from Contaminated Water: A Review. *J. Hazard. Mater.* **2003**, *97*, 219–243.
- (16) Demirbas, A. Heavy Metal Adsorption onto Agro-Based Waste Materials: A Review. *J. Hazard. Mater.* **2008**, *157*, 220–229.
- (17) Fu, F.; Wang, Q. Removal of Heavy Metal Ions from Wastewaters: A Review. *J. Environ. Manage.* **2011**, *92*, 407–418.
- (18) Hua, M.; Zhang, S.; Pan, B.; Zhang, W.; Lv, L.; Zhang, Q. Heavy Metal Removal from Water/Wastewater by Nanosized Metal Oxides: A Review. *J. Hazard. Mater.* **2012**, *211–212*, 317–331.
- (19) Cruywagen, J. J.; Heyns, J. B. B.; Rohwer, E. A. New Spectrophotometric Evidence for the Existence of  $\text{HCrO}_4^-$ . *Polyhedron* **1998**, *17*, 1741–1746.
- (20) Baruthio, F. Toxic Effects of Chromium and Its Compounds. *Biol. Trace Elem. Res.* **1992**, *32*, 145–153.
- (21) Banks, S. L. The Erin Brockovich Effect: How Media Shapes Toxics Policy. *Environ. Envtl. L. & Pol'y J.* **2003**, *26*, 219–251.
- (22) Cumin, W. Remarks on the Medicinal Properties of Madar, and on the Effects of Bichromate of Potass on the Human Body. *Edinburgh Med. Surg. J.* **1827**, *28*, 295–302.
- (23) Bloomfield, J. J.; Blum, W. Health Hazards in Chromium Plating. *Publ. Health Rep.* **1928**, *43*, 2330–2351.
- (24) Gmelin, C. G. Experiments on the Effects of Baryta, Strontia, Chrome, Molybdenum, Tungsten, Tellurium, Titanium, Osmium, Platinum, Iridium, Rhodium, Palladium, Nickel, Cobalt, Uranium, Cerium, Iron and Manganese, on the Animal System. *Edinburgh Med. Surg. J.* **1826**, *26*, 131–139.
- (25) Borneff, J.; Engelhardt, K.; Griem, W.; Kunte, H.; Reichert, J. Carcinogens in Water and Soil. XXII. Experiment with 3,4-Benzopyrene and Potassium Chromate in Mice Drink. *Arch. Hyg. Bakteriol.* **1968**, *152*, 45–53.
- (26) Stout, M. D.; Herbert, R. A.; Kissling, G. E.; Collins, B. J.; Travlos, G. S.; Witt, K. L.; Melnick, R. L.; Abdo, K. M.; Malarkey, D. E.; Hooth, M. J. Hexavalent Chromium is Cancerogenic to F344/N Rats and B6C3F1 Mice after Chronic Oral Exposure. *Environ. Health Perspect.* **2009**, *117*, 716–722.
- (27) Costa, M. Potential Hazards of Hexavalent Chromate in our Drinking Water. *Toxicol. Appl. Pharmacol.* **2003**, *188*, 1–5.
- (28) Costa, M. Toxicity and Carcinogenicity of Cr(VI) in Animal Models and Humans. *Crit. Rev. Toxicol.* **1997**, *27*, 431–442.
- (29) Connett, P. H.; Wetterhahn, K. E. In Vitro Reaction of the Carcinogen Chromate with Cellular Thiols and Carboxylic Acids. *J. Am. Chem. Soc.* **1985**, *107*, 4282–4288.
- (30) Kortenkamp, A.; O'Brien, P. The Generation of DNA Single-Strand Breaks During the Reduction of Chromate by Ascorbic Acid and/or Glutathione In Vitro. *Environ. Health Perspect.* **1994**, *102*, 237–241.
- (31) Zhitkovich, A.; Voitkun, V.; Costa, M. Formation of the Amino Acid-DNA Complexes by Hexavalent and Trivalent Chromium In Vitro: Importance of Trivalent Chromium and the Phosphate Group. *Biochemistry* **1996**, *35*, 7275–7282.
- (32) Linos, A.; Petralias, A.; Christophi, C. A.; Christoforidou, E.; Kouroutou, P.; Stoltidis, M.; Veloudaki, A.; Tzala, E.; Makris, K. C.; Karagas, M. R. Oral Ingestion of Hexavalent Chromium Through Drinking Water and Cancer Mortality in an Industrial Area of Greece – An Ecological Study. *Environ. Health* **2011**, *10*, 50.
- (33) Naz, A.; Mishra, B. K.; Gupta, S. K. Human Health Risk Assessment of Chromium in Drinking Water: A Case Study of Sukinda Chromite Mine, Odisha, India. *Exposure Health* **2016**, *8*, 253–264.
- (34) Tseng, C.-H.; Lei, C.; Chen, Y.-C. Evaluating the Health Costs of Oral Hexavalent Chromium Exposure from Water Pollution: A Case Study in Taiwan. *J. Cleaner Prod.* **2018**, *172*, 819–826.
- (35) Pehlivan, E.; Cetin, S. Sorption of Cr(VI) Ions on Two Lewatit-Anion Exchange Resins and their Quantitative Determination using UV-Visible Spectrophotometer. *J. Hazard. Mater.* **2009**, *163*, 448–453.
- (36) Sengupta, A. K.; Roy, T.; Jessen, D. Modified anion-exchange resins for improved chromate selectivity and increased efficiency of regeneration. *React. Polym.* **1988**, *9*, 293–299.
- (37) Schofield, W. C. E.; Badyal, J. P. S. Controlled Fragrant Molecule Release from Surface-Tethered Cyclodextrin Host-Guest Inclusion Complexes. *ACS Appl. Mater. Interfaces* **2011**, *3*, 2051–2056.
- (38) Memon, S.; Tabakci, M.; Roundhill, D. M.; Yilmaz, M. Synthesis and Evaluation of the Cr(VI) Extraction Ability of Amino/Nitrile Calix[4]arenes Immobilized onto a Polymeric Backbone. *React. Funct. Polym.* **2006**, *66*, 1342–1349.
- (39) Kirk, T. K.; Ibach, R.; Mozuch, M. D.; Conner, A. H.; Highley, L. Characteristics of Cotton Cellulose Depolymerized by a Brown-Rot Fungus, by Acid, or by Chemical Oxidants. *Holzforchung* **1991**, *45*, 239–244.
- (40) Kazakis, N.; Kantiranis, N.; Kalaitzidou, K.; Kaprara, E.; Mitrakas, M.; Frei, R.; Vargemezis, G.; Tsourlos, P.; Zouboulis, A.; Filippidis, A. Origin of Hexavalent Chromium in Groundwater: The Example of Sarigkiol Basin, Northern Greece. *Sci. Total Environ.* **2017**, *593–594*, 552–566.
- (41) Tiwari, A. K.; De Maio, M. Assessment of Risk to Human Health due to Intake of Chromium in the Groundwater of the Aosta Valley Region, Italy. *Hum. Ecol. Risk Assess.* **2017**, *23*, 1153–1163.
- (42) Ehrlich, C. D.; Basford, J. A. Recommended Practices for the Calibration and Use of Leaks. *J. Vac. Sci. Technol., A* **1992**, *10*, 1–17.
- (43) Wilson, M.; Kore, R.; Ritchie, A. W.; Fraser, R. C.; Beaumont, S. K.; Srivastava, R.; Badyal, J. P. S. Palladium-Poly(Ionic Liquid) Membranes for Permselective Sonochemical Flow Catalysis. *Colloids Surf., A* **2018**, *545*, 78–85.

- (44) Gutsche, C. D.; Nam, K. C. Calixarenes. 22. Synthesis, Properties, and Metal Complexation of Aminocalixarenes. *J. Am. Chem. Soc.* **1988**, *110*, 6153–6162.
- (45) Dieblod, A. C.; Chism, W. W. Characterisation and Metrology of Medium Dielectric Constant Gate Dielectric Films. In *High Dielectric Constant Materials: VLSI MOSFET Applications*; Huff, H. R., Gilmer, D. C., Eds.; Springer-Verlag: Berlin, 2005; p 486.
- (46) Lovering, D. *NKD-6000 Technical Manual*; Aquila Instruments: Cambridge, 1999.
- (47) Technical Note: FT-IR Spectroscopy ATR Accessories; PerkinElmer, 2004. [https://shop.perkinelmer.com/Content/technicalinfo/tch\\_atraccessories.pdf](https://shop.perkinelmer.com/Content/technicalinfo/tch_atraccessories.pdf) (accessed on March 31, 2019).
- (48) Evans, J. F.; Gibson, J. H.; Moulder, J. F.; Hammond, J. S.; Goretzki, H. Angle Resolved ESCA Analysis of Plasma Modified Polystyrene. *Fresenius' Z. Anal. Chem.* **1984**, *319*, 841–844.
- (49) Xia, L.; Akiyama, E.; Frankel, G.; McCreery, R. Storage and Release of Soluble Hexavalent Chromium from Chromate Conversion Coatings Equilibrium Aspects of CrVI Concentration. *J. Electrochem. Soc.* **2000**, *147*, 2256–2262.
- (50) Beer, A. Bestimmung der Absorption des Rothen Lichts in Farbigen Flüssigkeiten. *Annu. Phys. Chem.* **1852**, *162*, 78–88.
- (51) Georgiev, E. M.; Wolf, N.; Roundhill, D. M. Lower Rim Alkylammonium-Substituted Calix[4]arenes as “Proton-Switchable” Extractants for Chromate and Dichromate Anions. *Polyhedron* **1997**, *16*, 1581–1584.
- (52) Laboratory Operations and Quality Assurance Manual 1; U.S. Environmental Protection Agency, Analytical Services Branch, April 24, 2018. [https://www.epa.gov/sites/production/files/2018-05/documents/asb\\_loqam\\_042418.pdf](https://www.epa.gov/sites/production/files/2018-05/documents/asb_loqam_042418.pdf) (accessed on June 12, 2019).
- (53) Morsch, S.; Wood, T. J.; Schofield, W. C. E.; Badyal, J. P. S. A Combined Plasmachemical and Emulsion Templating Approach for Actuated Macroporous Scaffolds. *Adv. Funct. Mater.* **2012**, *22*, 313–322.
- (54) Rjeb, A.; Tajounte, L.; El Idrissi, M. C.; Letarte, S.; Adnot, A.; Roy, D.; Claire, Y.; Périchaud, A.; Kaloustian, J. IR Spectroscopy Study of Polypropylene Natural Aging. *J. Appl. Polym. Sci.* **2000**, *77*, 1742–1748.
- (55) Lin-Vien, D.; Colthup, N. B.; Fateley, W. G.; Grasselli, J. G. *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*; Academic Press, Inc.: San Diego, 1991.
- (56) Schofield, W. C. E.; Bain, C. D.; Badyal, J. P. S. Cyclodextrin-Functionalized Hierarchical Porous Architectures for High-Throughput Capture and Release of Organic Pollutants from Wastewater. *Chem. Mater.* **2012**, *24*, 1645–1653.
- (57) Brown, P. S.; Wood, T. J.; Badyal, J. P. S. Combining Plasmachemical Emulsion-Templating with ATRP to Create Macroporous Lipophilic Surfaces. *J. Colloid Interface Sci.* **2014**, *421*, 44–48.
- (58) Sharma, A. K.; Yasuda, H. Polymerization of Methane. *J. Appl. Polym. Sci.* **1989**, *38*, 741–754.
- (59) Ryan, M. E.; Fonseca, J. L. C.; Tasker, S.; Badyal, J. P. S. Plasma Polymerization of Sputtered Poly(tetrafluoroethylene). *J. Phys. Chem.* **1995**, *99*, 7060–7064.
- (60) Teare, D. O. H.; Schofield, W. C. E.; Garrod, R. P.; Badyal, J. P. S. Rapid Polymer Brush Growth by TEMPO-Mediated Controlled Free-Radical Polymerization from Swollen Plasma Deposited Poly-(maleic anhydride) Initiator Surfaces. *Langmuir* **2005**, *21*, 10818–10824.
- (61) Thomas, H. R.; O'Malley, J. J. Surface Studies on Multi-component Polymer Systems by X-ray Photoelectron Spectroscopy. Polystyrene/Poly(Ethylene Oxide) Diblock Copolymers. *Macromolecules* **1979**, *12*, 323–329.
- (62) Briggs, D. *Surface Analysis of Polymers by XPS and Static SIMS*; Cambridge University Press: Cambridge, 1998; pp 34–39.
- (63) Nitrate in Groundwater in Europe; European Environment Agency, 2019. <https://www.eea.europa.eu/data-and-maps/daviz/groundwater-nitrate-3> (accessed March 09, 2020).
- (64) *Chromium in Drinking-Water Background Document for Development of WHO Guidelines for Drinking-Water Quality*; World Health Organization: Geneva, 2003.
- (65) des Ligneris, E.; Dumée, L. F.; Kong, L. Nanofibers for heavy metal ion adsorption: Correlating Surface Properties to Adsorption Performance, and Strategies for Ion Selectivity and Recovery. *Environ. Nanotechnol., Monit. Manag.* **2020**, *13*, 100297.
- (66) Unnithan, M. R.; Vinod, V. P.; Anirudhan, T. S. Synthesis, Characterization, and Application as a Chromium(VI) Adsorbent of Amine-Modified Polyacrylamide-Grafted Coconut Coir Pith. *Ind. Eng. Chem. Res.* **2004**, *43*, 2247–2255.
- (67) Xu, X.; Gao, B.-Y.; Tan, X.; Yue, Q.-Y.; Zhong, Q.-Q.; Li, Q. Characteristics of Amine-Crosslinked Wheat Straw and its Adsorption Mechanisms for Phosphate and Chromium(VI) Removal from Aqueous Solution. *Carbohydr. Polym.* **2011**, *84*, 1054–1060.
- (68) Rayer, A. V.; Sumon, K. Z.; Jaffari, L.; Henni, A. Dissociation Constants (pKa) of Tertiary and Cyclic Amines: Structural and Temperature Dependences. *J. Chem. Eng. Data* **2014**, *59*, 3805–3813.
- (69) Muller, P. Glossary of Terms Used in Physical Organic Chemistry (IUPAC Recommendations 1994). *Pure Appl. Chem.* **1994**, *66*, 1077.
- (70) Roundhill, D. M.; Koch, H. F. Methods and Techniques for the Selective Extraction and Recovery of Oxoanions. *Chem. Soc. Rev.* **2002**, *31*, 60–67.
- (71) Elwakeel, K. Z. Removal of Cr(VI) from Alkaline Aqueous Solutions using Chemically Modified Magnetic Chitosan Resins. *Desalination* **2010**, *250*, 105–112.