**Dissolved Organic Matter Adsorption from Surface Waters by Granular Composites
versus Granular Activated Carbon Columns: an Applicable Approach**

Ofri B. Zusman¹ Mario L. Kummel¹, José M. De la Rosa² and Yael G. Mishael^{1}*

¹ Department of Soil and Water Science, The R.H. Smith Faculty of Agriculture, Food and Environment, The Hebrew University of Jerusalem, Israel

² Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS-CSIC), Av. Reina Mercedes 10, 41012, Seville, Spain.

Tel: 972-8-948-9171

* Corresponding author

yael.mishael@mail.huji.ac.il

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Abstract

Many new sorbents have been introduced as an alternative for granular activated carbon (GAC), the most common sorbent for dissolved organic matter (DOM) removal. In the current study, we developed an applicable granular composite based on a flocculant commonly employed for drinking water treatment adsorbed to montmorillonite. DOM adsorption from surface waters, Lake Kinneret and Suwannee River, with low and high specific ultraviolet absorption (SUVA), respectively, by composite and GAC columns, was studied. Adsorption of DOM from Suwannee River was significantly higher by the composite column, in comparison to the GAC column, while an opposite trend was obtained for the adsorption of DOM from Lake Kinneret. In-situ regeneration of the columns with a brine solution was extremely efficient and inefficient for the composite and GAC columns, respectively. Adsorption, of both waters, post-regeneration by the composite column was not compromised, while GAC effectiveness decreased. The opposite trend in DOM adsorption from Suwannee River and Lake Kinneret was explained by the different affinities of the sorbents towards various DOM molecules. Distinguishing between different DOM components adsorbed by GAC and the composite was supported by ^{13}C NMR and direct pyrolysis-GC-MS measurements. Furthermore, we demonstrated that the kinetics and adsorption at the equilibrium of five organic molecules to the composite and GAC can be correlated to their chemical-physical properties. Indeed, combining the properties of both sorbents, by integrating them into a single column, yielded higher DOM removal than by the individual columns. Furthermore, since DOM removal by GAC and by the composite, increases, and decreases with temperature, respectively, the integrated column, mitigates the changes in removal, stabilizing the adsorption performance. Such an integrated filter may minimize additional seasonal and water quality fluctuations.

1. Introduction

Dissolved organic matter (DOM), is a heterogeneous mixture of organic molecules that naturally occur in lakes, rivers and marine waters (Stevenson, 1994). The heterogeneity of the DOM is expressed both in the size of the molecules and in their chemical properties. The range of sizes can vary from single amino acid to macromolecule of up to 0.45 μm (Buffle et al., 1982; Thurman, 1985). DOM concentrations, components, and chemical properties vary considerably from one location to another and depend on a large number of variables, such as the origin of organic matter, temperature, ionic strength, pH, microbial community, etc. (Leenheer and Croué, 2003).

Surface water quality is affected by DOM concentrations which may pose undesired color, taste, and odor in drinking water (Kenefick et al., 1992; Mallevialle and Suffet, 1987). Furthermore, it forms complexes with many organic and inorganic pollutants (Aiken et al., 2011; Ding et al., 2019; Lubal et al., 1998; Mei et al., 2016; Senesi and Chen, 1989). In water treatment facilities DOM brings upon several problems, mainly the enhancement of biofilms growth on pipelines and membranes (Herzberg and Elimelech, 2007; Katz et al., 2014; Schneider et al., 2005; Tarchitzky et al., 2013). A health problem related to DOM is that upon chlorination it induces the formation of carcinogenic disinfection by-products (DBPs) like trihalomethanes and haloacetic acid (Fan et al., 2020; Grünwald et al., 2002; Heller-Grossman et al., 2001; Li et al., 2012).

Several studies show that dissolved humic substances, the main DOM component, induce DBPs formation and biofilm generation (Edzwald et al., 1985; Fan et al., 2020; Reckhow et al., 1990). The dissolved humic substances are classically termed fulvic and humic acids based on their solubility in an acidic and basic solution (Stevenson, 1994), but more recently these definitions have been questioned and new approaches have been suggested (Kleber and Lehmann, 2019; Lehmann and Kleber, 2015). Dissolved humic substances are usually characterized by high molecular weight, diverse hydroxyl and carboxyl groups with the majority

deprotonated at ambient pH, and they also bear high aromaticity which is the main contribution to the bulk DOM UV absorption (Stevenson, 1994). Common methods to measure DOM concentrations include total organic carbon (TOC), chemical oxidation demand (COD), and ultraviolet (UV) absorption (Matilainen et al., 2011). A simple and a good expression of the bulk DOM aromaticity is specific UV absorbance (SUVA) (Weishaar et al., 2003). $SUVA_{254}$ is defined as the UV absorbance at a wavelength of 254 nm normalized to the dissolved organic carbon (DOC) concentration.

There are several methods to decrease DOM concentrations such as flocculation/coagulation (Sillanpää et al., 2018), oxidation (Kainulainen et al., 1994; Wenk et al., 2013), membrane (Schäfer et al., 2001; Zhang et al., 2018; Zularisam et al., 2006), and sorption to solid surfaces (Fettig, 1999; Heijman et al., 1999). Activated carbon (AC) is the most excessively employed sorbent in water treatment plants all over the world based on its high surface area and affinity towards a wide range of organic pollutants (Dąbrowski et al., 2005; Gur-Reznik et al., 2008; Moreno-Castilla, 2004; Namasivayam and Kavitha, 2002). Granular activated carbon (GAC) is the common form of AC used in plants for DOM adsorption by filtration, due to its high hydraulic conductivity (Crittenden et al., 1993; Matilainen et al., 2006; Schreiber Bernd et al., 2007). Despite the wide use of GAC, it has many well-known disadvantages. The adsorption efficiency of DOM by GAC columns decreases rapidly, in industrial terms, and usually, after several months it reaches a low and constant removal (Chowdhury et al., 2013). The most common method to recover GAC is by thermal regeneration (approximately 700°C) (Bagreev et al., 2001; Sabio et al., 2004; San Miguel et al., 2002) which requires material transportation, is energy-intensive and sorption capacity is reduced post-regeneration (San Miguel et al., 2002; Sebastiani et al., 1994). The interactions of pollutants with GAC are mainly non-specific (Newcombe, 1999) and large molecules such as DOM might clog the pores (Li et al., 2003; Zhang et al., 2011). The drawbacks of such conventional sorbents have led to the development

of innovative materials including composites (Bhatnagar and Sillanpää, 2017; Kumari and Gupta, 2019; Ruiz-Hitzky et al., 2010).

In the past decades, polymer-clay composites have been widely explored and the high affinity of these sorbents towards several pollutants has been reported (Mukhopadhyay et al., 2020). One of the most common polymer studied is chitosan (Jang and Lee, 2019; Mukhopadhyay et al., 2020; Shi et al., 2019; Vakili et al., 2019) followed by many studies on the fabrication and use of polydiallyldimethylammonium chloride (PDADMAC)-clay composites as sorbents (Ganigar et al., 2010a; Gunister et al., 2013; Radian and Mishael, 2012; Ray et al., 2019; Sabarish and Unnikrishnan, 2018; Zadaka et al., 2008). Studies have also focused on new and advanced polymers for the development of composite sorbents (Ganigar et al., 2010a; Gardi and Mishael, 2018; Jean Serge et al., 2019; Ravi et al., 2020; Shabtai and Mishael, 2018, 2016; Zadaka et al., 2008). However, most of the studies did not address operational and applicable aspects of composite employment for water treatment such as: 1. the composites, as powder, cannot be employed in filtration columns, due to their low hydraulic conductivity 2. the polymers are not cheap and not necessarily approved for treating drinking water use 3. sorbent regeneration was not demonstrated 4. studying pollutant removal from real contaminated water (not synthetic) 5. comparing the removal of the newly developed sorbent to commercial products. To the best of our knowledge, the development and employment of granular composites for DOM adsorption in columns have not been explored.

In the current study, we developed an applicable filter, based on a granular composite sorbent, for the removal of DOM from surface waters. We focused on Lake Kinneret, the only lake in Israel which supplies drinking water to the surrounding city and villages. The composite sorbent is based on the clay-mineral, montmorillonite (MMT), and PDADMAC, a cationic polymer commonly used as a flocculant, approved for drinking water treatment and relatively cheap. We tested the adsorption of DOM from Lake Kinneret by columns of granular PDADMAC-MMT (GPDADMAC-MMT) composite and compared to the adsorption by GAC columns. The raw

water of Lake Kinneret is characterized by relatively very low dissolved humic substances content, only ~30% from the bulk DOM (Barkay-Arbel, 2013) unlike most surface waters in the world, which have a high content of humic substances, >50% (Korshin et al., 1999; Leenheer, 1981; Thurman and Malcolm, 1981). Lake Kinneret has a very low SUVA value (~1) while, surface waters around the world have higher SUVA values (~3) (Ates et al., 2007; Edzwald, 1993; Edzwald et al., 1985). Therefore, the adsorption of Suwannee River DOM, with a more representative SUVA of ~3.6, was explored as well.

2. Materials and methods

2.1 Material

Wyoming Na-montmorillonite SWy-3 (MMT) was obtained from the Source Clays Repository of the Clay Mineral Society (Columbia, MO), Poly(diallyldimethylammonium) chloride (average M_w 400,000-500,000), gallic acid, humic acid, tannic acid, and octanol were purchased from Sigma Aldrich. Toluene was purchased from Gadot-Group. Suwannee River NOM (2R101N) was obtained from the International Humic Substances Society (IHSS).

Lake Kinneret water was obtained from Tiberius filtration plant after undergoing pH adjustment, flocculation with alum and sand filtration prior to filtration by GAC (Table S1). The GAC used in this study was the virgin GAC (Hydraffin 30N, purchased from Benchmark Lt.) and the thermally regenerated GAC (Hydraffin 30N, purchased from Benchmark Lt.) employed in the Tiberius filtration plant.

The pH and the conductivity of the water are 6.6-7 and ~1300 $\mu\text{S}/\text{cm}$, respectively. Suwannee River water was prepared by adding the solid organic matter to distilled water with conductivity and pH adjusted to Lake Kinneret water.

2.2. Analytical Methods

The UV absorbance of the surface waters was measured at 200-300 nm by UV-Vis spectrophotometer (Thermo Scientific, Evolution 300, Waltham, MA). The UV absorption of

Lake Kinneret was measured by a 10 cm quartz cuvette due to a very low absorption by a 1 cm cuvette.

DOC concentrations were determined by a total organic carbon analyzer (Shimadzu, Japan) (range of 3 ppm to 100 ppm) And by laboratory total organic carbon analyzers (Sievers M5310 C, GE Analytical Instruments, USA) (range of 4 ppb to 50 ppm). Zeta potentials were analyzed with a Zetasizer Nano series (Malvern Instruments, UK). The amount of PDADMAC adsorbed on the MMT (0.1 g/g) was calculated by an element analyzer calculated for carbon (FlashEA 1112, Thermo). Thermal gravimetric analysis (TGA) and its derivative analysis (DTG) were performed by the Q500 Thermogravimetric Analyzer (TA Instruments, New Castle, USA.). The heating rate was 35 °C/min using the high resolution-dynamic program (sensitivity 1, resolution 2); temperature ranged from 30 to 800 °C. Infra-Red (IR) spectra were obtained by the FTIR spectrometer (Nicolet Magna-IR-550, Madison WI). The measurement conducted at room temperature with a range of 400-4000 cm^{-1} . GPDADMAC-MMT images were obtained by scanning electron microscope (Jeol 7800) equipped with a secondary electron detector. Imaging conditions were: 3 keV and Magnification of 10,000. Brunauer–Emmett–Teller (BET) surface area of the sorbents was measured by NOVA 220e-Series Surface Area Analyzers (Quantachrome Instruments). The sorbents were added to 9 mm tubes and the temperature was elevated gradually in the rate of 20 C°/1 h in each step, from 20 to 120 C° under vacuum. The adsorbed gas was nitrogen (N_2).

Direct pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) was performed using a double-shot pyrolyzer (Frontier Laboratories, model 2020i) attached to a GC/MS Agilent 6890N system. Cross-polarization magic angle spinning (CPMAS) ^{13}C NMR experiments were carried out with a Bruker Avance III HD 400 MHz spectrometer (Bremen, Germany).

2.3 Experimental Methods

2.3.1 Granular PDADMAC-MMT preparation

PDADMAC-MMT was prepared by mixing a suspension of 5 g/L Na-montmorillonite (10 L) to a 5 g/L PDADMAC solution (2 L) at room temperature (~25°C). The suspension was stirred (with a large magnet) for 24 hours and passed through a Buchner funnel to separate the solid from the suspension. The resulting product is a wet PDADMAC-MMT. To granulate the PDADMAC-MMT, the water content of the wet PDADMAC-MMT was determined by weighing a small amount before and after putting it in an oven overnight at 105°C. Afterward, the entire PDADMAC-MMT sample was weighed and put in an oven at 105°C, until the desired moisture (65-70% water) was reached. The PDADMAC-MMT was then forced through a 2.5 mm grid and re-inserted to the oven for final drying. Finally, the dry granules are sieved to 0.3 - 2.5 mm.

2.3.2 DOM adsorption by filtration

DOM adsorption by columns was performed at room temperature ~25°C. Glass columns (23 cm length, 1 cm diameter) were packed with 14 cm³ sorbents. Lake Kinneret (3 mg/L DOC) or Suwannee River waters (1.8-6.7 DOC, varied for different experiments) were pumped through the columns with a flow rate of 1.7 ml/min, equal to a velocity of 1.3 m/h and an empty bed contact time of 8 min (approximate the same contact time as the Tiberius filtration plant). Every few hours the effluent was collected, filtered with 0.45 µm PTFE syringe filters (simplepure) and DOM removal measured by the UV absorption and DOC concentration of the inlet and effluent. The experiments were performed in minimum duplicates and a maximum of ten repetitions. DOC measurement of Lake Kinneret was performed only for one repetition. Lake Kinneret DOM adsorption experiments, were performed also at controlled temperatures of 6°C (in a walk-in refrigerator), 27°C, and 40°C (in a hothouse). The GAC used in this experiment was the virgin GAC. Column regeneration was obtained by pumping a brine solution (2 M NaCl) through the columns (from the 25 °C experiments) with the same flow rate as the filtration experiments (1.7 ml/min). All of the volumes of the effluent were collected for mass balance and DOM discharged was

measured by UV absorption. DOC measurements were not conducted due to the extremely high conductivity of the sample.

DOM characterization of the sorbents, GAC, and GPDADMAC-MMT, was conducted pre and post DOM adsorption in the columns, by performing Py-GC/MS and ^{13}C NMR measurements. Samples (2 mg) were placed in small crucible capsules and introduced into a preheated micro-furnace at (500°C) for 1 min. The volatile pyrolysates were then directly injected into the GC/MS for analysis. Chromatographic conditions were similar to those described by De la Rosa et al., (2017). The compound assignment was achieved by taking advantage of ion chromatography via single-ion monitoring (SIM) for the major various homologous series and comparison with published data reported in the literature or stored in digital libraries (NIST and Wiley libraries).

All the ^{13}C NMR samples were homogenized and crushed in an Agatha mortar before being placed into zirconium rotors of 4 mm OD with KEL-F-caps. The rotors were spun at 14 kHz. A ramped ^1H -pulse was used during a contact time of 1 ms to circumvent Hartmann-Hahn mismatches. A 90° ^1H -pulse width of 2.4 μs was used for all spectra. The ^{13}C chemical shifts were calibrated relative to tetramethylsilane (0 ppm) with glycine (COOH at 176.08 ppm). Over 10,000 scans were accumulated for each sample, applying a pulse delay between each single scans of 300 ms. The spectra were quantified by integration of the following chemical shift regions (De la Rosa et al., 2018) using MestreNova 10 (Mestrelab Research S.L., Santiago de Compostela, Spain). Processing of the spectra consisted of a Lorentz-to-Gauss apodization (75 Hz), baseline and phase correction. It was impossible to acquire a valid spectrum from the GAC samples, despite changing the delay times, due to the abundance of polycondensed aromatic forms and the lack of effectiveness of the ^{13}C - ^1H cross-polarization. Similarly as described for activated carbons by De la Rosa et al (2018).

2.3.3 DOM adsorption - batch studies

The adsorption of five different dissolved organic molecules, toluene, octanol, gallic acid (GA), tannic acid (TA), Aldrich humic acid (AHA) (post-treatment as required (Kam and Gregory, 2001; Schmit and Wells, 2002)), by GPDADMAC-MMT and GAC was tested at equilibrium (reached within 24 hours). The sorbents (90 mg) were added to solutions (45 ml) of the dissolved organic molecules (12.5 mg/l) and for GA also a concentration of 50 mg/L was measured. The samples were agitated overnight and the adsorption was calculated by measuring the concentrations in the supernatant. GA, TA, and AHA were measured by UV absorption at 262, 276 and 254 nm, respectively. Toluene and octanol were measured by TOC. The kinetics of gallic and humic acid adsorption by powder (<0.14 mm) and granular (0.7-1.4 mm) AC and PDADMAC-MMT were studied. The sorbents (400 mg) were added to 200 ml solutions (12.5 mg/L) of gallic and humic acid. Samples were collected every couple minutes (0-400 min) and immediately filtered with 0.45 μ m PTFE syringe filters (simplepure). Dialysis experiment conducted with a 1000 D dialysis bags, filled with Lake Kinneret water (25 mL) inserted into DW (5 L). The DW was replaced every 2 days for 6 days. The absorption of the water inside the dialysis bag was measured at 254 nm.

3. Results and Discussion

3.1. PDADMAC-MMT characterization

PDADMAC-MMT composites, as a powder and as granules, were chemically and physically characterized by zeta potential, BET, TGA, FTIR, and SEM measurements (Figure 1). Zeta potential of MMT is -34 mV and upon PDADMAC adsorption (0.1 g/g) charge reversal was reached for the PDADMAC-MMT composite, +30 mV. The BET surface area of MMT is ~30 m²/g as reported in the literature (Barbier et al., 2000; Levy et al., 2019) while the BET of the PDADMAC-MMT (no significant difference between the powder and granules) was lower, 14-15 m²/g. The reduction in BET surface area was attributed to high polymer adsorption on the MMT

surface (Levy et al., 2019), since the BET surface area measurements, analyze the adsorption of nitrogen (N_2), which has little interaction with the polymers and high interactions with the clay surface (Carrado, 2000; Mayer, 1999). Despite the difference at the macro-scale, between the PDADMAC-MMT powder (0.04-0.14 mm) and the granules (1-2 mm), no significant changes were observed at the micro-scale, as observed from the SEM images (Figure 1C). The DTG profiles of the powder and granules were identical with a weight loss between 200- 600 °C (does not appear in the MMT sample), associated with the adsorbed polymer (~0.1 g/g). Hygroscopic water loss at the low-temperature ranges (~30-130 °C) was lower for the PDADMAC-MMT than for the MMT sample, indicating water exclusion by PDADMAC adsorption. The third peak of weight loss at the region of 600-750 °C correlates to the dehydration of structural water. As expected, the FTIR spectra of the powder and granules were identical (Figure S1) and similar to spectra reported in the literature for the adsorption of PDADMAC to MMT mainly via electrostatic interactions of the quaternary amine with the negatively charged clay surface

3.2. Surface water filtration by GPDADMAC-MMT and GAC columns

The removal of DOM from Suwannee River (Figure 2A) and Lake Kinneret (Figure 4A), with high (3.6-4.2) and low (~1) SUVA, respectively, by filtration with GPDADMAC-MMT and GAC columns, was investigated. Following the filtration, in-situ regeneration of GAC and GPDADMAC-MMT by brine (Figures 2B and 4B) and ex-situ regeneration of GAC by thermal reactivity were executed. Finally, the performance of the sorbents post-regeneration was demonstrated (Figures 2C and 4C).

3.2.1 Adsorption of DOM from Suwannee River by GAC and GPDADMAC-MMT columns

DOM removal from Suwannee River (adjusted to the DOC concentration of Lake Kinneret) was constantly high by the GPDADMAC-MMT column throughout the experiment, while the removal by the GAC column decreased dramatically (Figure 2A). The decrease in DOM removal by GAC

columns is well documented and explained in terms of pore-clogging by macromolecules (Li et al., 2003; Zhang et al., 2011). The sharp decrease in removal, obtained by UV_{254} absorption, suggests that there is a very high percentage of such macromolecules, mainly dissolved humic substances, among the UV absorbent molecules in the bulk DOM. The relatively poor DOM removal performance by the GAC, despite its high surface area, can also be explained by the lack of surface charge (Figure 1A), expressed by, the absence of electrostatic attraction. On the other hand, the removal by the GPDADMAC-MMT column was high since these dissolved humic substances form strong electrostatic interactions with the positively charged GPDADMAC-MMT.

The regeneration of the GPDADMAC-MMT columns by rinsing with brine solution was nearly 70% (of the adsorbed material), whereas, GAC regeneration by the brine was extremely low, ~6% (commercially, GAC is efficiently regenerated by thermal treatment) (Figure 2B). The high desorption from the GPDADMAC-MMT column, induced by an abrupt increase in the ionic strength, supports the suggestion that the main adsorption mechanism is electrostatic, while GAC adsorbed DOM molecules thorough other chemical and physical interactions. An important result is that nearly two-thirds of the regeneration occurs within the third pore volume, which is only 0.75% of total pore volume initially passed through the column. The performance of the GPDADMAC-MMT column post-regeneration was not compromised while the efficiency by thermally regenerated GAC (common regeneration method) decreased significantly (Figure 2C). It is well-known that the thermal regeneration of GAC decreases the surface area and increases the presence of acidic groups (Cazetta et al., 2013; Cheng et al., 2007; Guo and Du, 2012; Sebastiani et al., 1994). A negative charge surface will repel the negatively charged DOM molecules.

Many surface waters in the world have a higher concentration of DOM than Lake Kinneret (2-3 DOC mg/L), therefore, the removal of DOM from Suwannee River with higher DOC concentrations (~7 mg/L DOC) (Figure 3), was explored. As obtained for the low Suwannee River DOC concentration, DOM removal, measured by UV_{254} absorption was superior by the GPDADMAC-MMT columns in comparison to the degree of removal by GAC columns. Higher DOM removal by the GPDADMAC-MMT column was also determined by quantifying DOC concentrations in the inlet and effluent waters of the columns. Important to notice, the degree of DOM removal measured by UV_{254} absorption is nearly the same as the degree of removal measured by DOC concentration indicating that the fraction of UV absorbing molecules dominate the Suwannee River DOM.

3.2.2 Adsorption of DOM from Lake Kinneret by GAC and GPDADMAC-MMT columns

DOM removal by filtration, from Lake Kinneret (2-3 mg/L DOC), obtained through UV_{254} absorption and through DOC measurements showed an opposite trend than that observed for the removal of Suwannee River DOM (Figure 2A) i.e., higher removal by GAC columns vs. GPDADMAC-MMT columns (Figure 4A). This opposite trend can be explained in terms of the different SUVA values, high and low, for Suwannee River and Lake Kinneret, respectively. The high SUVA of Suwannee River indicates that a large fraction of the DOM is composed of dissolved humic substances as reported (Croue et al., 2000; Korshin et al., 1999; Watson et al., 2019), which have a high attraction to the positively charged GPDADMAC-MMT sorbent. Dissolved humic substances are characterized by high molecular weight, diverse hydroxyl and carboxyl groups with the majority deprotonated at ambient pH and also bear high aromaticity which is the main contribution to the bulk DOM UV absorption (Stevenson, 1994). In contrast, the low SUVA of Lake Kinneret indicates that only a small fraction of the DOM is composed of dissolved humic substances, explaining the low removal by the GPDADMAC-MMT. On the

other hand, GAC adsorbs efficiently nonpolar, aromatics and small DOM molecules (Freihardt et al., 2017; Katsigiannis et al., 2015; Lamichhane et al., 2016; Srivastava et al., 2006), due to its porosity and its relatively hydrophobic surface. According to studies, the majority of Lake Kinneret DOM is less than 1000 Dalton (Barkay-Arbel, 2013; Dubowski et al., 2018). In addition, just 30% of the DOC is humic acids (Barkay-Arbel, 2013) and the main fraction is aliphatic (Heller-Grossman et al., 1993), explaining the high removal by GAC. To support the literature, we dialyzed the water from Lake Kinneret with dialysis bags of 1000 Dalton and indeed, no UV absorption was measured inside the bags after 5 days in which the water was replaced twice. Similar to the regeneration by brine solution of the GPDADMAC-MMT column post-Suwannee River filtration (Figure 2B), the regeneration post-Lake Kinneret filtration was very effective (97% discharged), while GAC regeneration was very low (7% discharged) (Figure 4B). Accordingly, nearly two-thirds of the regeneration occurs within the fifth pore volume which is 1.25% from the total pore volumes pass through the column. Refiltration of Lake Kinneret water through the regenerated GPDADMAC-MMT column provided the same degree of DOM removal (obtained by UV_{254} absorption) as obtained by the virgin column, while, DOM removal by the thermally regenerated GAC column, impaired and the filtration efficiency decreased (Figure 4C). Unlike the dramatic reduction in the Suwannee River DOM adsorption by the thermally regenerated GAC, the compromise in the adsorption of Lake Kinneret DOM was moderate. The content of humic substances in Lake Kinneret is low and therefore, the reduction in DOM removal, due to electrostatic repulsion between the humic substances and the thermally regenerated GAC, is not as dramatic.

The main conclusions from comparing Lake Kinneret and Suwannee River filtration, by both sorbents, are that for surface waters with high SUVA values, filtration by GPDADMAC-MMT columns is an excellent alternative to virgin GAC and all the more so to thermally regenerated

GAC. However, for waters with low SUVA values, adsorption by virgin GAC is efficient, somewhat compromised once the GAC is thermally regenerated but higher than by the GPDADMAC-MMT.

These opposite trends in DOM adsorption from Suwannee River and Lake Kinneret may be explained by different affinities of various DOM molecules, with different physical-chemical properties, towards the sorbents. To test this hypothesis, the sorbents GAC and GPDADMAC-MMT were characterized by ^{13}C NMR and Py-GC/MS measurements, pre and post DOM adsorption.

3.3 Characterization of DOM adsorbed by GAC and by the GPDADMAC-MMT: ^{13}C NMR and Py-GC/MS measurement

The ^{13}C NMR spectra and Py-GC/MS of pre and post-DOM adsorbed by GPDADMAC-MMT are shown in Figure 5. The pyrochromatograms of GAC were composed of small peaks corresponding to benzene, toluene, styrene, alkylbenzenes, n-alkanes and a wide unresolved complex mixture (HUMP) typically composed by saturated/unsaturated hydrocarbons and highly condensed aromatic compounds (Liu et al., 2005; Ventura et al., 2008).

The GAC adsorbed with DOM included also short alkylbenzenes and long-chain n-alkanes.

The pyrochromatograms of GPDADMAC-MMT were composed of a series of heterocyclic (N) aromatic compounds. Particularly, series of methyl pyrroles, methyl indoles and methyl carbazoles, which are derived from the cracking and linking produced during the pyrolysis of the diallyldimethylammonium. The GPDADMAC-MMT adsorbed with DOM exhibited also carbazoles and anthraquinone, which are absent at the pre-DOM adsorbed GPDADMAC-MMT (Figure 5A).

The different detected organic compounds, originating from the adsorbed DOM on the GAC and the GPDADMAC-MMT samples, support our suggestion that different fractions of the DOM adsorbed to the sorbents.

¹³C NMR spectra of Suwanee River DOM is characterized mainly by aliphatic carbon (0-90 ppm), aromatic carbon (100-160 ppm) and by carboxylic carbon (~180 ppm). While there is an overlap at the aliphatic region between pre and post-DOM adsorbed GPDADMAC-MMT, the aromatic and the carboxylic region are present only at the post-DOM adsorbed GPDADMAC-MMT (Figure 5B). Indeed, the sample of the GPDADMAC-MMT adsorbed with DOM includes carboxyl-C and aromatic-C, supporting the adsorption of humic-like substances by the GPDADMAC-MMT. ¹³C NMR spectra for GAC are not presented since tuning of the GAC samples was not possible due to the high reflection of the excitation energy.

3.4 Adsorption of dissolved organic molecules at equilibrium by GAC and GPDADMAC-MMT

To directly test the different sorbent affinities, we measured the adsorption at the equilibrium of five dissolved organic molecules (12.5 mg/L) with different physical-chemical properties such as size (MW), charge (pKa), polarity (polar surface area), hydrophobicity (log K_{ow}), and aromaticity (number of rings), by the two sorbents (Figure 6A). The positive GPDADMAC-MMT surface adsorbed benzene, which has no polar sites or charge, with very low affinity (3% removal). Octanol has one alcohol group, increasing its adsorption to 27% due to the interactions with the negative dipole and therefore the adsorption of TA, a polyphenol molecule, further increases reaching 80% removal. The removal of negatively charged molecules, GA and AHA were complete (results not shown for GA). The adsorption to GPDADMAC-MMT clearly increases as the charge, polarity, and MW of the molecules increases due to electrostatic interactions and enthalpy gain, respectively (Radian et al., 2010).

The adsorption of these molecules to GAC demonstrates a different trend. GAC tends to adsorb small, aromatic and hydrophobic molecules. Benzene has all three characters and thus its removal is complete. GA is a small and aromatic molecule and although it is charged, it is

successfully removed by GAC. Octanol is a small aliphatic molecule thus adsorbed well (86% removal). TA and AHA are big polar and charged molecules, respectively, and therefore their adsorption is low-mediocre (28 and 47%, respectively).

The adsorption at the equilibrium of bulk DOM from Lake Kinneret and Suwannee River waters by GAC and by GPDADMAC-MMT, quantified by UV absorption and by DOC measurement (Figure 6B), follows the same trends as the filtration (Figure 2A, Figure 4A). The SUVA of the treated waters, Lake Kinneret or Suwannee River, by GPDADMAC-MMT was lower (SUVA 0.6 and 3.1, respectively) than the initial SUVA (1 and 3.7, respectively) since the GPDADMAC-MMT mainly adsorbed dissolved humic substances which usually contribute to the UV absorption. The SUVA of the treated waters, Lake Kinneret or Suwannee River, by GAC was lower (SUVA 0.3) and higher (SUVA 6.2), respectively, than the initial SUVA. As mentioned above, the majority of the UV absorbing molecules of Lake Kinneret are small, therefore well adsorbed by GAC explaining the reduction in SUVA. On the other hand, the majority of the UV absorbing molecules of Suwannee River are large and negatively charged, therefore not well adsorbed by GAC explaining the dramatic increase in SUVA.

3.5 Adsorption kinetics of dissolved organic molecules to GAC and GPDADMAC-MMT

The efficiency of molecule removal by adsorption to a sorbent is strongly dominated not only by the pollutant's affinity to the sorbent and by the capacity of the sorbent at equilibrium, but also by the kinetics of pollutant adsorption. More specifically the efficiency of filtration is time-dependent.

The adsorption kinetics of GA and AHA, with high affinity at equilibrium, to GAC and GPDADMAC-MMT, respectively, was studied (Figure 7A). Equilibrium was reached within 400 min and the trends fit those measured at equilibrium (Figure 6A). The advantage of AHA adsorption by the GPDADMAC-MMT is clear, while the advantage of GA adsorption by GAC is

somewhat less pronounced since its concentration is lower in the kinetics experiment (12.5 mg/L vs. 50 mg/L).

The kinetics of GA adsorption (normalized to maximum adsorption) is nearly the same by both sorbents (Figure 7C), but interestingly the kinetics of AHA adsorption by GAC is faster than its adsorption by the GPDADMAC-MMT (Figure 7B). This difference can be explained by the size of the organic molecules. Inhibition in the adsorption of macromolecules due to penetration into mineral pore systems has been reported (Ganigar et al., 2010b; Mishael et al., 2007). The slower adsorption kinetics of AHA (500-50000 Å) (Esfahani et al., 2015) to the GPDADMAC-MMT can be explained by its penetration into the granule porous system with adsorption also on internal surfaces and not only on the external surface. On the other hand, AHA may be excluded from the internal pore system of GAC due to size limitation. The kinetics of GA adsorption is nearly the same by both sorbents, since gallic acid is significantly smaller than AHA, and it can penetrate not only into the GPDADMAC-MMT but also into the pore system of GAC. To test whether the inhibition of AHA adsorption by GAC is due to size exclusion by the pore system of the granules, the kinetics of AHA adsorption by powder AC (PAC) was studied. As seen in Figure 7B the kinetics of AHA adsorption to GAC and PAC are identical, supporting no penetration of AHA in the pore system of the AC granules. The slower adsorption kinetic of AHA by the granular PDADMAC-MMT vs. the powder PDADMAC-MMT further supports our suggestion that the AHA penetrates the pore system of the GPDADMAC-MMT. Based on this concept, the kinetics of GA is slower to both granulated sorbents, GAC, and GPDADMAC-MMT, in comparison to its kinetics by the powder sorbents, as seen in Figure 7C.

3.6 Adsorption of DOM by integrated columns of GPDADMAC-MMT and GAC

In order to improve operational DOM removal from surface waters with low SUVA value such as Lake Kinneret, we propose employing more than one sorbent. We hypothesized that integrating GPDADMAC-MMT and GAC will yield optimal bulk DOM removal since each sorbent has a high

affinity towards DOM molecules with different physical-chemical properties. This suggestion, is supported by 1. the high and low regeneration, with a brine solution, of GPDADMAC-MMT and GAC, respectively (Figure 2B and 4B) 2. the high and low DOM adsorption from Suwannee River by GPDADMAC-MMT and GAC columns, respectively, vs. the low and high DOM adsorption from Lake Kinneret by GPDADMAC-MMT and GAC columns, respectively (Figure 2A and 4A), 3. The ^{13}C NMR and Py-GC-MS measurements performed, pre and post-DOM adsorption by the sorbents (Figure 5), and 4. The correlation between the physical-chemical properties of the adsorbing organic molecules and the sorbents (Figure 6A).

It must be emphasized that most of the operational time in water treatment plants, water filtration is by thermally regenerated GAC columns. For example, the GAC columns in the water treatment plant of Lake Kinneret are thermally regenerated every 4 years, the plant has been operating for 17 years, so for 2/3 of the operational time, regenerated GAC columns are in use with only 25% removal on average.

To test the suggestion that integrating GPDADMAC-MMT and GAC will yield optimal DOM adsorption, columns were filled with regenerated GAC and GPDADMAC-MMT (1/1 V/V) (Figure 8). Indeed, for Lake Kinneret (low SUVA water), the integrated columns demonstrated superior performance with 90% DOM removal, while the removal by regenerated GAC or GPDADMAC-MMT was about 75 and 40%, respectively. Three designs of integrated columns were tested, a homogenizes mix, a layer of GAC followed by a layer of GPDADAMAC-MMT and vice versa. The performance of the three designs was identically high.

The performance of the integrated column for DOM removal from Suwannee River (high SUVA water) was also tested (Figure S2). DOM removal by the integrated column was nearly the same as the removal by the GPDADMAC-MMT column. As discussed, the DOM of Suwannee River has a very large fraction of humic substances with a very high affinity towards the

GPDADMAC-MMT and low affinity towards GAC (Figure 2A). Therefore, DOM removal from surface waters with high SUVA will be more efficient by a GPDADMAC-MMT column.

The integrated column may have additional advantages based on the combination of two materials with different characteristics. For example, the adsorption of DOM to GAC increases moderately when the temperature rises (Schreiber et al., 2007, 2005) while the adsorption of organic molecules to composites in many cases decreases (Dinu and Dragan, 2010; Ma et al., 2012; Ye et al., 2009). Therefore, an integrated column would minimize seasonal filtration performance fluctuations.

The adsorption of Lake Kinneret DOM by the GAC column improved moderately as the temperature increased from 6 to 27 and 40°C (Table 1), simulating temperatures throughout the year. In contrarily, DOM adsorption by the GPDADMAC-MMT column decreased as the temperature increased. Indeed, DOM adsorption by the integrated column, averaged out the changes in removal, stabilizing the filtration performance.

4 Conclusions

- We developed an applicable polymer-clay composite sorbent, based on a flocculant commonly employed for drinking water treatment, for the adsorption of DOM from surface waters. The composite was granulated and therefore can be applied in filtration columns unlike most composites developed which are powders. We demonstrated efficient in-situ composite column regeneration with a brine solution, and also demonstrated efficient refiltration.
- DOM adsorption, from Suwannee River, by the composite column, was superior to that of the GAC column. An opposite trend was observed for the adsorption of DOM from Lake Kinneret i.e., higher removal by GAC vs. the composite columns. This opposite

trend was explained in terms of the different water compositions and SUVA values, high and low, for Suwannee River and Lake Kinneret, respectively.

- We demonstrated that the kinetics and adsorption at equilibrium of five organic molecules to the composite and GAC can be correlated to their chemical-physical properties. Therefore, combining the properties of both sorbents, by integrating them into a single column, yielded higher DOM removal than by the individual columns.
- An additional advantage of the integrated column was its ability to minimize seasonal filtration performance fluctuations. Since DOM removal by GAC and by the composite, increases, and decreases with temperature, respectively, the integrated column, averaged out the changes in removal, stabilizing the filtration performance.
- We suggested that the advantage of the integrated column will manifest itself also upon changes in water chemistry (pH, salinity, nutrients, etc.), DOM composition, and concentrations. The approach of integrating different sorbents for the filtration of complex water composition should be considered.
- Finally, from an economic point of view, the composite has a meaningful advantage since the cost of GAC (employed in Tiberius filtration plant) is 3.31 \$/Kg not including the costs of ex-situ thermal regeneration which are very high. On the other hand, the estimated cost of the composite including the materials and the granulation process is 2.56 \$/Kg i.e., 23% less than GAC. Also, the successful in-situ regeneration by a brine solution, we demonstrated, should be extremely cheap.

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DOM removal (%) by	Water passed		6 °C	27 °C	40 °C	Δ Removal
	volume (ml)	Pore volumes				
GAC	202	24	88	90	96	8
	2218	264	86	88	92	6
	2923	348	86	89	91	5
	4637	552	83	83	89	6
GPDADMAC- MMT	202	21	54	34	13	-41
	2218	236	51	46	37	-14
	2923	311	54	47	38	-16
	4637	494	52	46	39	-13
Integrated column	202	23	92	89	92	0
	2218	249	85	90	88	3
	2923	329	87	90	85	-2
	4637	521	82	87	83	1

Figure 1 - Characterization of PDADMAC-MMT and AC: (A) physical properties (B) DTG analysis profile of MMT and PDADMAC-MMT, (C) SEM images of granules and powder PDADMAC-MMT

^a (Skibinski et al., 2018), ND - not determined

Figure 2 – (A) Removal of DOM from Suwannee River (~2 mg/L DOC) by filtration with GPDADMAC-MMT and GAC columns, (B) regeneration of the columns with brine, and (C) refiltration of the brine regenerated GPDADMAC-MMT and thermally regenerated GAC.

Figure 3 – Removal of DOM from Suwannee River (~7 mg/L DOC) by filtration with GPDADMAC-MMT and GAC columns calculated by measuring UV absorption at 254 nm and by DOC content

Figure 4 – (A, D) Removal of DOM from Lake Kinneret (~2 mg/L DOC) by filtration with GPDADMAC-MMT and GAC columns calculated by measuring UV absorption at 254 nm and also (D) by DOC content, (B) regeneration of the columns with brine, and (C) refiltration of the brine regenerated GPDADMAC-MMT and thermally regenerated GAC.

Figure 5 – Sorbent characterization pre and post-DOM adsorption by (A) Py-GC/MS (B) ^{13}C NM

Figure 6 – The adsorption, at equilibrium, by GPDADMAC-MMT and GAC of (A). dissolved organic molecules (12.5 mg/L), toluene, octanol, GA (50 mg/L), TA, AHA, (B) DOM from Lake Kinneret and Suwannee River and the effect on the SUVA of the waters.

Figure 7 – (A) Kinetics of AHA and GA removal by GPDADMAC-MMT and GAC, Kinetics of removal (adsorbed (mg/g) per adsorption at equilibrium (mg/g) (Q_t/Q_e)) by powder and granular PDADMAC-MMT and AC (B) of AHA and of (C) GA.

Figure 8 - Removal of DOM from Lake Kinneret by filtration with GPDADMAC-MMT, regenerated GAC and integrated (regenerated GAC mixed with GPDADMAC-MMT) columns.

Highlights

- Drinking-water treatment cationic-polymer, was adsorbed to clay and granulated as a sorbent
- DOM filtration from high SUVA water by composite vs. GAC columns is very efficient
- The composite and GAC sorbents target different DOM molecules
- DOM filtration from low SUVA water by integrated column, composite+GAC, is efficient
- Integrated column mitigates temperature fluctuation effects, stabilizing performance

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☒ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Yael Mishael