

# Nanocomposite Sorbent for Organic Matter Removal from Contaminated Water

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## **Abstract**

The global water crisis has deepened, with drop of freshwater resources around the world quality of the water in constant decline. Surface water pollution is caused by a wide variety of natural and anthropogenic substances found in water in different concentrations. Dissolved organic matter (DOM) is a mixture of natural molecules found in all surface water sources. At high concentrations, DOM causes an undesirable odor, color and taste in the drinking water and even reacts with chlorine creating harmful substances that affect human health, some found to be carcinogenic. In water treatment facilities, DOM removal encounters several problems, mainly the enhancement of biofilms growth on pipelines and membranes, which diminishes the efficiency of the facilities .

In my research, I have developed and characterized a novel, hybrid, clay polymer nanocomposite, for efficient and rapid DOM removal. I examined the adsorption kinetics of a granular and powdered nanocomposite. A comparison was made between the nanocomposite and the most common industrial sorbent, activated carbon in the two sorbents forms (powder and granules).

The results of the study show that the composite is an extremely efficient sorbent for DOM removal and demonstrates fast adsorption kinetics. In addition, the nanocomposite was superior to the activated carbon, with a four times higher efficiency.

This research examined an applicable approach for industrial solution for DOM removal. The study has shown that clay polymer nanocomposites can be an alternative advantageous sorbent for water purification.

## **1. Introduction**

### **1.1 Global Water Crisis and Deterioration of Water Quality**

Although 70% of the earth is covered with water, only approximately 3% can be used for drinking (fresh water). Approximately two-thirds of the fresh water are found in icebergs that are not immediately accessible for human use. In addition, urbanization, climate changes and increased irrigation use have led to water shortage in various regions across the globe. As a result, there is a true concern that within the next few decades, humankind may suffer from an acute water crisis that will primarily impact low-income populations in developing countries.<sup>1</sup> Even Nowadays a shortage of drinkable water has already led to political instability and to increased morbidity of both children and adults. The water crisis is beginning to take a toll in a few areas of the State of Israel. The deepening crisis raises the importance and awareness of water supply and quality and has promoted research, which aims to find practical solutions for water contamination, including treatment of dissolved organic matter (DOM), whose presence in water is harmful to both agriculture and humans.

### **1.2 Dissolved Organic Matter (DOM)**

DOM is a natural and significant component of the aquatic ecosystem. The term DOM is used to describe a heterogenous mixture of organic molecules dissolved in water originating from a variety of biological and geological sources. The sizes of DOM molecules range from single amino acids to macromolecules, which are generally assumed to have a maximal size of 0.45  $\mu\text{m}$ .<sup>2</sup> DOM can be classified into 8 categories: Humic substances, which can be subcategorized as humic acid and fulvic acid, and six additional categories of non-humic substances. Humic substances have common chemical makeup, such as aromatic rings, phenol groups, and carboxylic groups, which leave these molecules in natural water environments (pH 7-8). Apart from the common groups, the specific chemical structure of each molecule has not been fully analyzed due to their structural complexities (Figure 1). Since the solubility of a molecule is a function of its size and charge, humic acids and fulvic acids can be separated by modifying the acidity of the solution. Due to its electric charge, fulvic acid is soluble under basic conditions, and owing to its small size, is also soluble under acidic conditions (even though it loses its electric charge). In contrast, humic acid is not sufficiently small to dissolve under acidic conditions. Fulvic and humic acids constitute more than 50% of the DOM in most surface water sources in the world.<sup>3</sup>

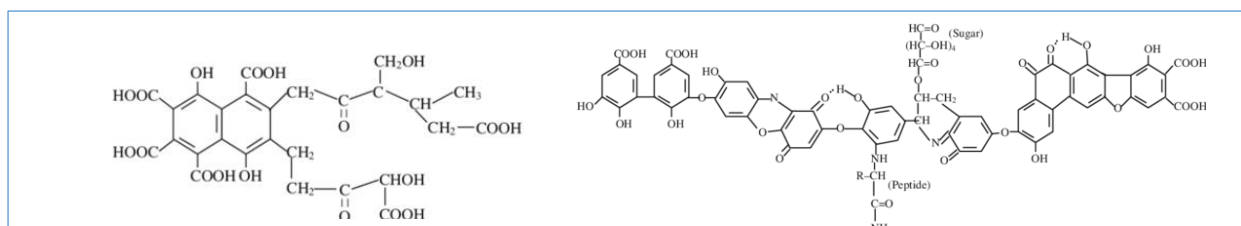


Figure 1: Model of a humic acid (right)<sup>4</sup> and fulvic acid (left)<sup>5</sup> molecule.

### 1.3 The Effect of DOM on Surface Water Quality

In the late 1980s, an increase in the quantity of DOM in surface waters was first reported in Sweden.<sup>6</sup> In the past few decades, several reports demonstrated that the increase in DOM concentrations in surface waters is a global phenomenon.<sup>7,8</sup> Climate change and reduced acidic rain precipitation can possibly explain the reported increase in DOM concentrations.<sup>9</sup>

The presence of DOM in drinking water causes several environmental and health problems. DOM form undesirable complexes with organic and inorganic substances in water and can cause undesirable color, odor, and taste, thereby affecting drinking water quality.<sup>10</sup> In addition, the presence of DOM in pipes and in membranes of water treatment facilities and in agricultural drip irrigation systems, can cause formation and accumulation of biofilms (concentrations of microorganisms in organic substances). The biofilms block the narrow openings of irrigation pipes thus rendering water treatment and desalination facilities nonfunctional. Some works have shown that the humic fraction is the primary cause of irreversible formation of biofilms in membranes and the undesirable watercolor.<sup>11</sup> In addition to environmental problems, DOM in water is also detrimental to human health. In chlorinated drinking water, the chlorine reacts with DOM in various chemical reactions, to create a range of byproducts. The chemical classification and concentration of these byproducts in drinking water are a function of many parameters, such as the chemical characteristics of the DOM, DOM concentration, acidity (pH), temperature, and others. Some byproducts are carcinogenic. The most common carcinogenic substances identified were trihalomethanes (THMs) and haloacetyoxide (HAAs). In the past few decades, more than 600 toxic byproducts have been identified.<sup>12</sup> Many studies have shown that the humic fraction plays a key role in the formation of byproducts. Considering the many problems posed by DOM in surface waters, it is essential to extract it, particularly the humic fraction, before use of the water for agricultural or drinking purposes.

### 1.4 DOM Extraction Methods

**1.4.1 Adsorption** – Commonly used DOM removal method involves adsorption to a solid substrate on filtration columns or in sedimentation tanks, where the contaminant is physically or chemically adsorbed (depending on the sorbent substrate). Each sorbent has different chemical properties, which include the ability to form hydrogen bonds, electrostatic bonds and dipole-dipole interactions. There are various substrates used for adsorption:

**1.4.1.1** Activated carbon (AC) – made of wood charcoal that underwent pyrolysis, and then exposed to high oxygen concentrations. The process results in AC with many microscopic pores and a subsequently high specific surface area (300-2,000 m<sup>2</sup>/g activated carbon). Due to its high surface area and diverse pore size, AC can adsorb materials of different sizes with high efficiency and is therefore used in a variety of industrial applications, such as gas purification, water and wastewater purification, air filtration and others.<sup>13</sup>

**1.4.1.2** Granular activated carbon (GAC) – GAC (Figure 2) adsorbs microcontaminants, e.g., pesticides, industrial chemicals, flavors, algae toxins from water and DOM, with high efficiency. GAC-based removal of DOM is highly efficient and can reach approximately 90% when using a new substrate, but after several filtrations, the filtration efficiency drops to approximately 20-30% due to pore blockage by the humic fraction,<sup>14</sup> which has a high molar mass. Since GAC adsorption efficiency rapidly declines, the substrate must be regenerated every few months. GAC is generally regenerated by heating the substrate to 700 °C; after each activation, the adsorption efficiency drops by approximately 20%. The heating process results in enlargement of the carbon pores, which reduces its ability to adsorb low-molar-mass molecules.<sup>15</sup> In addition, the activation process switches the electric charge of the carbon from neutral to negative, resulting in reduced efficiency in adsorbing negatively charged molecules, including the DOM humic fraction. Due to the high cost of the process and its many drawbacks, many water treatment facilities only regenerate the substrate once every few years, resulting in a generally low DOM filtration efficiency.

**1.4.1.3** Powder activated carbon (PAC) – Owing to its high surface area, PAC adsorbs a wide range of molecules with high efficiency. Due to its powder form, its hydraulic resistance is high, and it therefore can only be used in sedimentation tanks and not in filtration columns.

In light of the water quality problems and the strict regulations pertaining to drinking water quality, higher efficiency and cost-effectiveness water purification methods are needed.

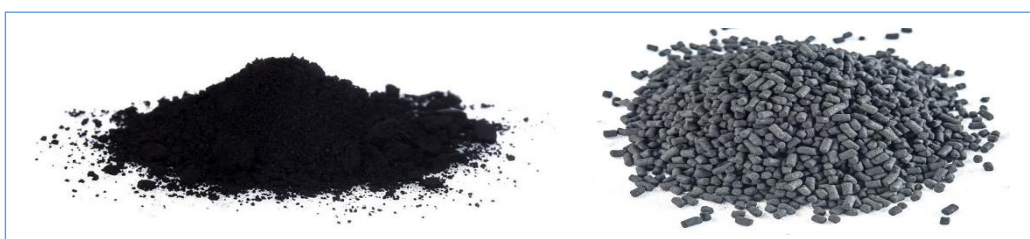


Figure 2: Granular activated carbon (right) and powder activated carbon (left)

## 1.5 Adsorption Substrates – Organoclays

In light of the need for improved alternatives for DOM removal from water, many works are advancing the development of complex adsorption substrates, including organoclays. Montmorillonite (MMT) is a common clay mineral with a chemical formulation of  $\text{Al}_2\text{H}_2\text{O}_{12}\text{Si}_4$ . The basic structure of MMT contains three layers: a tetrahedral, octahedral and tetrahedral layers (Figure 3). The tetrahedral layer is comprised of silicon atoms surrounded by oxygen

atoms ( $\text{SiO}_2$ ), while the octahedral layer is comprised of an aluminum atom surrounded by oxygen atoms ( $\text{Al}_2\text{O}_3$ ). Isomorphous exchange is a geochemical process which occurs over thousands of years, during which some of the silicon or aluminum atoms are exchanged for a metal of lower valence, such as iron or magnesium. This exchange leads to the formation of a negative charge on the clay surface. This charge forms a layer of inorganic cations along the surface area of the clay.

Organoclays are substances comprised of negatively charged clay minerals whose exchangeable inorganic cations have been substituted by organic cations. Cation exchange from inorganic to organic cations confers new properties to the surface area. Organoclays with a large surface area (particularly MMT) constitute very efficient adsorption substrates that can remove contaminants from the water, such as drugs, pesticides, oils and fuels, DOM and others.<sup>16</sup>

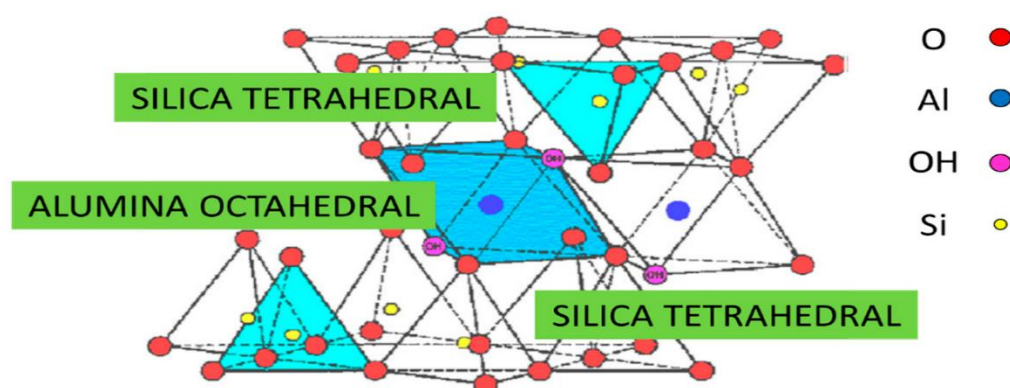


Figure 3: The three layers of montmorillonite clay.<sup>17</sup>

#### 1.5.1 Polymer-clay composites

Polymer-clay composites are a type of organoclay. These composites are comprised of polymer (organic) complexes adsorbed to mineral clay (inorganic). This method can be used to generate many types of substances that are impacted by the composite preparation technique, polymer type, mineral type and polymer conformation on the clay.<sup>18</sup> Adequate adsorption of a polycation (a positively charge polymer) to negatively charged clay minerals, results in a change in the surface electric charge of the clay from negative to positive, thereby enabling highly efficient adsorption of the negatively charged molecules.<sup>19</sup>

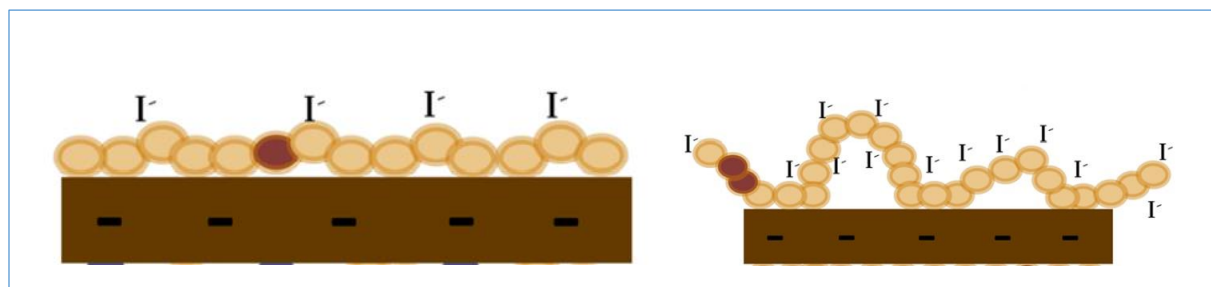


Figure 4. “Loops and tails” configuration (right) – many adsorption sites are free. “Trains” configuration (left) – most of the polymer is adsorbed to the mineral, subsequently leaving few available adsorption sites.<sup>20</sup>



As mentioned above, the conformation of the polymer (the spatial arrangement of the polymer) on the clay also affects the properties of the composite and its efficiency in adsorbing different contaminants.<sup>21,22</sup> There are two main conformations: “trains” and “loops and tails,” wherein the “loops and tails” configuration will generally adsorb with higher efficiency. This is due to the spatial arrangement of the polymer on the clay. While most of the surface area of the “train” polymers is adsorbed by the clay (leaving very few free positively charged sites on the polymer for adsorption), the “loop and tails” polymer binds in such a way that only certain parts are adsorbed to the clay, while the rest remain “free” in the water, and subsequently have more free positively charge adsorption sites (Figure 4).<sup>23</sup>

Despite the hundreds of articles published in the past few decades, detailing the characteristics of polymer-clay composites, a relatively small number compared the adsorption performance of composites to other sorbents, in general, and to industrial sorbents, in particular.<sup>24</sup> Some studies have shown that polymer-clay composites remove organic contaminants with higher efficiency than GAC,<sup>25,26,27</sup> while others have shown that GAC is more efficient.<sup>28</sup> Nevertheless, with regards to adsorption kinetics, polymer-clay composites have been found superior to AC.<sup>29,30</sup>

## 1.6 Adsorption Kinetics

The adsorption rate of a contaminant on a substrate (adsorption kinetics) is an important factor in industria decontamination processes, as the contact time between the contaminant and the sorbent is short. Adsorption kinetics is especially impotant in water industries, since the water in sedemination tanks and particularly in filtration columns, are in contact with the sorbent for a short and limited period of time (for example, in industrial filtration columns, the average contact time is approximately 10 minutes). Therefore, there is a need for efficient sorbents that is also characterized by rapid adsorption kinetics. The adsorption kinetics is influenced by a range of factors including the contaminant and sorbent concentrations, temperature, contaminant size, sorbent pore size, and others. Solvents diffuse through water in porous substrtes, there is an additional diffusion – pore diffusion (Figure 5). The two types of diffusion are distinct, as in the pores, solvent diffusion behavior is different and is dependent on the pore size.<sup>31</sup>

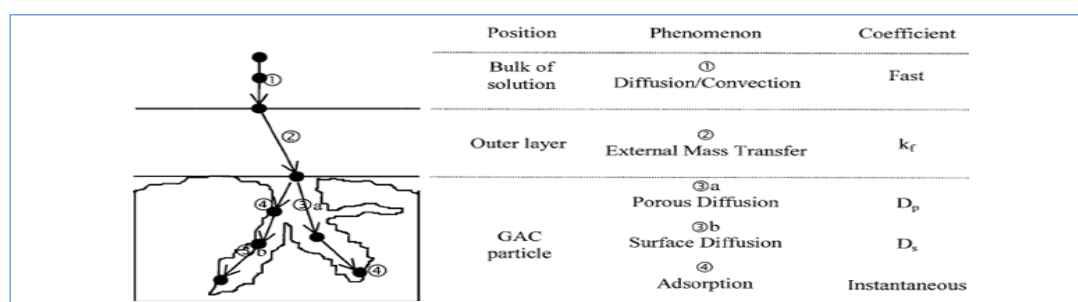


Figure 5: General diffusion (1) and particle diffusion (3a) in granular activated carbon (GAC)<sup>32</sup>



### 1.6.1 Kinetic order of reaction

There are three basic orders of kinetics, which describe the relationship between two reacting substances: zero-order reaction, first-order reaction and second-order reaction.

- A zero-order reaction is a reaction in which the reaction rate is independent of the concentration of the reactants ( $[A]_t = -kt + [A]_0$ ).
- A first-order reaction is a chemical reaction that depends on the concentration of only one reactant ( $\ln([A]_t/[A]_0) = -kt$ ).
- A second-order reaction describes a state in which the concentration of the two reactants affects the reaction rate ( $1/[A]_t = kt + 1/[A]_0$ ).

### 1.6.2 Analysis of granular polymer-clay composite kinetics

The vast majority of water treatment facilities use filtration columns that require sorbent substrates with high hydraulic conductivity (essential for water to flow through the filters). Powder polymer-clay composites are practically impervious and therefore cannot be used as a sorbent substrate in filtration columns. In order to use polymer-clay composites in the water industry, they must be in a granular form. Most studies assessing the adsorption kinetics of polymer-clay composites focused on powder composites. A comprehensive review article found that of 100 published articles relating to adsorption kinetics of contaminants by polymer-clay composites,<sup>33</sup> only one<sup>34</sup> compared between granular and powder polymer-clay composites. To the best of our knowledge, no other studies have been conducted on this topic; therefore, this research area requires additional and extensive research.

The present work compared the adsorption kinetics of fulvic acid by a powder vs. granular polymer-clay composite, and compared their efficiency to that of GAC and PAC.

## 2. Materials and Methods

### 2.1 Materials

MMT Wyoming Na-Mt (Montmorillonite)  $Al_2H_2O_{12}Si_4$  (CEC = 0.8 mmole  $g^{-1}$ ) was purchased from The Clay Mineral Society (Columbia MO) and poly (vinyl benzyl trimethyl ammonium chloride polymer ( $C_6H_5CH_2N(Cl)(CH_3)_3$ ) was purchased from Scientific Polymer Products Inc. Fulvic acid from the Suwannee River was obtained from the International Humic Substances Society (IHSS). Hydriffin 30 N GAC and PAC were purchased from Corporation Donau Carbon.

### 2.2 Experimental Method

#### 2.2.1 Preparation of powder polymer-clay composite

MMT clay was suspended in distilled water to a concentration of 5 g/L. In parallel, a polymer PVCT solution (27% polymer) was dissolved in distilled water to a concentration of 2.5 g/L. Both the solution and suspension were mixed with a magnetic stirrer for approximately one hour, until a homogenous solution/suspension was obtained. To form the composite, the polymer solution was then mixed with the clay suspension at a 1:2 ratio, by dripping the polymer solution into the clay suspension using a peristaltic pump. To separate the water from the composite, the composite solution was passed through a Buchner funnel lined with 12-15  $\mu\text{m}$  filter paper, attached to a pump. A sample of the filtrate was taken for spectrophotometric analysis, to determine the percent of the polymer in the composite. Solid nanocomposite that remained on the filter paper was scraped off into a receptacle with distilled water, which was then centrifuged at 10,000 rpm for 16 minutes, after which, the supernatant was aspirated. This washing process was repeated three times to remove the polymer that was not adsorbed to the clay. Then, the composite was frozen for 24 hours and lyophilized. After drying, the composite was ground with a mortar and pestle and passed through 0.14 mm sieve.

### 2.2.2 Characterization of the composite and polymer

To determine the clay/polymer loading in the prepared composite, solutions of distilled water and varying concentrations of polymer were prepared and spectrophotometrically analyzed to prepare a calibration curve. As mentioned above, a sample of the filtrate was collected and its UV absorbance was measured using a Thermo Scientific, Evolution 300 device (Waltham MA), at a wavelength of 254 nm. The absorption results were compared to the calibration curve and the loading percentage was subsequently calculated. In addition, loading was also evaluated by elemental analysis of the dry composite, using a FlashEA 1112 Thermo device. To test the effect of the polymer on the spacing between the clay layers, a sample of the MMT clay and of the composite were subjected to X-ray diffraction analysis using a Philips PW1830/3710/3020. To check whether there was a surface charge switch (negative  $\rightarrow$  positive) after adsorption of the polymer on the surface area of the clay, the zeta potential (the surface charge of the sorbent) of the composite was determined using the Malvern Instruments, UK device. The composite was also characterized by thermal gravimetric analysis (TGA) using a Q500 thermogravimetric analyzer (TA Instruments, New Castle, USA).

### 2.2.3 Granulation of the composite

A process identical to the steps described in section 2.2.1 was performed, until the step of filtration of the composite from its solution by pouring it into a Buchner. To determine the wetness of the composite, the wet composite was dried at 105  $^{\circ}\text{C}$  in an oven, for approximately 24 hours. After determining the wetness, the wet composite was dried in an oven until it reached an optimal wetness of approximately 70%. The composite was then passed through a 0.85-1.4 mm sieve, and the granules were heated in an oven for 24 hours, until completely dried.

### 2.2.4 Sorbents in the experiment

The kinetics analysis was performed using the following four sorbents:

- Granular polymer-clay composite comprised of MMT clay and PVCT polymer  
Particle size: 0.85-1.4 mm.
- Powder polymer-clay composite comprised of MMT clay and PVCT polymer  
Particle size: <0.14 mm.
- Granular activated carbon  
Particle size: 0.85-1.4 ( $\pm 0.5$ ) mm.
- Powder activated carbon  
Particle size: <0.14 mm.

### 2.2.5 Kinetics experiment

A solution containing 14 mg/L fulvic acid in distilled water (pH=6.5) was placed on a shaker. A sorbent at a concentration of 2 g/L was added to the solution. Every few minutes from the start of the experiment, a 2 mL sample was taken from the solution. The last sample was taken 24 hours after the start of the experiment, which was defined as the adsorption equilibrium time (reached when the concentration of the contaminant in the solution does not change). The sample was passed through a 0.45 filter, and its UV absorbance was measured at a wavelength of 254 nm. The absorbance results were compared to those of the original solution (before the sorbent was added) and the concentration of fulvic acid in the sample was calculated. The results were processed and fit to the appropriate kinetic order of reaction and the kinetic constant was calculated using a Python code and the matplotlib library to model the results. The experiment described above was repeated three times to determine the standard deviation for each of the four adsorbents in 2.2.4.

## 3. Results

### 3.1 Characterization of the Composite

#### 3.1.1 Zeta Potential

The zeta potential of MMT, PVCT, the composite and of AC were measured to confirm charge shift of the clay upon polymer adsorption (Table 1).

Table 1. Zeta potential of the composite, clay and polymer.

Composite PVTC-MMT	PVTC	MMT	Activated Carbon
+35.2 mV	+44.2 mV	-38.9 mV	-40 mV

The electrical charge of the clay was negative and measured -38.9 mV, while the electrical charge of the polymer was positive +44.2 mV. The zeta potential of the composite was positive and measured +35.2 mV, indicating successful synthesis. The zeta potential of AC was -40 mV.

### 3.1.2 Elemental Analysis

Table 2: Results of elemental analysis of the composite

Organic substance (%)	N – Nitrogen (%)	C – Carbon (%)	H – Hydrogen (%)	Si – Silicon (%)
10.625	1.06025	9.5953	1.82235	0.03875

CHNS (elemental analysis) of a sample of the composite was performed to determine the loading percentage of the polymer to the clay ((polymer mass/composite mass) \*100) (Table 2). The percentage of carbon in the composite stood at 9.6%, namely, the polymer loading efficiency was ~10%, since the polymer is the only organic component in the composite.

### 3.1.3 Thermogravimetric Analysis

The percentage of mass loss of the clay, polymer and composite as a function of temperature increase (TGA) was measured between 23-800 °C, to determine the loading efficiency of the polymer to the clay (green line, Figure 4). The slope (derivative) of the curve (derivative analysis) indicates the temperature at which significant mass loss occurs (blue line, Figure 6).

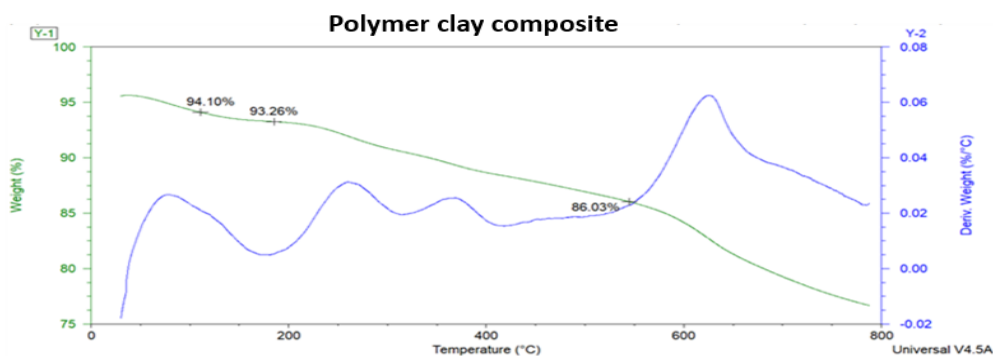


Figure 6. Mass loss in the composite at temperatures 23-800 °C.

Mass loss of the composite was observed at all temperatures, where the most loss occurring at 200-550 °C, which is ascribed to the combustion of the organic material in the polymer. At 200-550 °C, there was a 8-9% drop in the mass of the composite, namely, the percentage of polymer in the composite was 8-9%, similar to the results obtained from the elemental analysis (Table 2).

### 3.1.4 X-Ray Diffraction (XRD)

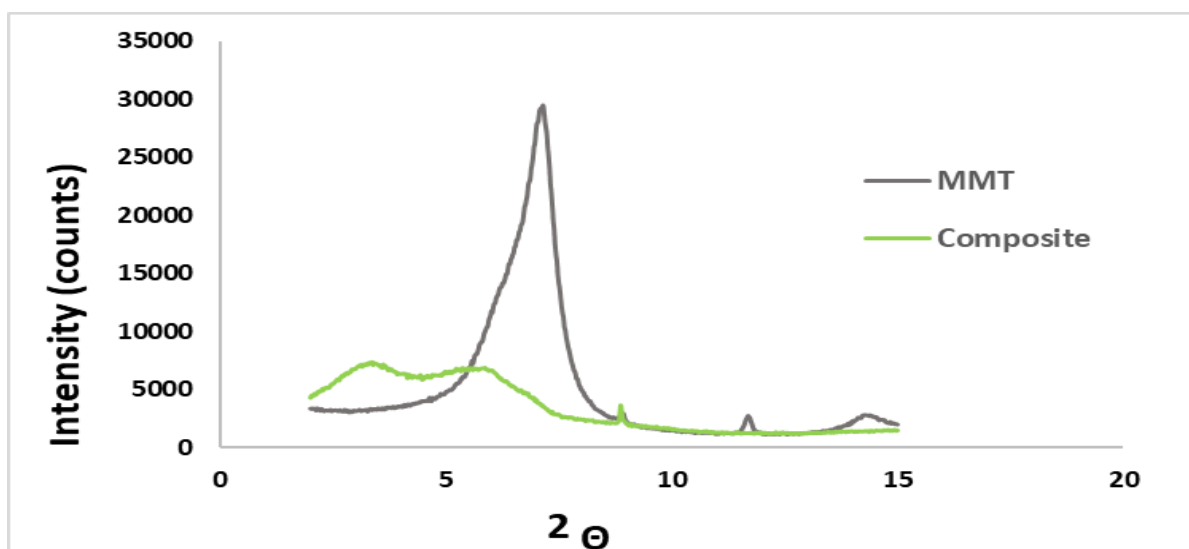


Figure 7: Basal spacing in the clay and in the composite (XRD)

An increase in the inter-layer spacing in the clay (Basal spacing) indicates polymer penetration between the layers. In addition, a change in the spacing and identification of variable distances may indicate multiple conformations. During adsorption, the polymer penetrates the clay layers, and thereby increased the basal spacing.<sup>35</sup> To determine if the polymer was indeed in between the clay layers and to characterize the polymer conformations on the clay, the basal spacing of the clay and of the composite were measured and the results were compared.

The XRD measurements exhibited a significant peak (Figure 7, grey line), which reflected a basal spacing of 12.407 nm. This result agrees with the basal spacing of MMT (Zusman et al., 2021). In the graph of the composite, two peaks, with angles smaller than those of the clay graph, were observed, and indicated two different interlayer spacings of 15.705 nm and 26.429 nm in the composite (Figure 7, green line). The right peak in the graph of the composite, reflecting a basal spacing of 15.07 nm, can likely be attributed to the “trains” configuration,

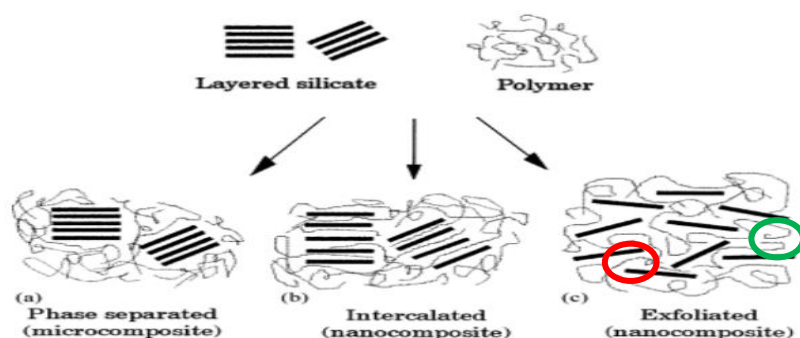


Figure 8: “Loops and tails” (green circle) and “trains” (red circle) configurations in the same composite form two different interlayer spacings in the clay (3c).<sup>36</sup>

while the left peak reflecting an interlayer spacing of 26.429 nm can likely be attributed to the “loops and tails” configuration, as this configuration takes up more space than the “trains”, resulting in enlargement and greater separation of the clay layers than the “trains” configuration

(Fig. 8).<sup>37</sup> Assignment of the two small peaks of the polymer-clay composites to “loops and tails” and “trains” configurations” has been reported by several other groups.<sup>38,39,40</sup>

### 3.1.5 Scanning Electron Microscope (SEM)

To show the differences between the surface areas of the two forms of the composite – powder and granular, the composite was photographed under a JSM-7800F, JEOL, Japan scanning electron microscope (SEM).

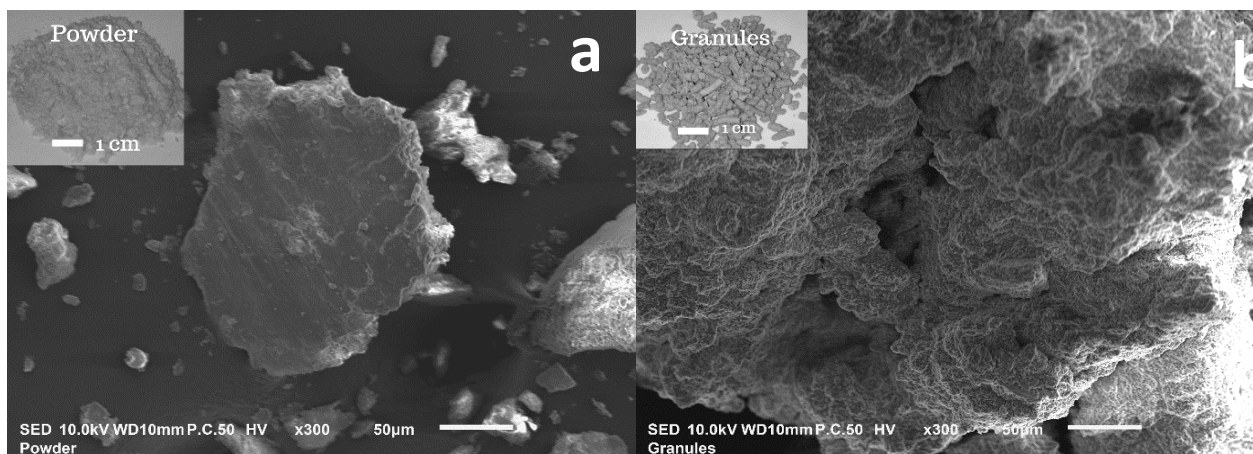


Figure 9. SEM images of the (a) powder and (b) granular composite at a resolution of 50  $\mu\text{m}$ .

## 3.2 Adsorption Kinetics Experiment

To assess the effect of the type of sorbent in the solution on the adsorption kinetics of fulvic acid, a kinetics experiment was performed, in which the adsorption efficiency of the composite and the carbon, in their two forms, were measured (Figure 10).

At equilibrium, adsorption of fulvic acid by the composite was more efficient than by AC, in both powder and granular forms. The powder composite adsorbed more efficiently than all the other sorbents forms, reaching a 100% adsorption of the contaminant at equilibrium, while the granular composite adsorbed approximately 40%. In contrast, PAC adsorbed approximately 25% of the contaminant and GAC adsorbed only approximately 10% (Fig. 10a).

Normalization of the adsorbed contaminant mass at a given time by the contaminant mass adsorbed at equilibrium ( $Q_t/Q_e$ ) enables calculation of the adsorption kinetics (Figure 10b). A close look at the first few minutes on the graph shows that the adsorption kinetics of the powder composite is faster than that of the granular composite. The adsorption kinetics of the ACs could not be compared, since the GAC did not provide relevant results, due to its steady and static adsorption activity. In addition, the graph shows that the powder composite and the PAC had identical adsorption kinetics.

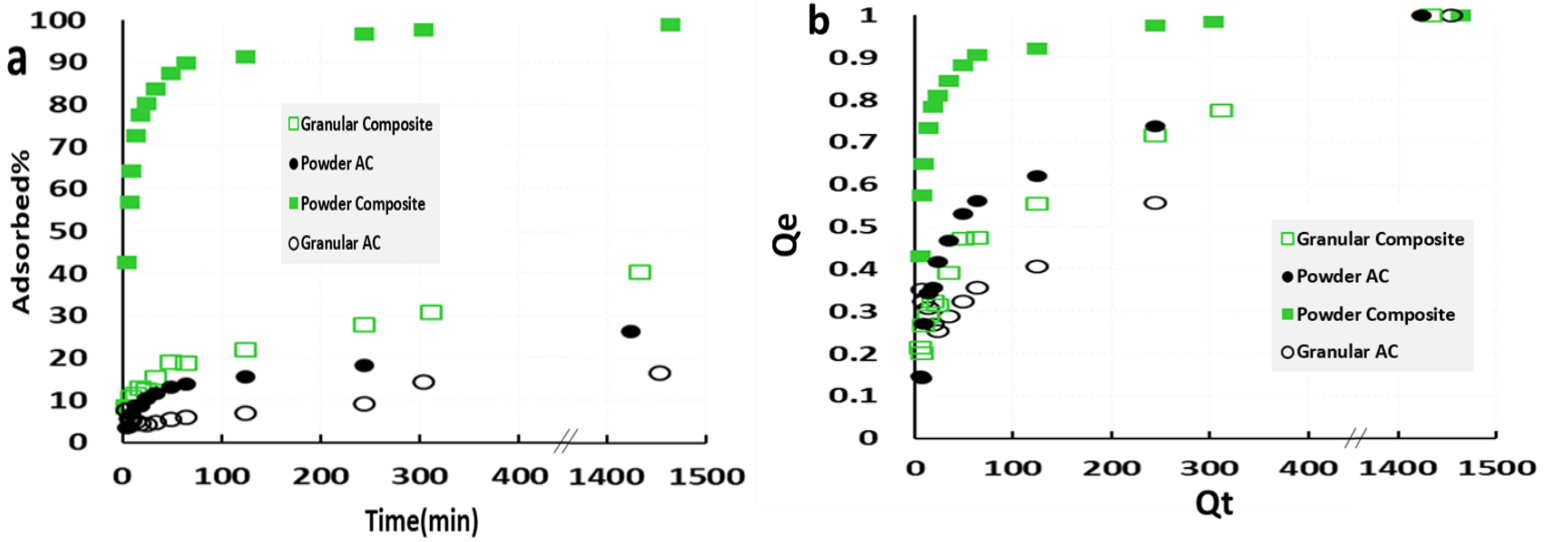


Figure 10: (a) Percentage of fulvic acid adsorbed as a function of time. (b) Mass of adsorbed contaminant at a given time / mass of contaminant adsorbed at equilibrium.

### 3.3 Kinetics Constants and Kinetic Order of Reaction

The results of the experiment were analyzed using Python code and the matplotlib library to fit the results to one of the kinetic orders of reaction mentioned in the introduction (1.6).

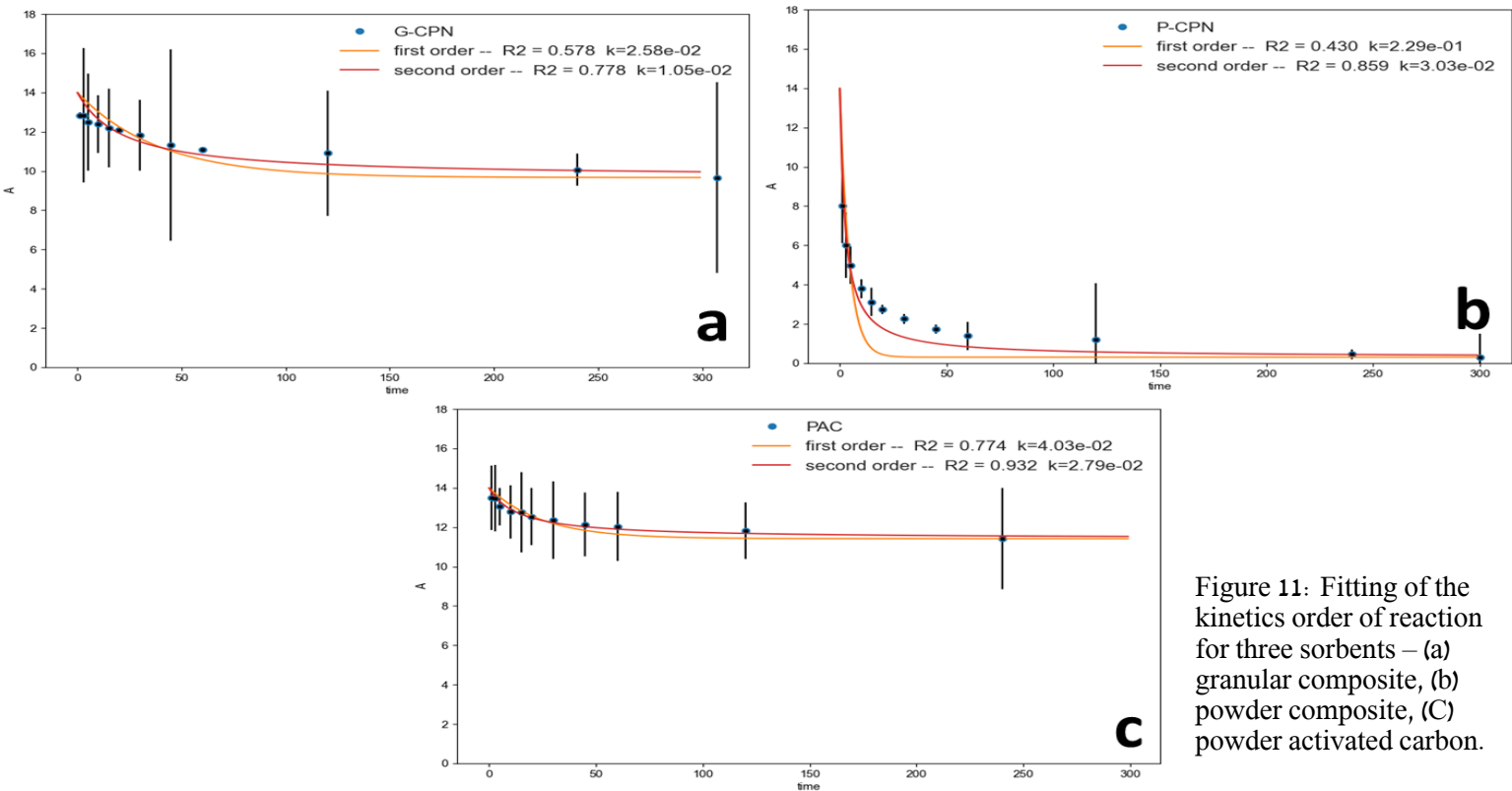


Figure 11: Fitting of the kinetics order of reaction for three sorbents – (a) granular composite, (b) powder composite, (C) powder activated carbon.

The code generates a graph for each sorbent, which presents three functions – (1) experimental results, (2) first-order reaction model and a (3) second-order reaction model.



All three experiments fit a second-order reaction very well. Namely, the adsorption mechanism of all tested sorbents was affected by both the concentration of the sorbent and by the concentration of the contaminant (Figure 11, Table 3).

Table 3: Order of reaction and kinetics constant of the three sorbents

Adsorbent	Kinetics order of reaction	K – Kinetics constant	R <sup>2</sup>
Powder composite	Second	0.03	0.859
Granular composite	Second	0.01	0.778
Powder activated carbon	Second	0.028	0.932

## 4. Discussion

In this work, a polymer-clay composite (a hybrid material composed of an organic polymer and inorganic clay with combined properties of the two components) was synthesized in order to reach rapid and efficient adsorption of fulvic acid and compared it with a commercial sorbent, namely activated carbon. Furthermore, the effect of an additional pore range in the sorbent on the adsorption kinetics of the two sorbents was assessed by comparing between powder and granular forms.

### 4.1 Adsorption Efficiency

The results of the adsorption experiment showed that the fulvic acids were adsorbed more efficiently by the composite as compared to the AC sorbents. At equilibrium, the powder composite adsorbed four times more fulvic acid than the PAC and GAC; 100% vs. 26% for the powder and 40% vs. 10% for the granular form (Figure 10a). The higher affinity of the fulvic acid to the composite on the one hand and its low affinity to the AC on the other hand, can be explained by the electric charge on the surface of the sorbents. While the surface of the composite is positively charged, the surface of the AC is negative (Table 1). As explained in the introduction, fulvic acids are aromatic, with a negative charge in a neutral aqueous environment<sup>30,41</sup>. Therefore, during adsorption, there is a strong electrostatic attraction between the composite and the fulvic acid, while there is electrostatic repulsion between fulvic acid and the AC. Both the AC and the composite have aromatic rings and there are therefore also Pi-Pi bonds. These bonds (which are relatively weak), together with van der Waals bonds, likely contribute to the little adsorption there is by AC.

## 4.2 Kinetics

The adsorption kinetics is primarily active within the first few minutes of the experiments. Considering the graph (Fig. 10b), the mathematical model and the kinetic orders of reaction (Figure 11), it was found that the powders had identical adsorption kinetics (Table 3). This is likely a coincidence (since the materials are different, the adsorption kinetics are likely to be different, which was not the case).

In addition, the adsorption kinetics of the granular composite was three-fold slower than the powder composite. As explained in section 1.6 of the introduction, granular sorbents have an additional range of pores, characterized by larger pores, a range which, as said, does not exist in powder sorbents. Addition of this pore range affects the adsorption kinetics of the sorbent, where studies, including a study published in 2020 showed that the effect inhibits adsorption of the contaminant and subsequently slows the kinetics.

A study conducted in recent years compared the adsorption kinetics of a larger molecule (humic acid) to that of a very small molecule (gallic acid). The publication proposed that due to its size, the large molecule does not penetrate the additional pore range in the granules, while the small molecule does, therefore, the adsorption kinetics of the small molecule by the granules is slower. The fulvic acid molecule is significantly smaller than that of humic acid and significantly larger than that of gallic acid. Therefore, with regards to kinetics adsorption of fulvic acid, with no knowledge of the pore size in the sorbents we used, we could not determine whether there would be penetration into the additional pore range in the granular composite. Based on the study results that showed faster adsorption kinetics to the powder composite, we assume that the fulvic acid indeed penetrated the granular pore range (composite), which led to a slowdown of the adsorption.

SEM images collected at a 50  $\mu\text{m}$  resolution, supported the claim that the contaminant molecules penetrated to the pore range of the granular composite (Figure 9). The images visually showed the distinct differences on the surface of the powder vs. the granular composites. While the powder composite was characterized by a rather flat surface, the granular composite was characterized by a porous and branched surface, with cavities that provided an additional pore range.

An additional factor that should be considered is the duration for each sorbent to reach maximum adsorption. As shown in the graph (Figure 10a), the powder composite reached maximum adsorption of 100% after 4 hours. All other sorbents, and, most importantly, PAC, took more time and showed lower efficiency (26% removal for the PAC), and, therefore, despite the similar adsorption kinetics between the two, we found a clear advantage in the adsorption performance of the powder composite.

### **4.3 Significance of this Research**

To the best of our knowledge, the composite prepared for these experiments is novel and has never been previously studied. The adsorption efficiency of the powder composite clearly showed that the composite can serve as a superior alternative to AC. The adsorption efficiencies of the powder and granular composites were significantly higher than their counterpart forms of AC. As explained in the introduction, the various industrial needs, and, primarily, the need for sorbents with high hydraulic conductivity, require granular sorbents as adsorption substrates in filtration columns. The adsorption performance of the granular composite demonstrate that it is a preferable sorbent for fulvic acid removal from surface waters than GAC, which, as said, serves as an industrial sorbent in most water treatment facilities today.

As mentioned above, despite the research-worthy potential of granular composites, to the best of our knowledge, apart from a single study, the correlation between granular and powder polymer-clay composites has not been studied. In this work, I partially clarified the differences between the surface of the two forms. These differences may be observed in additional studies of other composites and may constitute an inclusive characterization. Understanding the correlation between granular and powder polymer-clay composites will assist in optimizing the adsorption mechanisms of granular composites to closely resemble the powder sorbents and to integrate them into the water purification industry as an alternative to the common methods, which are limited and require upgrading.

### **4.4 Future Research**

I would like to propose research directions that can be based on and further enhance the current work, with the goal of providing a broader and more comprehensive picture of the granular composite prepared in this work. It would be of interest to assess the effect of regeneration process in a concentrated salt solution on the substrates DOM removal efficiency. As stated in the introduction, every few months, it is necessary to regenerate GAC to restore its efficiency, however, the process always results in a lower efficiency as compared to a new, unused substrate. Regeneration of a sorbent substrate is an important and critical process for all sorbents, and it is therefore important to understand how it will affect the composite prepared in this study.

## 5. References

- <sup>1</sup> Jury, W. A. & Vaux, H. J. The Emerging Global Water Crisis: Managing Scarcity and Conflict Between Water Users. *Advances in Agronomy* vol. 95 1–76 (2007).
- <sup>2</sup> Nebbioso, A. & Piccolo, A. Molecular characterization of dissolved organic matter (DOM): A critical review. *Analytical and Bioanalytical Chemistry* vol. 405 109–124 (2013).
- <sup>3</sup> Linnik, P. N., Ivanechko, Y. S., Linnik, R. P. & Zhezherya, V. A. Humic substances in surface waters of the Ukraine. *Russ. J. Gen. Chem.* 2013 8313 **83**, 2715–2730 (2014).
- <sup>4</sup> Wang, S., health, C. M.-E. geochemistry and & 2006, undefined. Effect of natural organic matter on arsenic release from soils and sediments into groundwater. *Springer*(2006) ) doi: 10.1007/s10653-005-9032-y.
- <sup>5</sup> Wang, S. & Mulligan, C. N. Effect of natural organic matter on arsenic release from soils and sediments into groundwater. *Environmental Geochemistry and Health* vol. 28 197–214 (2006).
- <sup>6</sup> Forsberg, C. & Jr., R. C. P. A darkening of Swedish lakes due to increased humus inputs during the last 15 years. <https://doi.org/10.1080/03680770.1989.11898741> **24**, 289–292 (2017).
- <sup>7</sup> Eikebrokk, B., Vogt, R. D. & Liltved, H. NOM increase in Northern European source waters: discussion of possible causes and impacts on coagulation/contact filtration processes. *Water Supply* **4**, 47–54 (2004).
- <sup>8</sup> Worrall, F. & Burt, T. P. Trends in DOC concentration in Great Britain. *J. Hydrol.* **346**, 81–92 (2007).
- <sup>9</sup> Matilainen, A. *et al.* An overview of the methods used in the characterisation of natural organic matter (NOM) in relation to drinking water treatment. *Chemosphere* **83**, 1431–1442 (2011).
- <sup>10</sup> Kenefick, S. L., Hrudey, S. E., Prepas, E. E., Motkosky, N. & Peterson, H. G. Odorous substances and cyanobacterial toxins in prairie drinking water sources. in *Water Science and Technology* vol. 25 147–154 (IWA Publishing, 1992).
- <sup>11</sup> See Kenefick (1992) at 10.
- <sup>12</sup> Fan, Z., Yang, H., Li, S. & Yu, X. Tracking and analysis of DBP precursors' properties by fluorescence spectrometry of dissolved organic matter. *Chemosphere* **239**, 124790 (2020).
- <sup>13</sup> Suzuki, M. Activated carbon fiber: Fundamentals and applications. *Carbon N. Y.* **32**, 577–586 (1994).
- <sup>14</sup> Matilainen, A., Vieno, N. & Tuhkanen, T. Efficiency of the activated carbon filtration in the natural organic matter removal. *Environ. Int.* **32**, 324–331 (2006).
- <sup>15</sup> Boere, J. A. Combined Use of Ozone and Granular Activated Carbon (GAC) in Potable Water Treatment; Effects on GAC Quality After Reactivation. <http://dx.doi.org/10.1080/01919519208552294> **14**, 123–137 (2008).
- <sup>16</sup> Shabtai, I. A., Lynch, L. M. & Mishael, Y. G. Designing clay-polymer nanocomposite sorbents for water treatment: A review and meta-analysis of the past decade. *Water Research* vol. 188 116571 (2021).
- <sup>17</sup> Caccamo, M. T., Mavilia, G., Mavilia, L., Lombardo, D. & Magazù, S. Self-Assembly Processes in Hydrated Montmorillonite by FTIR Investigations. *Mater.* 2020, Vol. 13, Page 1100 **13**, 1100 (2020).
- <sup>18</sup> See Shabtai (2021) at 16.
- <sup>19</sup> Arya, V. & Philip, L. Adsorption of pharmaceuticals in water using Fe<sub>3</sub>O<sub>4</sub> coated polymer clay composite. *Microporous Mesoporous Mater.* **232**, 273–280 (2016); See also Shabtai (2021) at 16.
- <sup>20</sup> Kohay, H., Izbicki, A. & Mishael, Y. G. Developing Polycation-Clay Sorbents for Efficient Filtration of Diclofenac: Effect of Dissolved Organic Matter and Comparison to Activated Carbon. *Environ. Sci. Technol.* **49**, 9280–9288 (2015).
- <sup>21</sup> Kohay, H., Bilkis, I. I. & Mishael, Y. G. Effect of polycation charge density on polymer conformation at the clay surface and consequently on pharmaceutical binding. *J. Colloid Interface Sci.* **552**, 517–527 (2019).

- 
- <sup>22</sup> Levy, L., Izbtski, A. & Mishael, Y. G. Enhanced gemfibrozil removal from treated wastewater by designed “loopy” clay-polycation sorbents: Effect of diclofenac and effluent organic matter. *Appl. Clay Sci.* **182**, 105278 (2019).
- <sup>23</sup> Shabtai, I. A. & Mishael, Y. G. Efficient Filtration of Effluent Organic Matter by Polycation-Clay Composite Sorbents: Effect of Polycation Configuration on Pharmaceutical Removal. *Environ. Sci. Technol.* **50**, 8246–8254 (2016). See also Kohay, H. (2015) at 20; Kohay, H. (2019) at 21; Levy, L. (2019) at 22; and .
- <sup>24</sup> See Shabtai, I. A. (2021) at 16.
- <sup>25</sup> Zusman, O. B., Kummel, M. L., De la Rosa, J. M. & Mishael, Y. G. Dissolved organic matter adsorption from surface waters by granular composites versus granular activated carbon columns: An applicable approach. *Water Res.* **181**, 115920 (2020).
- <sup>26</sup> Gardi, I., Nir, S. & Mishael, Y. G. Filtration of triazine herbicides by polymer-clay sorbents: Coupling an experimental mechanistic approach with empirical modeling. *Water Res.* **70**, 64–73 (2015).
- <sup>27</sup> Zadaka, D., Nir, S., Radian, A. & Mishael, Y. G. Atrazine removal from water by polycation–clay composites: Effect of dissolved organic matter and comparison to activated carbon. *Water Res.* **43**, 677–683 (2009).
- <sup>28</sup> See Kohay, H. (2015) at 20 and Shabtai, (2016) at 23 and Zusman, O. B. (2020) at 25.
- <sup>29</sup> Radian, A. & Mishael, Y. Effect of Humic Acid on Pyrene Removal from Water by Polycation-Clay Mineral Composites and Activated Carbon. *Environ. Sci. Technol.* **46**, 6228–6235 (2012). See also Kohay, H. (2015) at 20.
- <sup>30</sup> Shabtai, I. A. & Mishael, Y. G. Catalytic polymer-clay composite for enhanced removal and degradation of diazinon. *J. Hazard. Mater.* **335**, 135–142 (2017).
- <sup>31</sup> Piai, L. *et al.* Diffusion of hydrophilic organic micropollutants in granular activated carbon with different pore sizes. *Water Res.* **162**, 518–527 (2019).
- <sup>32</sup> Viegas, R. M. C., Campinas, M., Costa, H. & Rosa, M. J. How do the HSDM and Boyd’s model compare for estimating intraparticle diffusion coefficients in adsorption processes. *Adsorption* **20**, 737–746 (2014).
- <sup>33</sup> See Shabtai, I. A. (2021) at 16.
- <sup>34</sup> Zusman, O. B., Kummel, M. L., De la Rosa, J. M. & Mishael, Y. G. Dissolved organic matter adsorption from surface waters by granular composites versus granular activated carbon columns: An applicable approach. *Water Res.* **181**, 115920 (2020).
- <sup>35</sup> See Kohay, H. (2015) at 20 and Shabtai, (2016) at 23
- <sup>36</sup> Alexandre, M. & Dubois, P. Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials. *Mater. Sci. Eng. R Reports* **28**, 1–63 (2000).
- <sup>37</sup> See Kohay, H. (2015) at 20 and Shabtai (2016) at 23.
- <sup>38</sup> Fu, Q. *et al.* Pharmaceutical and Personal Care Products: From Wastewater Treatment into Agro-Food Systems. *Environ. Sci. Technol.* **53**, 14083–14090 (2019).
- <sup>39</sup> Radian, A. & Mishael, Y. G. Characterizing and Designing Polycation–Clay Nanocomposites As a Basis for Imazapyr Controlled Release Formulations. *Environ. Sci. Technol.* **42**, 1511–1516 (2008).
- <sup>40</sup> Churchman, G. J. Formation of complexes between bentonite and different cationic polyelectrolytes and their use as sorbents for non-ionic and anionic pollutants. *Appl. Clay Sci.* **21**, 177–189 (2002).
- <sup>41</sup> Filius, J. D., Lumsdon, D. G., Meeussen, J. C. L., Hiemstra, T. & Van Riemsdijk, W. H. Adsorption of fulvic acid on goethite. *Elsevier* (1999).