minerals
MDPI

Review

Applications of Chemically Modified Clay Minerals and Clays to Water Purification and Slow Release Formulations of Herbicides

Tomas Undabeytia [1], Uri Shuali [2], Shlomo Nir [2,*] and Baruch Rubin [2]

[1] Institute of Natural Resources and Agrobiology, IRNAS-CSIC, Reina Mercedes 10, 41012 Seville, Spain; undabeyt@irnase.csic.es
[2] The R.H. Smith Faculty of Agriculture, Food and Environment, The Hebrew University of Jerusalem, Rehovot 76100, Israel; ushuali@gmail.com (U.S.); rubin@mail.huji.ac.il (B.R.)
* Correspondence: shlomo.nir@mail.huji.ac.il; Tel.: +972-8-9489172 or +972-54-882-0412

Abstract: This review deals with modification of montmorillonite and other clay-minerals and clays by interacting them with organic cations, for producing slow release formulations of herbicides, and efficient removal of pollutants from water by filtration. Elaboration is on incorporating initially the organic cations in micelles and liposomes, then producing complexes denoted micelle- or liposome-clay nano-particles. The material characteristics (XRD, Freeze-fracture electron microscopy, adsorption) of the micelle– or liposome–clay complexes are different from those of a complex of the same composition (organo-clay), which is formed by interaction of monomers of the surfactant with the clay-mineral, or clay. The resulting complexes have a large surface area per weight; they include large hydrophobic parts and (in many cases) have excess of a positive charge. The organo-clays formed by preadsorbing organic cations with long alkyl chains were also addressed for adsorption and slow release of herbicides. Another examined approach includes "adsorptive" clays modified by small quaternary cations, in which the adsorbed organic cation may open the clay layers, and consequently yield a high exposure of the siloxane surface for adsorption of organic compounds. Small scale and field experiments demonstrated that slow release formulations of herbicides prepared by the new complexes enabled reduced contamination of ground water due to leaching, and exhibited enhanced herbicidal activity. Pollutants removed efficiently from water by the new complexes include (i) hydrophobic and anionic organic molecules, such as herbicides, dissolved organic matter; pharmaceuticals, such as antibiotics and non-steroidal drugs; (ii) inorganic anions, e.g., perchlorate and (iii) microorganisms, such as bacteria, including cyanobacteria (and their toxins). Model calculations of adsorption and kinetics of filtration, and estimation of capacities accompany the survey of results and their discussion.

Keywords: clay-based formulations; slow release formulations; micelle–clay composites; modeling of filtration; field experiments of weed control

Citation: Undabeytia, T.; Shuali, U.; Nir, S; Rubin, B. Applications of Chemically Modified Clay Minerals and Clays to Water Purification and Slow Release Formulations of Herbicides. *Minerals* **2021**, *11*, 9. https://doi.org/10.3390/min11010009

Received: 10 November 2020
Accepted: 18 December 2020
Published: 24 December 2020

1. Introduction

"Herbicides" are used for weed management in annual and perennial crops and in non-agricultural areas. They comprise approximately 46% of the total global use of pesticides [1]. Herbicides can be applied by a variety of means including ground and aerial sprayers, either pre-emergence on bare soil, or post-emergence, when the crop is present—as a directed spray or over-the-top. Regardless of the application method used, all herbicides reach the soil as the parent substance, or as degradation products and might be exposed to various dynamic processes. Depending on soil composition, structure, pH and water content, the applied herbicide (or its byproducts) can be taken up by plants and other macro- and/or micro-organisms. It might be adsorbed to clay and organic matter surfaces, chemically decomposed, volatilized, or photodegraded. The herbicide can migrate from the site of application and be eroded by run-off or leach down to deeper soil layers [2]. It should be noted that only the herbicide fraction present in the soil solution is available for biological activities.

Herbicides are generally applied after the active ingredient (ai) is mixed, dissolved, encapsulated, or dispersed (formulated) in or with other “inert” or “non-active” components that form different types of formulation [3]. Depending on the physical and chemical characteristics of the ai, the formulation can be in a state of gas, gel, solid (e.g., powder or granules), or a liquid (solution, suspension, or emulsion). A formulation may contain adjuvants that ensure dilution in carriers, maximize delivery to- and bioavailability-in plant and soil, enable stability in storage, and minimize health and environmental hazards. Adjuvants, which are also known as “inerts” may include wetting agents, humidifiers, stabilizers, stickers, oils, and surfactants that optimize the delivery of the herbicide to its target organism, enhance rain-fastness, reduce drift, and its desired behavior in soil and environment, [3,4].

The end-user may apply the formulation directly or spray it following dilution in water or oil. The type of applied formulation might greatly affect the behavior of the ai in the environment [5], thus modifying their control efficacy of the target weed or causing damage to non-target organisms.

Misused herbicides often pose a real hazard to the environment by application above the permitted use-rate, at the wrong time, and unintended spills, thus contaminating soil and water resources and damaging non-target species.

We report here on the use of surface-modified clay minerals, which are nanoparticles as carriers of herbicides, serving as a basis for environmentally-friendly formulations. The surface properties of the clay mineral (montmorillonite), or clay is modified from hydrophilic and negatively charged by adsorption of short- or long-alkyl chain quaternary ammonium cationic surfactants as monomers, micelles, or vesicles. The capacity of these complexes to bind herbicides is particularly advantageous with anionic compounds that are weak acids such as sulfonylurea herbicides, which are negatively charged in soils having neutral or basic pH [6,7].

These organoclay formulations have been designated to protect the environment from the harmful effects of irrational and uncareful use of herbicides, as well as to protect the agrochemicals from loss of activity due to photodegradation [8,9], volatility [10], and leaching or migration to the deep soil layers [11,12].

“Water purification.” The herbicides, which are discussed in Section 2 in the role of weed control, are considered in Section 3 as pollutants, which have to be removed from water, together with other chemicals and harmful microorganisms. In Europe the EC Drinking Water Directive (80/778/EC) stated that no single pesticide should exceed 0.1 $\mu g\ L^{-1}$ and total pesticides should not exceed 0.5 $\mu g\ L^{-1}$. Carter [13] presented a list of samples analyzed in England and Wales in which residue levels exceeded 0.1 $\mu g\ L^{-1}$; thus, isoproturon samples from surface-water exceeded the limit in 19.5% of the cases and groundwater samples were in excess in 1% of the cases. Observations of excessive concentrations of particular herbicides in water resulted in forbidding their use in given countries or regions.

Other pollutants whose purification is discussed are dissolved organic matter (DOM), (or natural organic matter (NOM)), pharmaceuticals, inorganic anions, and bacteria, including Cyanobacteria and their toxins.

“DOM.” The presence of DOM in drinking water can have negative effects due to: (a) color, taste, and odor; (b) interference with water treatment processes; (c) promotion of biofilms in water pipes; and (d) association with Cl_2 to form harmful disinfection by-products (trihalomethanes).

“Pharmaceuticals.” Pharmaceutical compounds (PhACs) are found in the environment at trace concentrations but are biologically active. Hence, they might occasionally cause more harm than other pollutants in the environment and are frequently denoted the hazards of the future. The comprehensive research of this issue involves testing the stability of the PhACs against chemical and/or biological degradation, as well as the biological effects of the parent molecules and their metabolites. Studies have emphasized that conventional water treatment processes cannot remove certain PhACs completely from source water [14–18].The review mentions quite a few studies which employed a sequence of several purification elements.

"Bacteria." For brevity, the review of removal of microorganisms is limited to bacteria. Removal of viruses and cryptosporidium was presented and discussed in [19] and reviewed by Nir and Shuali [20]. Chlorination has been the main strategy for disinfecting drinking water and wastewater, by inactivating pathogenic microorganisms. When the water includes organic molecules at concentrations of the order of mg/L, undesirable production of trihalomethanes (THMs) and haloacetic acids (HAAS) occurs, due to chlorination at high doses, whereas reduced efficiency in eliminating some epidemic microorganisms occurred at low doses [21]. Disinfection by chloramines results in formation of nitrosamines [22]. Ozone is powerful in removal of microorganisms, but its application results in formation of nitrosamines [23] and cyanogen halides [24]. Supplementing disinfection by removal of pathogenic microorganisms by filtration provides extra safety, in addition to decreasing the risk from harmful byproducts [25–27]. The cyanobacteria discussed produce toxins, which are harmful to humans and animals. The review deals with removal of the cells and their toxins.

The review emphasizes model calculations of adsorption and kinetics of filtration, since the calculations enable better planning of laboratory and pilot scale experiments, and also expose cases of synergism and antagonism in removal of pollutants. Estimations of capacities accompany the survey of results and their discussion

2. Slow Release Formulations of Herbicides

2.1. Modified Surfaces of Clay-Minerals and Clays by Organic Cations: Nomenclature

The focus is on the design and tests of herbicide formulations of slow release and on purification of water from chemical pollutants and from microorganisms. In the design of formulations for slow release formulations (SRF) of hydrophobic herbicides based on a clay backbone, the surfaces of negatively charged clays, or clay-minerals which are hydrophilic have to be neutralized and become somewhat hydrophobic by adsorbing organic cations. A general nomenclature, which will be used refers to the complexes formed as:

(1) Organo-clays.
(2) Micelle- and liposome-clays. In (i) the adsorbing organic cations reside initially as monomers in a water solution, whereas in (ii) most of the organic cations are initially in micelles, or vesicles (Figure 1).

2.2. Preparation and Tests of Herbicide Formulations of Slow Release

The stages include:

a. Preparation of the herbicide formulation.
b. Determination of release of the herbicide from the formulation in a water medium and in a soil environment.
c. Determination of leaching.
d. Determination of weed control in pot or column experiments.
e. Field experiment which includes determination of weed control, leaching, and resulting crop yield.

These stages involve several technologies. In the presentation the actual experimental procedures and results will be presented as illustrations.

2.3. Slow Release Formulations Hydrophobic and Neutral Herbicides

The preparation follows two steps:

a. Formation of organo-clays by adsorbing the chosen cations on the clay mineral montmorillonite.
b. Addition of an herbicide solution to the organo-clay particles. This stage can optionally occur in the same solution used in (a), and it involves a sorption of a fraction of the herbicide molecules, followed by possible stages of centrifugation, collection and drying of the pellet, followed by its grinding.

The experimental studies with clays modified with small quaternary alkylammonium cations were accompanied by modeling. The modeling of herbicide adsorption was adequately accomplished by employing the Langmuir equation, whose use enabled simulations and predictions for a variety of situations, such as several concentrations of the herbicides and organoclays at equilibrium, and also an acceptable description of the kinetics of adsorption.

The modeling of adsorption of organic cations at equilibrium employed a model [28] which considers the following elements:

(1) The total amount of the cation adsorbed consists of: (A) cations residing in the double layer region, and (B) cations bound to surface sites.
(2) The electrostatic Gouy–Chapman equations are solved for a solution or dispersion containing ions of several valences and particles whose surfaces are charged and partially neutralized by cation binding.
(3) The concentration of surface sites is explicitly considered, since it affects the depletion of cations from solution as a result of adsorption.
(4) The extension to interactions of organic cations with clays, or clay-minerals [29–32], considered that monovalent organic cations can form neutral complex, in which one cation is complexed with one surface site, and positively charged complexes, where two cations form a complex with one surface sites of a clay-mineral, such as montmorillonite.

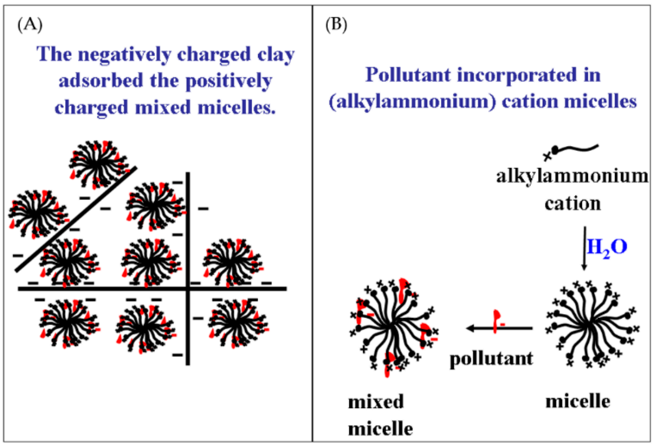


Figure 1. (**A**) The powder of the clay-mineral, such as Na-montmorillonite or a clay, such as Na-bentonite is introduced and a complex is spontaneously formed by interactions of the posi-tively charged micelles with the negatively charged clay-mineral or clay. In this scheme the mi-celle-clay complex includes the herbicide. In the absence of herbicide or pollutant molecules this Figure represents a scheme of the first stages of preparation of a micelle-clay complex. It should be noted that the sizes of micelles are in the nanometer range, whereas the lateral dimensions of the clay platelets (whose projections in the plane of the page are seen) are about 1 μm and their width is about 1.5 nm. (**B**) The salt of an organic cation with a long alkyl chain is introduced into a vessel with water. Above a concentration denoted critical micelle concentration (**CMC**) micelles of the cation form spontaneously in sizes of a few nanometers. The red colored molecules "pollutant" are herbicide molecules in the case of a preparation of slow release formulations of herbicides.

Structural formulae of several herbicides which were studied in the context of slow release formulations, and organic cations, which were used in modifying clays and clay minerals are shown in Figure 2.

In "adsorptive" clays, those modified with small quaternary cations, the adsorbed organic cation prop opens the clay layers revealing a high exposure of the siloxane surface for adsorption of organic compounds. The sorption of hydrophobic molecules is enhanced by additional interactions between the adsorbate and the preadsorbed organic cation on the clay surface [33,34]. It was shown that organo-clays which were formed by the small organic cations benzyltrimethylammonium (BDMHdA) and phenyl trimethylammonium (PTMA) interacting with montmorillonite yielded the most efficient sorption and best slow release formulations of the hydrophobic herbicides alachlor, metolachlor and acetochlor [10–12,35,36]. Thus a group of four organoclays based on four cations (Figure 2), which also includes benzyltriethylammonium (BTEA) and benzyltributylammonium (BTBA), exhibits a sequence PTMA > BTMA > BTEA > BTBA, which reflects their efficiency to sorb the above hydrophobic herbicides and reduce their leaching. This sequence indicates that a smaller size of the organic cations was advantageous. It was suggested that a significant contribution to enhanced sorbed amounts of the above hydrophobic herbicides was due to interactions between the phenyl rings of herbicide molecules and organic cations, which was favored by the smaller cations, PTMA and BTMA. The adsorption affinity of the herbicides increased when the BTEA loading was increased up to the cation exchange capacity (CEC) of montmorillonite, but for organo-clays based on BTMA or PTMA, maximum sorption was achieved when the loading of the cations was about 5/8 of the CEC. This result was explained by model calculations for the adsorption of the organic cations PTMA and BTMA by montmorillonite, which yielded relatively larger fractions of charged complexes consisting of 2 cation molecules and a surface site. In the cases of PTMA and BTMA the fractions of charged complexes were at least 27% and 14–18% at a loading corresponding to the CEC, respectively. In the case of BTEA the fraction of charged complexes was several-fold smaller. The tendency to form self-association between the adsorbed cations implies that their phenyl rings are less available for interaction with herbicide molecules, which results in reduced sorbed amounts of the above herbicide molecules by montmorillonite. In addition, it can be expected that the positively charged sites will be less hydrophobic. In the case of BTEA the interaction between the phenyl groups of the herbicides and the cations, and the fraction of charged complexes is smaller; hence, the sorbed amounts increase with the loading of BTEA up to the CEC, which results in neutralizing the negative charges of the clay-mineral. The same pattern described above was also observed in the case of the hydrophobic herbicide norflurazon interacting with montmorillonite preadsorbed by BTMA or BTEA. These examples illustrate that optimal sorption of hydrophobic herbicides may occur for incomplete charge neutralization of a clay-mineral.

FTIR studies in Table 1 below which is selected from Table 3 in [36] also support this explanation.

Table 1. FTIR vibration bands (cm^{-1}) of Alachlor and Alachlor sorbed on Montmorillonite and its complexes [a].

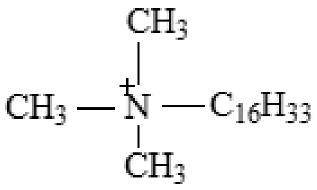
Free Alachlor	Band of C Aromatic- H 793
Clay	809
Clay-BTMA 0.5	815
Clay-BTMA 0.8	809
Clay-BTEA 0.5	810
Clay-BTEA 0.8	810

[a]: The infrared spectra of the organo-clay were subtracted from the corresponding spectra of alachlor-clay or alachlor–organo-clay.

The out-of-plane C-aromatic–H deformation vibration of alachlor molecules was shifted from 793 cm^{-1} for free alachlor to 809 cm^{-1} for alachlor sorbed on montmorillonite and montmorillonite-BTMA 0.8 mmol/g, but a larger shift to 815 cm^{-1} was observed for alachlor sorbed on montmorillonite-BTMA 0.5 mmol/g (Table 1). This shift indicates interaction of the aromatic ring of alachlor with both the clay and organo-clays, but the interaction appears stronger for the 0.5 mmol/g load of BTMA. On the other hand, the corresponding shift is the same for both loads of BTEA on the clay-mineral montmorillonite.

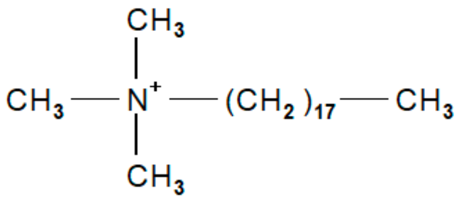
Reactivity of organoclays synthesized by adsorption of long carbon chain quaternary ammonium cations (“organophilic” clays) to hydrophobic herbicides is different than that of adsorptive clays. In this case it was reported that higher loading of the cations on the clay surface, yields more sorption of the herbicide. At high loading, the herbicide is partitioned into the hydrophobic phase created by interactions between the long alkylammonium backbones [37]. Therefore, the sorption of herbicide molecules will be a function of the arrangement of the organic cation on the clay surface which is dependent not only of the organic loading but also of structural characteristics of the clay. Increasing the organic phase will induce transitions on the clay surface from a flat monolayer to a bilayer lying parallel to the clay platelets, followed by a pseudo-molecular trilayer and finally to a paraffinic structure of very high affinity for hydrophobic molecules [38]. Clays with lower charge density will create voids between the hydrocarbons, which facilitate the accommodation of the herbicide and enhance interactions between them, in addition to interactions of polar moieties of the herbicide molecules with siloxane surface or headgroups of the surfactant [39]. Clay-based formulations by using organophilic clays have been described for bentazone [40], hexazinone [41,42], picloram [41] terbuthylazine and diuron [43], simazine [44], atrazine [45], ethofumesate [46]. With few exceptions, the use of organophilic clays usually provides slow release formulations with very low active substance (ai). An approach to raise its content is described in the following section.

Surfactants



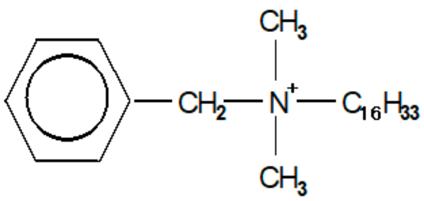
$CH_3-\overset{+}{N}(CH_3)_2-C_{16}H_{33}$

HDTMA

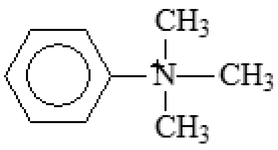


$CH_3-N^{+}(CH_3)_2-(CH_2)_{17}-CH_3$

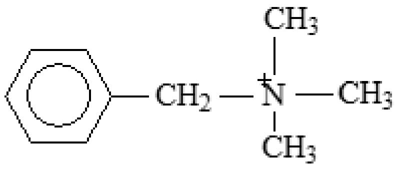
ODTMA



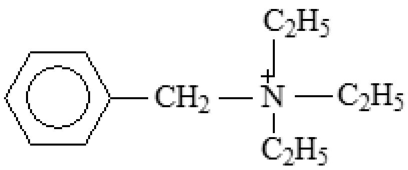
BDMHDA



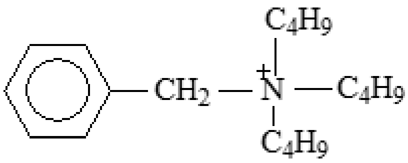
PTMA



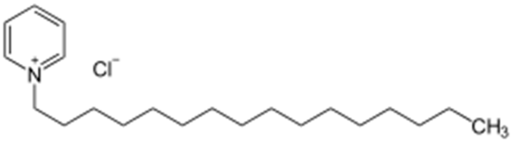
BTMA



BTEA

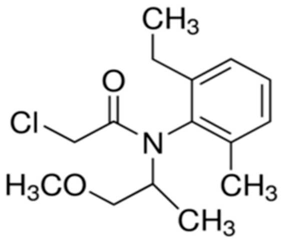


BTBA

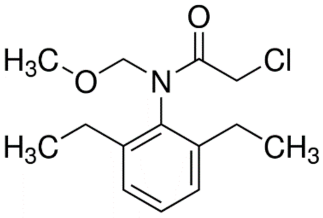


CPy; HDPy

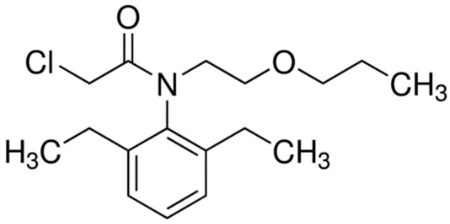
Herbicides



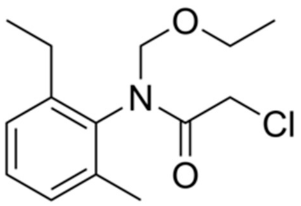
Metolachlor



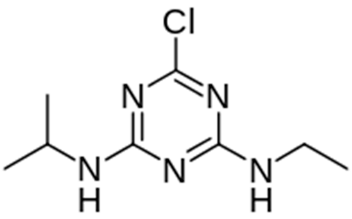
Alachlor



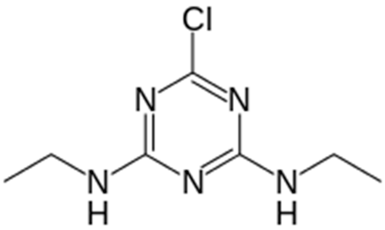
Pretilachlor



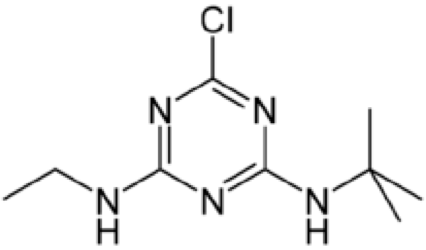
Acetochlor



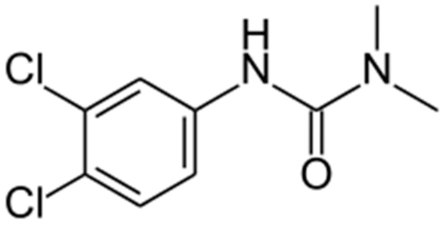
Atrazine



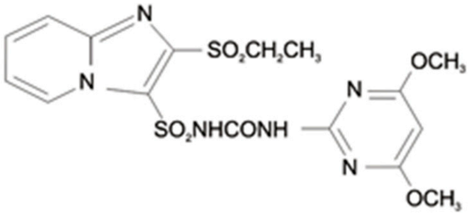
Simazine



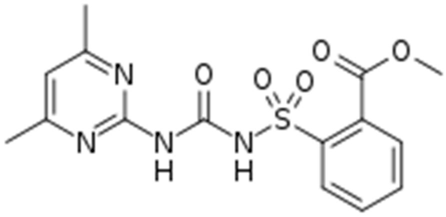
Terbutylazine



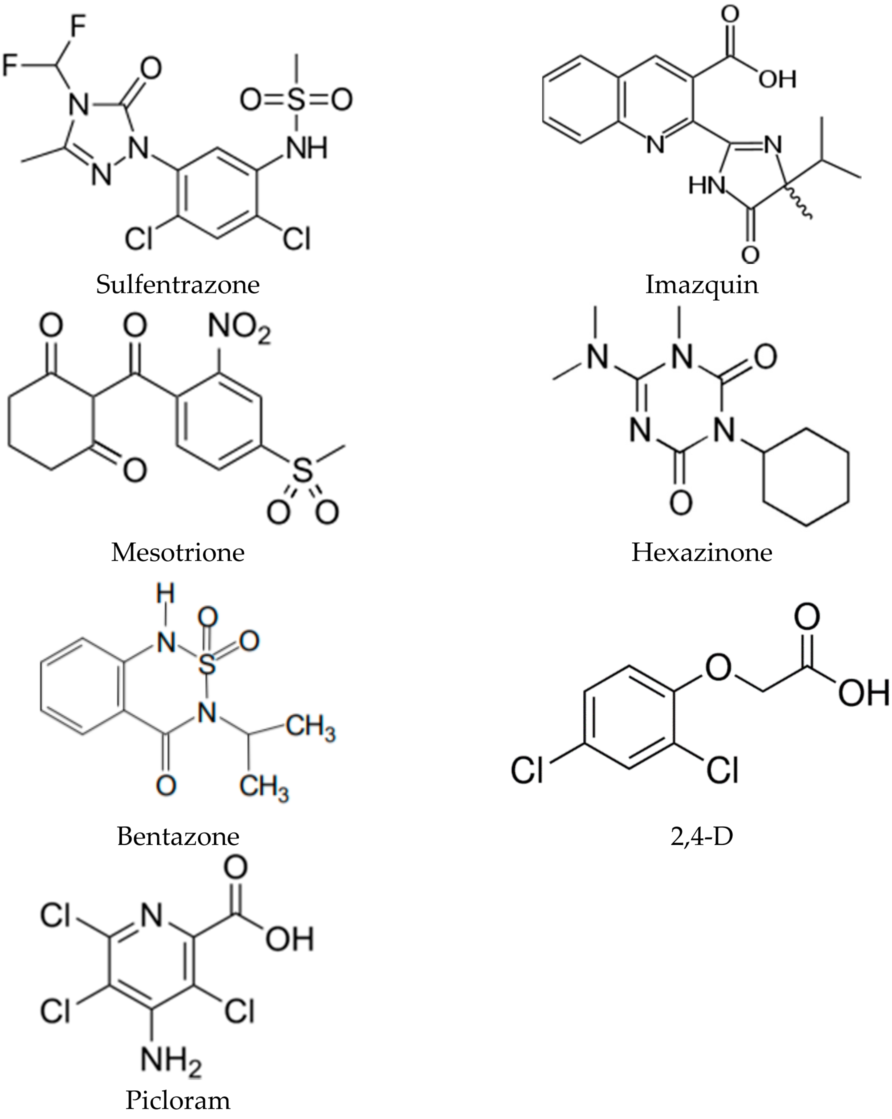
Diuron



Sulfosulfuron



Sulfometuron



Sulfentrazone
Imazquin
Mesotrione
Hexazinone
Bentazone
2,4-D
Picloram

Figure 2. Surfactants and Herbicides.

2.4. The Micelle– and Liposome–Clay Complexes

Anionic herbicides, such as sulfometuron (SFM) and sulfentrazone (SFZ)) (Figure 2) are very efficient in weed control, but their leaching poses a threat to neighboring fields and underground water [46–48]. The procedure described in Section 2.3 yielded minimal sorption of SFM, which is a weak acid, whose solubility in water increases at high pH, and its leaching and lateral mobility increase. Our approach was based on using an organo-clay whose surface had been modified to positive by suitable organic cations, which could cause charge reversal up to half (or more) of the cation exchange capacity (CEC) of montmorillonite, (or sepiolite). Irrespective of the degree of charge reversal achieved, the fraction of SFM adsorbed remained minimal. It was attempted to enhance the adsorption of SFM molecules on the backbone of the clay-based formulation, by incorporating their hydrophobic parts in a hydrophobic environment. Two solutions explored in parallel were denoted: (i) a micelle-clay [6,7], and (ii) a liposome-clay formulation [49].

In the micelle-clay approach, the idea was to incorporate the anionic herbicide in the positively charged micelles of quaternary ammonium cations (QACs), which would be later adsorbed by the negatively charged clay-mineral montmorillonite. This is illustrated in Figure 1. As a part of the design, the QAC chosen was octadecyltrimethylammonium (ODTMA), which includes an alkyl chain with 18 carbon atoms (Figure 2). Its CMC (critical micelle concentration) is 0.3 mM, which implies that at such concentration micelles of

ODTMA are spontaneously formed. At higher ODTMA concentrations, e.g., 12 mM, 11.7 mM of ODTMA are in micellar form, whereas ODTMA monomers are present at a concentration of 0.3 mM. This implies that at such concentration 97.5% of ODTMA cations in solution are in micellar form. Other frequently used micelles were composed of the organic cation benzyldimethylhexadecylammonium (BDMHDA), which has a phenyl ring; its alkyl chain includes 16 carbon atoms, and its CMC is 0.6 mM (Figure 2). Its choice was intended to maximize the interactions with the micelle-clay complex of herbicides which also possess a phenyl ring.

The micelles are spherical, or close to spherical; the positively charged head groups of the cations occupy the external surface, where they interact well with water (Figure 1). The interior, which is devoid of water is held together by van der Waals interactions between the hydrophobic alkyl chains. The spontaneous formation of the micelles reflects the fact that the system of water-ODTMA, or water-BDMHDA molecules reaches a state of minimal free energy, where the formation of micelles minimizes the disturbance to formation of water–water interactions by the organic cations in solution and the alkyl chains have maximal contacts between themselves, whereas the positively charged head groups interact well with water. For QACs with a shorter chain, the CMC is larger. The first set of experiments also tested the outcome with the widely used cation, hexadecyltrimethylammonium (HDTMA) whose alkyl chain includes 16 carbon atoms, and its CMC is accordingly 1 mM. The tests indicated that the binding affinity of HDTMA to montmorillonite was significantly smaller than that of ODTMA, which was a better choice for preparing SFM formulations for slow release [6,7].

The micelle-clay formulations, succeeded to lower significantly the leaching of SFM and enhance its biological activity. The same procedure of preparation of formulations of slow release on the basis of micelle-clay was also successful for the anionic herbicides sulfosulfuron [50], and sulfentrazone [51]. In the case of sulfentrazone the micelles were composed of BDMHDA.

Tests on sulfosulfuron (SFS, Figure 2 [50]), indicated that the order of addition of components, i.e., SFS, ODTMA, and clay-mineral yielded the same large fraction of adsorbed SFS (98%) in the preparation of a formulation based on 5 g/L montmorillonite, 5 mM ODTMA and 0.25 mM SFS. This finding was significant for encouraging future possible applications of the micelle-clay system for water purification by filtration, where the filter is filled with a dry complex and a solution of pollutants is to be purified by adsorption in the course of its passage through the filter.

In a comparative study by using metolachlor and sulfentrazone for the design of SRFs [52], it was reported that solubilization of SFZ in the ODTMA micelles was found to be higher than that of metolachlor (MTC). These loaded micelles with the herbicides were further sorbed on montmorillonite. This higher solubilization was explained by the following mechanisms: SFZ is solubilized by two ways: (a) The cationic ODTMA micelles enhance SFZ dissociation, resulting in SFZ-anion formation which binds electrostatically to the cationic micelles; (b) SFZ molecules can interact with the hydrophobic micelle core (solubilized into the micelle). In contrast, MTC solubilization in micelles was attributed only to its partitioning between the hydrophobic core and the water solution, and therefore was lower than the solubility obtained for SFZ.

A methodical approach for the synthesis of micelle-clay formulations was designed and its viability was experimentally tested. This approach consisted of the determination of the solubility of the herbicide into the surfactant micelles, and the binding affinity of the surfactant to the clay surface, which permits to determine theoretically the fraction sorbed for any clay/surfactant ratio and optimize its sorption. In a further step, the amount of ai in the final formulation can be estimated by considering that the same proportionality between the ai and the micelles in solution was maintained during the sorption of the loaded micelles with the herbicide [53]. This approach permits to test a priori the viability of any clay-surfactant system in obtaining a herbicide formulation with few experimental data determined previously. The herbicides mesotrione, metribuzin, and flurtamone, and three ethoxylated surfactants, the non-ionic alcohol alkoxylates berol B048 and berol B266, and the tallow alkyl ethoxylated amine Ethomeen T15 (ET15), were assayed with the fibrous clay mineral sepiolite. Unlike flurtamone (no formulations were feasible), formulations of metribuzin and mesotrione were obtained with ai content up to 5% for metribuzin with B266 and 16% for mesotrione with ET15. Whereas the alcohol alkoxylates were adsorbed by forming hemimicelles by H-bonding with the silanols present on the clay surface; ET15 was adsorbed by exchange with Mg ions; its ethoxyl units were penetrating into sepiolite tunnels developing an admicelle sorbed structure [53,54]. The loci of solubilization of the herbicides were different in the micelles of the three surfactants: flurtamone inside the hydrophobic core; metribuzin resided in the palisade layer of the micelles and mesotrione in the micelle/water interface [55]. Therefore, the use of this tool is promising.

In a similar approach to micelle-clay systems, liposomes, which form spherical surface aggregates defined by a double bilayer of surfactant limiting an inner water aqueous compartment, were used for encapsulation of herbicides and further sorption on clay minerals for the preparation of slow release formulations [49]. The clay mineral used was montmorillonite. As observed with micelle-clays, an optimal vesicle/clay formulation of anionic herbicides, such as sulfometuron and sulfosulfuron, by using cationic surfactants such as didodecyldimethylammonium bromide (DDAB) and dioctadecylammonium bromide (DDOB) can be obtained for vesicle/clay ratios such that most of the vesicles are adsorbed without undergoing premature decomposition. Otherwise, this would result in release to solution of pre-bound anionic herbicide molecules, which in turn, do not adsorb on the negatively charged clay mineral platelets or adsorb inefficiently on clay platelets adsorbed by the positively charged monomers [6,56]. Unlike SRFs by using hydrophilic clays, the use of longer alkyl chain instead, as in the case of DDOB, did not enhance the sorption of the ai, because of the faster permeabilization of the herbicide from the vesicles when they were sorbed [56]. Liposome-clay formulations were also obtained by replacing cationic surfactants with the neutral lipid phosphatidylcholine (PC), which poses a zwitterionic structure. The integrity of vesicles after sorption is not maintained. After an initial sorption by few contact points of the vesicles on the clay surface, they started to flatten out from the periphery to the center resulting in a bilayer vesicle with grows up by incorporating lipids from other vesicles sorbed in its vicinity up to developing a supported planar bilayer (SPB), as determined with DDAB and PC vesicles by fluorescence measurements, freeze-fracture electron microscopy, X-ray diffraction, and FTIR spectroscopy [49,56–59]. In the particular case of PC, the lipids are interacting with the clay surface by electrostatic interactions with the choline moiety of its headgroup. Herbicides are sorbed within the SPB by interactions with the alkyl chains of the lipid molecules in addition to water bridges with the head-polar moieties of PC [57,60]. PC-clay formulations with high ai were obtained for the herbicides atrazine (up to 9% *w:w*) and alachlor (up to 40% *w:w*) [58]; metribuzin (up to 25% *w:w*) [61]; and diuron (up to 28% *w:w*) [62].

2.4.1. Release Experiments

An efficient procedure enabled to estimate the release of the herbicide from organoclay formulations under irrigation conditions by a “soil funnel experiment” [50]. The herbicide formulation was applied on a thin soil layer deposited on filter paper inside a Buchner funnel (10 cm diameter), and irrigated with 50 mm of water. Ten fractions of the irrigated water solution were collected. The leached herbicide concentration was determined analytically by HPLC. The Rehovot sandy soil was chosen because of its minimal interaction with the herbicides. This inert soil enabled to test our new formulations under extreme conditions of leaching. It is expected that the leaching of the anionic herbicides will be similar in clay-rich soils because of the weak interaction of these herbicides with the negatively charged clay particles. The results of release in the funnel experiment (Table 2) demonstrate a dramatic decrease in the rate of release of herbicide from the micelle-clay formulation, in comparison with the release from the commercial one, (Monitor). Similar results were obtained for the new micelle-clay formulations of the anionic herbicides, sulfometuron [6,7], and sulfentrazone [51], in comparison with their commercial formulations. Similar advantage of slow release was also found in the case of hydrophobic herbicides, such as acetochlor [12].

Mobility of designed formulations was also followed by using soil columns. The efficiency of sulfentrazone and metolachlor from micelle-clays [52] was demonstrated along soil layers at several depths by using a bioassay based on shoot growth inhibition of a test plant foxtail. A significant improvement in weed control and reduced leaching, in comparison with the commercial formulations was obtained with both micelle-clay formulations. In the case of metolachlor, the new formulation yielded more growth inhibition in the layer 0–3 cm and significantly less inhibition at depths above 15 cm, than the commercial formulation (Dual Gold), indicating less leaching of the active substance with the application of the new formulation, and good biological activity of the herbicide. In the case of sulfentrazone, the new formulation yielded 100% inhibition in the layer below a depth of 3 cm vs. less than 50% inhibition by the commercial formulation Boral.

A good correspondence was obtained between the release experiments by using "soil funnels" and the leaching studies with "soil columns". After six irrigation events in "soil funnels", the release of metribuzin from PC-clay formulations prepared with ai contents of 17 and 25% *w:w* was reduced by 73 and 56%, respectively [61]. Soil columns of 16 cm length which were watered with 70 mm of rain after herbicide application, and sliced after 24 h to determine the remaining amount at several depths, yielded a better performance of the PC-clay formulations than the commercial (Eclipse 70) (Figure 3). In the case of the commercial formulation, retention of the herbicide in the upper two soil layers was significantly lesser than those with PC-clay ones. The amount remaining in the upper layer was 20% of the amount applied of the commercial formulation. In comparison, the remaining herbicide in PC-clay formulations amounted to 33% herbicide for PC-clay (17%) and 30% for PC-clay (25%). In the following segment, the amounts were also higher for PC-clay formulations, whereas that of the commercial formulation was significantly higher for the following layer. This leaching pattern was paralleled with the reduction in fresh weight per shoot of *Setaria viridis* in the two upper layers. Enhanced bioactivity by using PC-clay formulations was impressive in the upper layer (Figure 3b).

Table 2. Sulfosulfuron release in the "funnel" experiment (% of total applied).

Wash #	Commercial	Micelle-Clay
1	77.60	0.45
2	14.97	0.42
3	1.45	0.40
4	0.93	0.39
Total	99.91	3.67

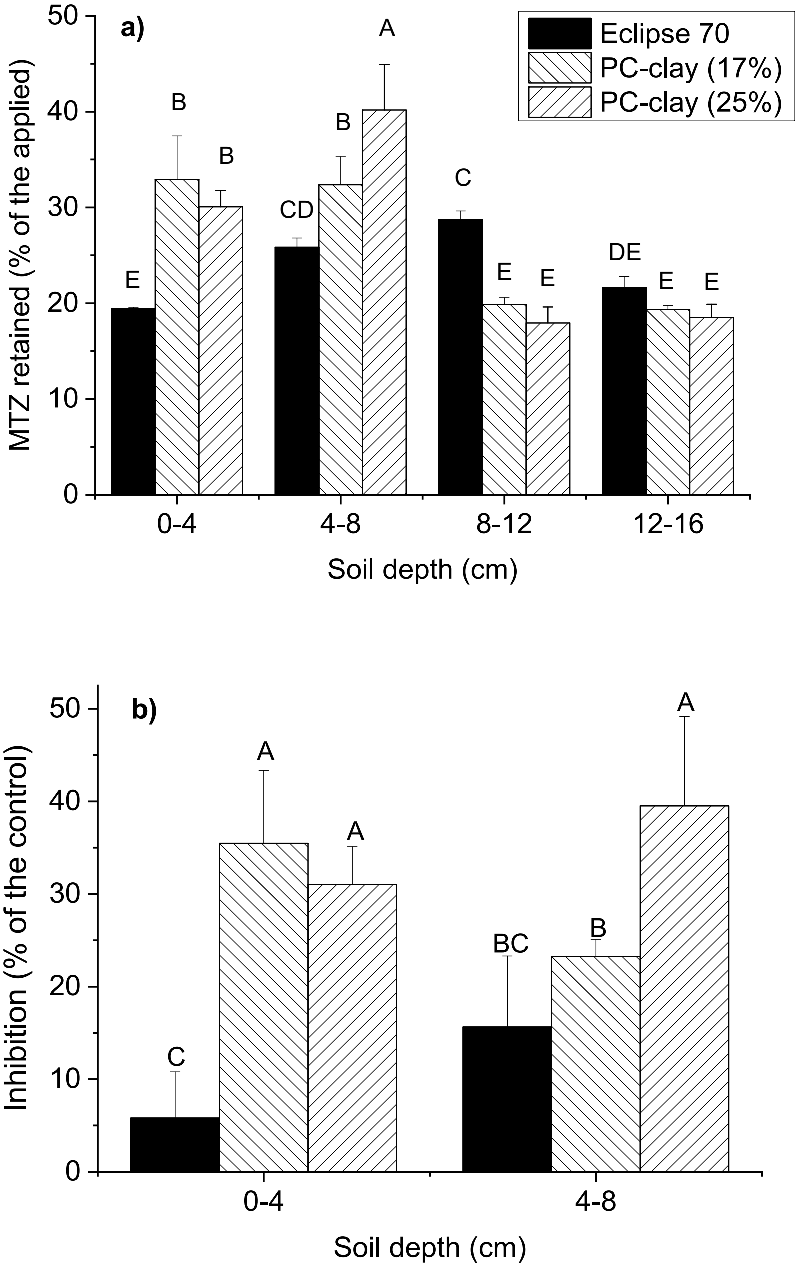


Figure 3. Percentage retained in soil column experiments (**a**) and herbicidal activity in the upper segments (**b**). Means followed with the same letter are not significantly different according to Student's multiple range test at $p = 0.05$.

2.4.2. Field Experiments

There are very few studies focusing on the comparison in the performance and reduced leaching of the clay-based formulations vs. the commercial products, under field conditions, which is the ultimate validation. In this section, three studies are presented by using slow release formulations prepared from three different approaches: an adsorptive clay [12], a clay-liposome complex [60], and a clay-micelle [54].

(a) **Organoclay Formulations of Acetochlor**

A slow release formulation of acetochlor was obtained by sorbing the herbicide on montmorillonite-PTMA at a cation load of 0.5 mmol/g clay [12].

Wheat seeds were sown on 20 November 2000, in sandy soil at the Faculty's Experimental Farm using an experimental planter (140 kg seeds/ha) on prepared beds. Five rows were sown in each plot (1.2 m × 8 m, 25 cm high bed). On the following day, acetochlor (1.5 kg as/ha) was applied either as the commercial formulation (EC; Harness, 90% ai) or the organo-clay formulation in a randomized block design with 5 replications. The commercial formulation was applied in 270 L/ha of water, whereas the organo-clay formulation was applied in a volume of 2.2 m^3/ha using a motorized knapsack sprayer. A few hours later the whole field was sprinkler irrigated (500 m^3/ha) at a rate of 5 mm/h. Wheat seedlings emerged 7 days later. Following the first irrigation of 500 m^3/ha, the experimental plots were irrigated one week later with additional 100 m^3/ha. The rainfall was measured automatically by a meteorology station. The total rainfall during the 2 months period was 127 mm.

Leaching of acetochlor applied in soil columns filled with soil taken from the field and sprayed by the herbicide formulations demonstrated that the slow release formulation was mostly active at low depths of the columns, whereas the commercial formulation was mostly active at the larger depths. Table 3 below emphasizes that the activity of the organo-clay based formulation of acetochlor was mostly in the top 5 cm layer in the field, i.e., the layer where the majority of weed seeds are expected to reside.

The dissipation of the ai from the upper 5 cm was monitored. On each of the 5 following weeks after planting, 1.5 kg of the upper 5 cm soil was sampled from each plot using a big spatula. The soil was transferred to two pots (6.5 cm × 6.5 cm surface area), and 10 seeds of green foxtail (*Setaria viridis*) were planted. The pots were arranged in a complete randomized design with five replications. Three weeks after planting, plant height was measured and inhibition rate was calculated for the average plant height in each pot.

Percent of shoot growth inhibition was calculated according to the following formula: % Growth Inhibition = $100*(P_c - P_t)/P_c$
In which P_c and P_t are the shoot height of the untreated control and the treated samples.

Table 3. Effect of acetochlor formulations on growth inhibition of the test plant green foxtail in soil taken from the upper 5 cm of soil in a field experiment in Rehovot as determined weeks after application.

Time (Weeks)	% Growth Inhibition	
	Clay-PTMA 0.5	Commercial Formulation (EC)
2	100	38 ± 7
4	93 ± 3	6 ± 6
6	74 ± 6	2 ± 5

Effect of acetochlor formulations applied in field study on green foxtail growth was determined several weeks after application. Soil samples were collected from field plots at a depth of 0–5 cm. Total irrigation (including rain) was equivalent to 60, 70, 92, 142, 146 mm on 2, 3, 4, 5, 6 weeks after application, respectively. The organo-clay based formulation contained 4% acetochlor. The results are presented in Table 3.

Following irrigation of 600 m^3/ha, and 127 mm rainfall, the formulation based on exchanging clay with PTMA at 0.5 mmol/g clay was found very effective in weed control even 6 weeks after application, whereas the herbicidal activity of the commercial EC formulation was significantly lower. The herbicidal activity of acetochlor adsorbed on clay exchanged with PTMA resulted in 97 to 74% growth inhibition as determined by shoot height for 2 to 6 weeks after application.

The organo-clay formulations, unlike the EC formulation, gave excellent weed control for extended periods, which is attributed to slow release of the ai from the organo-clay complex into the topsoil layer. From the environmental point of view, the maintenance of the ai of the herbicide in the topsoil layer reduces the hazard of contamination of ground water.

(**b**) PC-clay Formulations of Alachlor

A field experiment was conducted to test the efficiency reduced leaching of a PC-clay formulation of alachlor with a very high ai load (40% *w:w*) vs. the commercial formulation Alanex (48% *w:v*) in plots randomly sown with oats (*Avena sativa*) as a test plant [60]. The amounts at several soil depths were extracted 59 and 99 days after treatment (DAT), and compared with the predictions of data by using PEARL model, a chromatographic model widely used in the European Union (**EFSA**) for registration of herbicide formulations [63]. This model was parametrized for slow release with the chemical and physical properties of the herbicide molecule, type of soil, the experimental half-life ($T_{1/2}$) in soil and in-vitro release kinetics that were determined by laboratory experiments. At the end of the experiment, the plants shoots were harvested and the bio-efficacy of the formulations was evaluated by weighing the fresh shoot biomass.

Fifty nine DAT (Figure 4), the total amounts recovered were similar for the commercial and the PC-clay formulations, 77 ± 7% and 83 ± 5%, respectively, but the distribution along the soil profile differed. A higher retention was observed at the upper layer for the PC-clay formulation than for the commercial (49 ± 1% vs. 36 ± 1%) and the opposite trend in the following layer (21 ± 3% vs. 29 ± 1%). Model predictions were pretty good for both formulations. At 191 DAT, the residual amounts were similar for both formulations within the upper 20 cm, but at the deepest layer, the experimental amount was much higher for the commercial formulation (28 ± 1%) than for the PC-clay based formulation (18 ± 1%). In this case, the predictions were greatly overestimated in the first two layers whereas underestimated in the deepest layer for the commercial formulation. No statistical difference was noticed in the crop yield.

The behavior of the PC-clay formulation clearly showed a slow release of the ai with a larger accumulation in the upper layer at 59 DAT, and lower recovery at the deepest layer at 191 DAT, while maintaining identical bioactivity.

This study showed the great discrepancy obtained between the laboratory and field experiments. The degradation T1/2 of the herbicide under constant laboratory-controlled conditions of moisture at field capacity, and temperature (20 °C), was 13 days, so that the herbicidal activity should be completely dissipated after 59 and 191 DAT. This was explained by climatic factors such as oscillation in soil moisture content and temperature, and the effect of drying and wetting cycles.

In addition, the use of predictive models based in part on experimental constants determined under laboratory conditions should be handled carefully. The model greatly overestimated the residing amounts in the upper layers. Chromatographic models, such as PEARL are used to evaluate the leaching of pesticides to the groundwater, by using, as criterion, the amount leached at 1 m depth [60]. At this depth, a good concordance may be expected with the measured concentrations, and in case of overestimating the real values, the safe criterion established would remain valid. However, the use of this type of models to evaluate the persistence of herbicides in tops soils may drive to wrong conclusions. One reason for this variation is the effect of microbial adaptation for degrading the herbicide. This study reinforces the need of conducting field experiments.

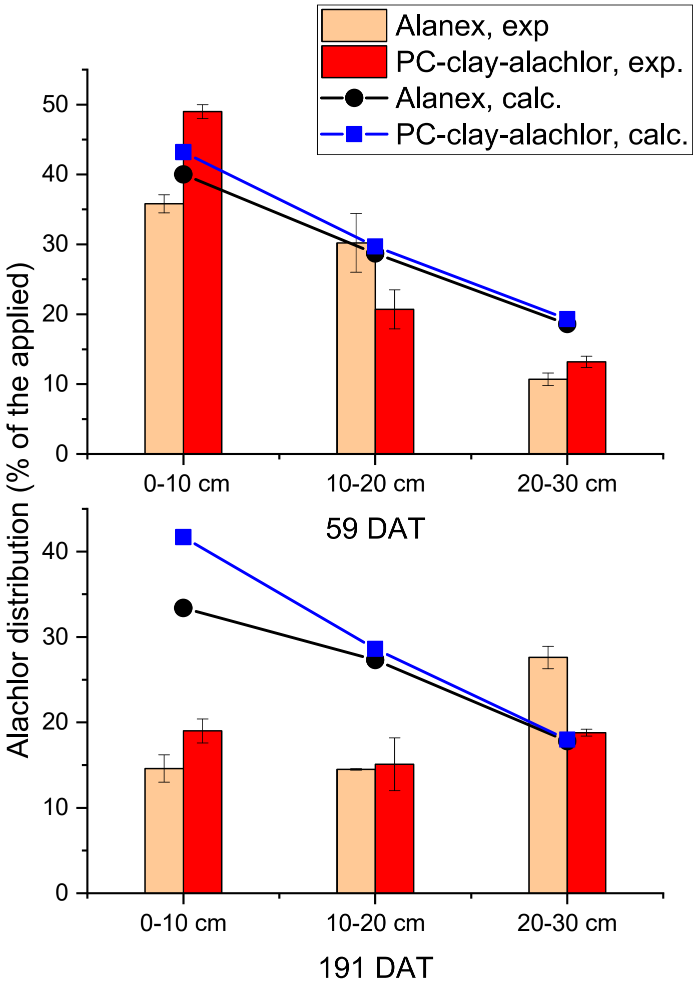


Figure 4. Distribution of alachlor applied as a commercial formulation (Alanex, 48% ai EC) and as a PC-clay formulation (40% ai) in soil depth 59 and 191 DAT. (Adapted from [60].).

(c) Clay-ET15 Formulations of Mesotrione

A micelle-clay formulation of the herbicide mesotrione with a content of 15% ai *w:w* was also tested against the commercial formulation Callisto (10% *w:v*). The clay-based formulation was made of the fatty amine ethoxylated surfactant Ethomeen T15 (ET15). The formulations were used as post-emergence in a maize crop with sunflower as a model of broadleaf weed between maize rows. As previously, the herbicide was extracted from the soil at several depth levels 10 and 30 DAT. At the end of the experiment the crop yield was determined.

The amount extracted at 10 DAT was about 7-fold higher for the micelle-clay-ET15 formulation relative to the commercial one in the upper layer, and about three-fold in the following layer (Figure 5). At the lowest depth, the amount of mesotrione was similar for both formulations. At 30 DAT, dissipation pattern is completely different. The residual amount in the upper layer is minimal for both formulations, and the amount determined at the largest depth was 4-fold higher for the commercial formulation. This behavior was explained by the fast-driven dissipation of this herbicide in soils via microbial degradation (its half-life in this soil was 10 d). Slow release was responsible for the large detection of the herbicide in the upper layers at 10 DAT. The microbial flora which is larger at these upper layers, degrades the herbicide that is slowly released and thus accessible. However, the herbicide migrated to the deepest layer is hardly degraded, increasing the risk for groundwater pollution. Again, no statistical difference was noticed in the crop yield at the end of the experiment.

Slow release formulations prepared from three different approaches: an adsorp-tive clay, a clay-liposome complex, and a clay-micelle, are shown in Table 4.

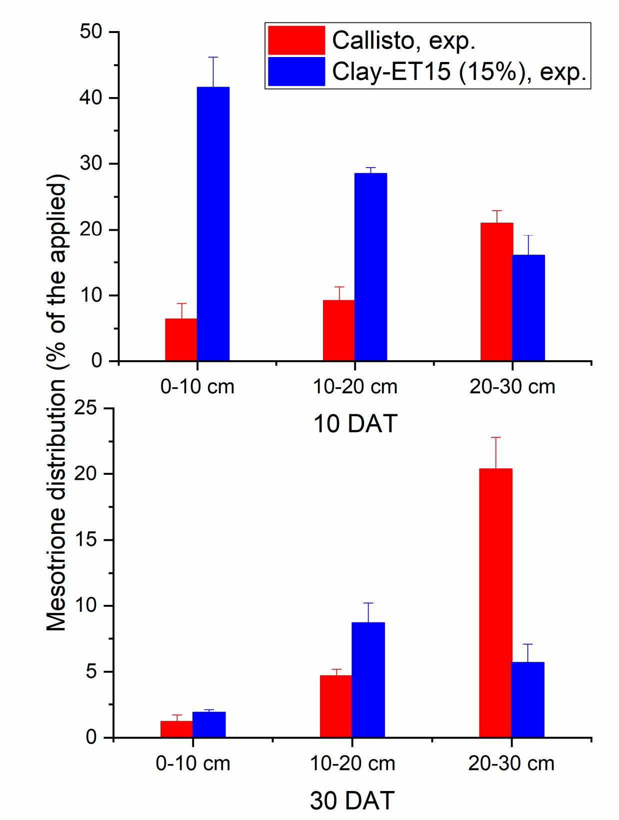


Figure 5. Mesotrione distribution applied post-emergence as a commercial formulation (Callisto, 10% ai *w:v*) and a micelle-clay-ET15 (15% ai *w:w*) in soil depth 10 and 30 DAT. Adapted from [54].

Table 4. Slow release formulations (SRFs) of several representative herbicides, based on quaternary ammonium cations (QACs)-clay composites; Montmorillonite (MMT).

Surfactant Modifier	Herbicide	Clay/Mineral Clay	Reference; [Remarks]
Hexadecyltrimethyl-ammonium (HDTMA)	Bentazone	MMT	Carrisoza et al. 2000 [40]
	Hexazinone	MMT	Celis et al., 2002 [64]
			Celis et al., 2005 [42]
	Acetochlor	MMT	Kaluderovich et al. [65]
	Picloram	MMT	Celis et al., 2002 [41]
	Pretilachlor	Bentonite	Wu et al., 2020 [66]
	Sulfometuron	MMT	Mishael et al., 2002 [6] [Micelle-clay].
	Sulfosulfuron	MMT	Mishael et al. 2003 [50] [Micelle-clay].
	Sulfentrazone	MMT	Polubesova et al., 2003 [51] [Micelle-clay].
		MMT	Ziv and Mishael, 2008 [52]. [Micelle-clay].
	Diuron	MMT	Celis et al., 2007 [43].
	Terbutylazine	MMT	Celis et al., 2007.

	MCPA	MMT	Celis et al., 2007.
	2,4-D	Bentonite (also zeolite, composed mainly by clinopetilolite) MMT MMT	Shirvani et al., 2014 [67]
	Atrazine	Bentonite	Hermosin et al., 2006 [68]. Trigo et al., 2010 [45]. Dutta et al., 2015 [34]
Benzyldimethyl-hexadecylammonium (BDMHDA)	Sulfentrazone	MMT	Polubesova et al. 2003 [51] [Micelle-clay].
Octadecyltrimethyl-ammonium (ODTMA)	Sulfometuron	MMT	Mishael et al., 2002 [6,7] [Micelle-clay].
	Sulfosulfuron	MMT	Mishael et al. 2003 [50] [Micelle-clay].
	Sulfentrazone	MMT	Polubesova et al. 2003 [51] [Micelle-clay].
	Metolachlor	MMT	Ziv and Mishael, 2007 [52]. [Micelle-clay].
Dioctadecyldimethyl-ammonium (DDOB)	Bentazone	MMT	Carrizosa et al., 2000 [40]
	Hexazinoe	MMT	Celis et al., 2002 [64]
Didodecydimethyl-ammonium (DDAB)	Sulfometuron	MMT	Undabeytia et al., 2003 [49] [Vesicle-clay]
	Sulfosulfuron	MMT	Undabeytia et al., 2003 [Vesicle-clay]
N-cetylpyridine	2,4-D	Bentonite (also zeolite: clinopetiolite)	Shirvani et al. 2014 [67]
Phosphatidylcholine (PC): 74% distearyl PC and 26% 1-palmitoyl-2stearyl PC.	Alachlor	MMT	Sanchez-Verdejo et al, 2008 [58,59] [Vesicle-clay]
		MMT	Undabeytia et al., 2008, [57] [Vesicle-clay]
	Atrazine	MMT	Tejada et al., 2017 [69]. [Vesicle-clay]
		MMT	Sanchez-Verdejo et al, 2008 [69] [Vesicle-clay]
	Diuron	MMT	Undabeytia et al., 2008 [57] [Vesicle-clay]
	Meribuzin	MMT	Tejada et al., 2017. [69] [Vesicle-clay]
		MMT	Undabeytia et al. 2012 [62] [Vesicle-clay]
		MMT	Undabeytia et al. 2010 [60] [Vesicle-clay]
Phenytrimethylammonium (PTMA)	Metolachlor	MMT	El-Nahhal et al., 2000 [11]
	Alachlor	MMT	El-Nahhal et al., 2000

	Acetochlor	MMT	El-Nahhal et al., 2001 [12]
	Bentazone	MMT	Carrisoza et al, 2000 [40].
	Hexazinone	MMT	Celis et al., 2002 [64]
		MMT	Celis et al. 2005 [42]
	Diuron	MMT	Celis et al., 2007 [43]
	Terbutylazine	MMT	Celis et al., 2007
	MCPA	MMT	Celis et al., 2007.
	Atrazine	MMT	Trigo et al., 2010 [45]
		Bentonite	Dutta et al., 2015 [34]
Octadecylammonium (ODA)	Bentazone	MMT	Carrisoza et al, 2000 [40]
	Hexazinone	MMT	Celis et al., 2002 [64]
			Celis et al., 2005 [42]
	Picloram	MMT	Celis et al., 2002 [41]
Trioctylmethylammonium (TOMA)	Atrazine	Bentonite	Dutta et al., 2015 [34]
Tallow alkyl ethoxylated amine (ET15)	Mesotrione	Sepiolite	Galan-Jimenez et al. 2020 [54]

3. Removal of Pollutants from Water

Since filtration is a main procedure in water purification, the clay-composites, which have been demonstrated to be very good adsorbents have become natural candidates for the materials filling the filters. It turned out that the powdered composites had to be mixed with granulated materials, such as sand, in order to enable flow in the filter. Consequently, efficient filtration required to develop granulation procedures of the clay-composites.

3.1. Granulation of Clay-Composites

The search of optimal ratios between the organic cations and clay-minerals or clays in the preparation of micelle-clay composites required to consider the distribution of the cations used between micelle and monomer states [6,70]. A large ratio between the clay and the organic cations (e.g., ODTMA or BDMHDA) yielded poor results for achieving efficient herbicide formulations, and removal of pollutants by filtration was poor, since adsorption of the cations as monomers by the excess clays shifted the distribution of the cations in the suspension towards decomposition of the micelles. An optimal ratio was 12 mM of organic cation per 10 g/L of the clay-mineral sodium montmorillonite (which amounted to 8 mM of e^-). For this ratio the clay-mineral (or clay) is loaded by an excess of positive charge of 0.5 of the CEC. Under such condition, the fraction of organic cation (ODTMA) remaining un-adsorbed in solution during the preparation of the complex was close to zero for the large concentrations of the components used. Usually a ratio of 2:4.5 w/w between the salt and clay was used for loading the cation at 50% of charge reversal of the clay. The stages of preparation of granulated micelle-clay complexes based on ODTMA are detailed in Nir et al. (2015) [71] and Nir and Ryskin (2019) [72] were

(1) Incubation of ODTMA-Br in tap water at temperatures between 38 °C and 50 °C for 1–3 h, which was the time needed for complete dissolution of the cation ODTMA. At the end of the dissolution most of the cation ODTMA was in micellar form and the solution became clear. At lower temperatures, e.g., 22–24 °C the liquid looked opaque.

(2) A gradual addition of the clay (sodium-bentonite) during 1 h while stirring the solution for 3 h. This procedure produced a micelle-clay complex which was left to sediment for 1 h.

(3) Filtration of the sediment (or cake) in a membrane filter press to a final water content of 45 to 50%; heating was applied when the water content in the cake was larger by placing the cake in an oven at temperatures between 60 to 100 °C. When needed, the cake was broken by a knife crusher or by a mixer.
(4) Granulation of the crushed cake was accomplished by a two-stage machine. First a shredder was used to obtain the desired granule size; the second stage involved production of spherical granules.
(5) Drying of the granular micelle-clay was in an oven at 50 to 60 °C for about 24 h or more, until no further weight loss was observed, corresponding to 3% humidity.
(6) The granules were sieved by a vibrational equipment for selection of suitable particle size fractions, whose dimensions were 400 × 400 mm. The sizes of the sieve holes chosen were based on the required particle sizes and the diameters were between 0.3, or 0.4 and 2 mm. More than 85% of the material was granules in the range of the chosen sizes. The choice of particle size requires a compromise. The smaller particles exhibited a larger efficiency of adsorption of pollutants, but the presence of smaller particles in a filter results in a larger chance of clogging. The granulated particles which deviate from above stated standards can be reprocessed.

3.2. Modeling of Filtration Kinetics

3.2.1. Introduction

This section follows the presentation in Nir et al. [7,73], and Nir and Shuali [20]. Here an equation which considers convection, adsorption, and desorption (according to the Langmuir formalism) is presented and solved numerically for filtration, which includes several pollutants. In Section 3.2.2, the treatment of the possible complications in filtration of solutions including several pollutants is presented. In fact, a solution may include many solutes, but when their binding affinities (K-values, Equation (3.3)) are very small relative to that of a single dominant pollutant. Reasonable simulations and predictions can be executed by considering explicitly just one solute, as in the case of removal of perchlorate by a filter which included the micelle (ODTMA)-clay complex [71]. The treatment employs the Langmuir equation which ignores changes in affinity due to changes in surface potential, on account of a relatively small coverage of the adsorbing surfaces of particles in the filter.

Here is presented a solute transport model, which accounts for site specific and also competitive adsorption processes according to the formalism of the Langmuir equation. The proposed model ignores mechanical dispersion for the flow through the filter, which can be justified when solute transport is dominated by adsorption rather than diffusion and dispersion. Nir et al. [73] demonstrated that for a relevant range of kinetic parameters and flow velocities the calculated values of our numerical program agree very well with those according to STANMOD [74].

3.2.2. Adsorption and Convection in a Column Filter

The equations below are for a solution with several solutes. By using i = 1 in the equations below, and avoiding the summation in Equation (3) these equations are reduced to the case of a single solute.

The column filter is of length L and a cross section A, and is filled with material whose molar concentration of adsorbing sites is R_0. The beginning and end parts of the filter are at the coordinates X = 0 and X = L, respectively. We consider a situation where a solution containing several (i=1…m) pollutants is provided at given concentrations, C_{0i}, i.e., Ci(X, t) = C_{0i} for X ≤ 0, where t denotes the time.

$$dCi(X,t)/dt = -v \times \partial Ci(X,t)/\partial X - C_i \times Ci(X,t) \times R(X,t) + D_i \times RLi(X,t) \quad (1)$$

in which,

RLi(X,t) is the molar concentration of occupied sites of type i.

v denotes the flow velocity in the filter, which is given by

$$v = Q_v/(A \times f) \quad (2)$$

in which Q_v is the flow rate (volume/time) and f is the fraction of pore volume out of the total volume of the filter. R(X,t) denotes the molar concentration of free adsorbing sites, i.e.,

$$R(X, t) = R_0 - \sum RLi(X,t) \quad (3)$$

C_i are the forward rate constants of adsorption ($M^{-1}min^{-1}$) and $D_i(min^{-1})$ are the rate constants of dissociation. The quantities $Ki = C_i/D_i$ are the affinity coefficients of pollutant i.

The filter was divided to n planar sections of width $\Delta X = L/n$. The numerical solution employs the approximation

$$-\partial\, Ci(X,t)/\partial\, X = (Ci(X,t) - Ci(X + \Delta X, t))/\Delta X \quad (4)$$

and a Taylor expansion:

$$Ci(X, t + \Delta t) = Ci(X,t) + (dCi(X,t)/dt) \times \Delta t \quad (5)$$

and similarly for RLi(X,t), which satisfies the equation:

$$dRLi(X,t)/dt = C_i \times Ci(X,t) \times R(X,t) - D_i \times RLi(X,t) \quad (6)$$

A Fortran program solves these equations numerically. A non-trivial test on the mass conservation of pollutants and adsorbing sites was incorporated; mass conservation is only satisfied when using a sufficiently small-time interval Δt, and a narrow width ΔX in equations 3.4 to 3.6. The relative errors encountered were below 0.1% and could be further reduced for a smaller Δt. Setting v = 0 in Equation (1) gives a reduction to adsorption/desorption in dispersion, whereas ignoring adsorption/desorption reduces the situation to convection only, and the solution eventually yields constant concentrations, C_{oi}, within the whole filter.

Statistical Criteria.

The statistical criteria for the goodness of the fits were the closeness of R^2 to unity, and RMSE, the root mean square error, which is given by

$$RMSE = [\sum(y_{i,exp} - y_{i,calc})^2/(n - m)]^{0.5} \quad (7)$$

in which $y_{i,exp}$ and $y_{i,calc}$ are experimental and calculated values of percent removal from water of given pollutants by the filter, n is the number of data points and m is the number of parameters. In our case the parameters are R_0, C_i, and D_i. It is intended to first determine the parameters methodically from a single solute case, one at a time, albeit sequential determination is possible.

3.2.3. Effect of Volume Filtered, Flow Rate, Flow Velocity, Filter Length, Concentration of Surface Sites, and Pollutant Concentration on Solute Removal

A detailed analysis, including numerical examples which illustrate the effects of different factors on the kinetics of filtration and on the capacity of the filter to purify water from given pollutants is presented in [20,73]. For brevity only, a general description is presented here.

The flow rate is given by Equation (3.2) as a product of the flow velocity by the cross-sectional area. Hence, it is sufficient to discuss the effect of flow velocity on the quantities C_i/C_{i0}.

$(C_0 - C)/C_0 = 1 - C/C_0$ is the fraction of the solute retained in the filter, which corresponds to the given sample, e.g., the value of $C/C_0 = 0.02$ corresponds to 98% removal. Generally, a reduced efficiency of removal arises upon increase in flow rate, or flow velocity. In addition, due to a reduced capacity of the filter in terms of the volume which satisfies the criterion of maximal allowed concentration of a solute in the filtered water per kg of the included material. Of course, a larger velocity corresponds to a reduced contact time, and a reduced efficiency, or capacity.

In case it is needed to enhance the flow velocity by a given factor, it is possible to achieve this outcome without a loss in filtration efficiency by multiplying the length of the filter by the same factor. In fact, inspection of Equation (1) indicates that multiplication of filter length and flow velocity, v, by the same factor does not modify the outcome. This implies that operating a laboratory filter at a small flow velocity during filtration can yield useful information on filtration through a large filter, where the flow velocity is larger.

An enhancement of the concentration of adsorbing sites (R_0) enables to increase in proportion the filter capacity and the flow rate. The fact that an increase in the concentration of the active material, say by a factor of three should give a threefold larger capacity is accepted by common sense, but the results indicate that the increase in filtered volume was accompanied by a threefold increase in flow rate and flow velocity. It was pointed out that an increase in flow velocity results in a reduction of the capacity. If an x-fold increase in R_0 is not accompanied by a similar increase in flow velocity, but filtration is carried out at the same flow velocity as before, this implies an increase in capacity per mass of the material included in the filter, i.e., enhanced purified volume per unit mass, e.g., in units of m^3/kg of material. An enhancement of about threefold was observed in purification of grey water [75] when filling the filter columns exclusively by a granulated micelle-clay complex instead of its mixture with excess sand at a w/w ratio of 1:30. A similar effect was reported in Nir et al. [71].

It can be expected that the volume of pollutant solution that can be purified by the filter in accord with the regulations is expected to diminish when the pollutant concentration increases.

Two patterns of dependence of capacity on pollutant concentration emerge:

(i) In this pattern, the calculations [20] showed that the volume of pollutant solution that can be purified by the filter when reducing the pollutant concentration 100-fold (from 10 ppm to 0.1 ppm) is increased 4.76-fold, or vice versa, a 100-fold increase of pollutant concentration increases the price of the filtration 4.76-fold. More examples are provided by our experimental results.

(ii) The second pattern occurs for a very large K-value. In this pattern the volume of solution that can be purified by such a filter can decrease linearly or even steeper with an increase in pollutant concentration.

The analysis in Nir et al. [20,73] also elaborates on the effect of the kinetic parameters (Ci, Di) and Ki -values on the capacity and filtration efficiency at different stages.

3.2.4. Peculiar Effects in Kinetics of Filtration of a Solution Including Several Pollutants

The analysis of competition between two pollutants for adsorption by filter sites in [73] demonstrated that in multi-pollutant systems, the kinetics of filtration may exhibit some unexpected results, which were illustrated for the case of two pollutants. The pollutants were chosen to have the same initial solution concentrations and to compete for the same sites. Their kinetic parameters were $C_1 = 60\ M^{-1}\ min^{-1}$, $D_1 = 0.06\ min^{-1}$, $K_1 = C_1/D_1 = 1000\ M^{-1}$; $C_2 = 6\ M^{-1}.min^{-1}$, $D_2 = 0.0006\ min^{-1}$, and $K_2 = 10,000\ M^{-1}$. Since $C_1 >> C_2$, it might be expected (see Table 3.4.1A, from [73]) that initially, i.e., for the first volumes of solution passing through the filter, the fraction adsorbed and the concentration of filter sites occupied by pollutant #1, are larger than the corresponding values for pollutant #2. However, since $K_2 >> K_1$, this trend is reversed at a later stage, and eventually the emerging concentration of pollutant #1 is larger than that of #2, whereas the concentration of filter sites occupied by pollutant #2 predominates. The example chosen illustrates an unexpected result that at a certain stage the emerging concentration of pollutant #1 exceeds the value of C_{01}, because the molecules of pollutant #2, whose affinity of adsorption is larger, gradually replace those of the first one from the filter sites. With more volumes passing and a decrease in the concentration of filter sites adsorbed by the first pollutant, its concentration in the emerging effluent decreases and approaches the value of C_{01}. This theme was further elaborated in Table 3.4.1B in [20].

The experimental results in Table 6 in [73] demonstrated that in a solution which included the neutral herbicide, bromacil, and the anionic herbicide, sulfentrazone, after the passage of 10 L of water through a filter which included a micelle-clay complex mixed with sand, the emerging concentrations of bromacil exceeded its initial concentration.

Another type of peculiarity was reported by [57] that the affinity of atrazine for adsorption by a certain liposome-clay complex increased in the presence of alachlor. On the other hand, a negative effect of sulfentrazone on the adsorption of bromacil was noted [73].

3.3. Removal of Pollutants from Water

3.3.1. Removal of Herbicides from Water

In the Introduction it was mentioned that in Europe no single pesticide should exceed 0.1 μg L^{-1} and total pesticides should not exceed 0.5 μg L^{-1}. The limits set on herbicide concentrations in water by EPA [76] and WHO [77] are less strict. A few given examples of "Maximal Contaminant Level" (MCL) allowed are:

Diquat 20 μg/L, simazine 4 μg/L, atrazine 3 μg/L, alachlor 2 μg/L [76]. The corresponding values for isoproturon and metolachlor according to [77] are 9 and 10 μg L^{-1}, respectively**.**

Polubesova et al. [70] focused on the removal from water of hydrophobic and anionic herbicides by powdered complexes of ODTMA and BDMHDA with montmorillonite at 6.5 g of complex per filter; at 100/1 w/w ratio of sand to complex. More than 99% of alachlor, sulfentrazone, chlortoluron, and sulfosulfuron were removed from solutions of 10 mg/L; 97% of alachlor was removed from a solution of 0.005 mg L^{-1}, (about 0.15 μg L^{-1} emerging).

The results of [73] demonstrated a much larger efficiency of removal of both bromacil and sulfentrazone by the micelle-clay filter than by a filter with Granulated active Carbon (GAC) at room temperature, and more so at 35 °C and 50 °C. It should be pointed out that due to the fact that the kinetic coefficients C_1 and D_1 are inversely proportional to the viscosity of the medium, analysis of adsorption results in dispersion gave larger values of these parameters than the results obtained from filtration, since filters are characterized by larger viscosities. The K-values are independent of viscosity according to the model. The results reported in [73] yielded the same value of $K = 10^4\ M^{-1}$ for bromacil as previously obtained from measurements in suspension [70].

Lelario et al. [78] studied removal of sulfentrazone using micelle-clay granulated composites. One of the aims of this study was to compare the efficiency of removal of this anionic herbicide by BDMHDA-, or ODTMA-clay. The results demonstrated that ODTMA-clay was more efficient than BDMHDA-clay for filtration of sulfentrazone. These results were in contrast to the results of [70] for adsorption in dispersion or by filtration, which utilized powdered complexes mixed with sand at large excess.

The explanation of the different behavior exhibited in the results of filtration by the granulated complexes is explained by the larger release of monomeric BDMHDA cations during filtration in comparison with ODTMA ones. Larger release of BDMHDA than ODTMA cations was demonstrated In [79], for powdered complex and by [80] for granulated complexes. Hence, in filtration, where the released cation can bind to one or more of the anionic sulfentrazone molecules, the dimers or oligomers formed would have a chance of emerging from the filter. This effect will be significantly larger in the case of BDMHDA- than ODTMA-clay granulated complex. Thus, ODTMA-clay is expected to be more efficient than BDMHDA-clay for filtration of sulfentrazone.

3.3.2. Removal of DOM from Water by Filtration

Removal was described in [81]. DOM, (or NOM) are large anionic molecules which include molecular masses in the range of 1–100kDa, are in general humic acids (HA) and fulvic acids (FA), which can form complexes and aggregates with large molecular masses. DOM molecules can bind other organic molecules and transport them to ground water. These molecules, which are rich in acidic (carboxylic acids) groups, are also hydrophobic [82].

HA removal employed a column filter (5 to 20 cm), which contained a mixture of quartz sand and a complex micelle–montmorillonite. The complex ODTMA-montmorillonite was in powdered form. Almost complete removal of HA (3.3 mg/L) from 100 L was achieved at a flow rate of 50 mL min^{-1}. The comparison with GAC mixed with sand implies that HA removal by GAC is significantly less efficient than by the micelle–clay complex.

3.4. Removal of Pharmaceuticals

The comprehensive research of this issue involves testing the stability of the PhACs against chemical and/or biological degradation; the metabolites formed, as well as the biological effects of the parent molecules and metabolites.

The presentation in this section will focus on the removal of PhACs from water by the micelle–clay complex, or in combination with other procedures. Modeling of this removal in dispersion will be presented, since most of the results were frequently summarized in terms of such studies, rather than by filtration. The two most frequently used forms of the linear Langmuir equation will be presented. Equation (8) below is the Langmuir–Scatchard equation for adsorption of a single pollutant at equilibrium. It gives a linear relation between the quantity Y and r, in which r denotes the bound molar concentration of the pollutant divided by the molar concentration of adsorbing particles, which can include a total number, N of sorbed molecules of the pollutant per the adsorbing particles, and P denotes the molar concentration of the pollutant which remains un-adsorbed in dispersion.

$$Y = r/P = K \times N - K \times r \quad (8)$$

The quantities P and r are determined experimentally. The slope of Y vs. r equals—K, which was defined two line after Equation (3), and the intercept equals K × N, from which N is obtained. Another widely used form of the Langmuir equation is given by Equation (9) below.

$$Ce/Q_e = 1/(kQ_{max}) + Ce/Q_{max} \quad (9)$$

Ce and k, which are similar to P and K, but have the units of mg L^{-1} and L mg^{-1}; Q_e and Q_{max}, which have the units mg g^{-1} stand for RP (molar concentration of bound pollutant) and R_0, respectively. It can be noted that the last two equations have the same form but use different units.

3.4.1. Removal of Antibiotics

(a) **Tetracycline and Sulfonamide Antibiotics**

Removal was described in [83]. Antibiotics are used for the treatment of human and animals diseases, but larger amounts are used with the aim to prevent diseases and promote growth of livestock and poultry. The presence of antibiotics in the environment can change the microbial ecology and increase the evolution of antibiotic-resistant pathogens. Treatment of raw wastewater frequently results in accumulation of antibiotics residues, which pose a threat as aquatic contaminants [84]. In addition, the presence of antibiotics can cause disturbance in water treatment processes, which are based on bacterial activities.

Tetracycline and sulfonamide antibiotic groups are widely used and undergo slow degradation and transformation [85]. Polubesova et al. [83] studied the removal of several antibiotics from water by BDMHDA–montmorillonite complexes in a comparison with removal by GAC. For the passage of 1 L of an initial solution of 10 mg L^{-1} the removal by BDMHDA-clay filter (6.5 g) was between 94 and 99.9%, whereas the GAC filter yielded removal between 45 and 89%.

The presence of FA, or HA had little effect on the removal efficacy of both antibiotics, when tested by the micelle-clay filter, but was significantly reduced when GAC was used.

(**b**) **Removal of Amoxicillin Trihydrate and Cefuroxime Axetil**

Removal was described in [86]. Amoxicillin is a most used antibiotic within the penicillin class, which also includes cefuroxime. The study showed that amoxicillin trihydrate, and cefuroxime axetil spiked into wastewater were completely removed by a sequential wastewater treatment plant, which included activated sludge, ultrafiltration (hollow fiber, and spiral wound membranes with 100 kDa and 20 kDa-cutoffs), GAC column, and reverse osmosis (RO). In parallel, the study aimed to test whether the purification by a micelle-clay complex could supplement this sequence.

Adsorption isotherms employing GAC and micelle (ODTMA)–clay complex as adsorbents were generated in a dispersion which included synthetic water. The results fitted the Langmuir equation. In the case of Amoxicillin, the parameters determined were Q_{max} of 100 mg g^{-1} and 90.9 mg g^{-1}, and K- values of 0.158 L mg^{-1} and 0.229 L mg^{-1} for amoxicillin trihydrate sorbed by GAC and ODTMA-clay, respectively. Overall the micelle-clay was significantly better sorbent than GAC

3.4.2. Removal of Several Non-Steroidal Anti-Inflammatory (NSAID) Drugs

(**a**) **Removal of Diclofenac**

Removal was described in [87]. The presence of ionized carboxyl group in diclofenac (DC) results in its low sorption and high mobility in the soil. No diclofenac degradation was detected in pure water or sludge during one month. This study dealt with an efficient method for the removal of diclofenac from water by micelle-clay composites. In addition, diclofenac was spiked into wastewater and was completely removed by a sequential wastewater treatment plant. Adsorption of DC in dispersion by charcoal and a composite micelle ODTMA–clay (montmorillonite) was investigated. Analysis by the Langmuir isotherm in the presentation by Equation (3.9) yielded good fits. Q_{max} for the micelle–clay complex was 153.8 mg g^{-1} and the affinity constant k was 0.070 L mg^{-1}. The corresponding values for charcoal were 158.7 mg g^{-1} and 1.2×10^{-3} L mg^{-1}, respectively. The implication is that, on w/w basis, there is about 3% more sites for adsorption of DC on charcoal than those on the micelle–clay complex, but the affinity coefficient of the complex is 58-fold larger than that of charcoal. Interestingly, from the cation exchange capacity of montmorillonite, (which is 0.8 mmol g^{-1} clay) and the fact that the clay comprised 4.5/6.5 of the weight of the micelle (ODTMA)–montmorillonite, it follows that the number of adsorption sites of the complex (which are positively charged) is 0.55 mmol g^{-1} complex. By taking the molecular weight of DC as 295 Da, the above value is close to that deduced from Q_{max}, which is 0.52 mmol g^{-1} complex. A conversion of the value obtained for k (0.070 L mg^{-1}) yields 21,000 M^{-1}, which is slightly larger than the largest K-value obtained in [83], i.e., for oxytetracycline (20,000 M^{-1}).

Filtration experiments with a solution containing 300 ppm of diclofenac demonstrated poor removal by GAC, in contrast to very efficient removal by micelle-clay filters. Filtration of DC solutions at concentrations of 8 and 80 ppb yielded almost complete removal at flow rates of 30 and 60 mL min^{-1}.

Estimates of the capacity of DC removal in terms of cubic meters of diclofenac solutions which can be purified per one kg of granulated complex have a large degree of uncertainty, because most of the measurements of filtration used the powdered complex. The estimates are based on C_1= 40 to 60 M^{-1} min^{-1} and R_0 = 1 M^{-1} for a filter whose length is 1.6 m and a flow velocity of 10 m h^{-1}. For an initial solution including 10 μg L^{-1} which has to be purified to 0.1 μg L^{-1} the estimates are 18 to 30 m^3 kg^{-1}. For the criterion in [78] the capacity to purify a solution of 1 μg L^{-1} to 0.5 μg L^{-1} yielded for the liposome-clay based on DDAB a capacity of 39 m^3 kg^{-1}. For purification of a solution of diclofenac 1 μg L^{-1} to 0.5 μg L^{-1} a recent calculation based on the granulated ODTMA-clay yielded a value of 38 m^3 kg^{-1} ODTMA-clay, whereas a reduction of diclofenac concentration from 10 μg L^{-1} to 0.5 μg L^{-1} yielded for ODTMA-clay a capacity of 32 m^3 kg^{-1}. All these values indicate that the application of both composites may be economical for purifying water from residues of diclofenac, because regeneration may be cheap and will double the capacity.

Another composite studied for removal of DC was that formed by sorption of a cationic starch on montmorillonite [88]. Filtration experiments showed synergism in the removal of DC in the presence of the anionic pharmaceutical sulfamethoxazole (SMX), instead of expected competition. This was due to the fact that the SMX molecules lose their anionic character by forming very polarized hydrogen bonds, which provide new sorption sites for DC through hydrophobic interactions with its aromatic and apolar moieties. Therefore, synergism in the removal of negatively charged molecules in complex matrixes, which is usually neglected, may be also operating, allowing a larger treated volume of water by the filter.

(**b**) **Removal of Ibuprofen**

Ibuprofen is used for analgesic and fever-reducing effects, and at higher doses, anti-inflammatory effects. It is extensively used as non-prescription drug. Ibuprofen molecules occur as anions at neutral pH and are not readily adsorbed by sludge in treated waste water, remaining in the aqueous phase. Ibuprofen has been shown to be significantly biodegraded during the warm season, but much less during the cold season.

Ibuprofen in pure water and in Al-Quds activated-sludge was resistant to degradation for one month. The sequential system yielded complete removal of ibuprofen from spiked wastewater samples, (625 L including 40 mg L^{-1} of ibuprofen, [89]).

Batch experiments of ibuprofen adsorption were carried out by using micelle-clay and GAC as sorbents. The simulation of the results of batch experiments by the Langmuir equation resulted in a slight advantage of GAC. However, the kinetics of ibuprofen adsorption was 20-fold faster for the micelle–clay complex than for GAC, which resulted in a much more efficient retention of ibuprofen in a filter which included the ODTMA–clay complex. The filtration compared initial solutions of ibuprofen in the range of several mg L^{-1}. Table 5 demonstrates experimental and calculated filtration results of an ibuprofen solution at an initial concentration of 110 μg L^{-1} by the micelle–clay powdered complex mixed with excess sand. The system (in duplicate) included two filters in series. The predictions yield RMSE value of 6.9, i.e., within experimental errors and an acceptable value of R^2, which was 0.92.

Table 5. Removal of ibuprofen through filtration (average concentration 109.8 ppb) by two columns in series, each including a mixture of a micelle–clay complex with excess sand (1:100, w/w): Experimental and calculated results.

V(L)	Emerging Concentration ppb	% Removed Exp.	% Removed Calc.[a]
		Column 1	
9.0	2.3	97.9	92.3
15.0	5.3	95.2	86.5
30.0	41.6	62.1	70.0
		Column 2	
9.0	0.32	99.7	99.6
15.0	0.22	99.8	99.1
30.0	0.5	99.5	96.0

[a] The flow rate was 50 mL min^{-1}.; R_0 = 0.013 M^{-1}; C_1 = 140 M^{-1}min^{-1}; D_1 = 0.004 min^{-1}.The RMSE = 6.9 and R^2 = 0.92. Selected results from [90].

Removal of Mefenamic Acid and Naproxen

Mefenamic acid is used for the relief of short-term moderate pain such as muscular aches and pains, menstrual cramps, headaches, and dental pain [91]. Naproxen is commonly used for fever, and inflammation, and for reducing pain and stiffness caused by migraine, osteoarthritis, and kidney stones [92].

Both mefenamic acid and naproxen were stable in distilled water. Mefenamic acid was stable in Al-Quds University activated sludge during a period of more than a month, whereas naproxen underwent biodegradation within three days in activated sludge giving O-desmethyl-naproxen. The micelle-clay complex exhibited very fast kinetics of adsorption of the metabolite O-desmethyl-naproxen.

Overall the same procedure of removal of mefenamic acid from 620 L spiked by 40 mg L^{-1} by the sequence of purification elements in Al-Quds Waste Water Treatment Plant (WWTP) was carried out as described for Ibuprofen in the previous section. Samples taken after passing the reverse osmosis (RO) unit demonstrated that practically complete removal of mefenamic acid was achieved (99.5%). It was concluded that incorporation of micelle-clay filters in WWTPs is promising in both cases.

Removal of Statins from Water [93]

The statins Atorvastatin (ATO), Rosuvastatin (RST) and Simvastatin (SIM) are frequently prescribed for reducing human blood cholesterol. Adsorption results by activated carbon and the ODTMA–clay complex in batch experiments were well simulated by the Langmuir equation; the values of R^2 were between 0.915 and 0.987. The results demonstrated the superior efficiency of adsorption of these statins by the micelle–clay complex. Filtration using columns which included the active component, the micelle–clay complex, or GAC mixed at a 1:50 (w/w) with excess sand demonstrated significantly larger efficiency of the micelle-clay in removal of all these statins from water, in comparison with activated carbon. The sequential treatment elements of the WWTP at the Al-Quds University Campus removed completely the spiked statins each separately at a concentration of 1 mg L^{-1} from a sludge reservoir of 1000 L.

Removal of Spironolactone

Spironolactone (SP) prevents the body from absorbing too much salt and keeps potassium levels from getting too low. It has been used to treat inflammation, allergy and diseases related to adrenal cortex insufficiency. SP is soluble in alcohol, benzene, and chloroform; it is poorly soluble in water. Similarly to the previously reviewed PhACs in Section 3.4, adsorption of SP in aqueous dispersions was well described by Langmuir isotherms, showing a better removal by the micelle–clay complex than by activated carbon. A small-scale filtration of water solutions indicated better removal of SP by the micelle–clay complex than by GAC. Kinetic studies on both pure water and wastewater after secondary treatment, demonstrated that SP underwent degradation to its hydrolytic derivative, canrenone, in both media. More than 90% of spiked SP was removed together with its newly identified metabolites [94].

Removal of Paracetamol

Paracetamol, which is also known by the name acetaminophen is used to treat pain and fever, but unlike Ibuprofen (Section 3.4.2(b)) it does not reduce inflammation. It is soluble in water and alcohol. Adsorption of paracetamol and its biodegradation product (*p*-aminophenol) by GAC and a composite micelle (ODTMA)–clay, were determined in dispersion at 25 °C. Adsorption was adequately described by a Langmuir isotherm. Kinetic studies of paracetamol and p-aminophenol removal demonstrated that the micelle–clay complex is efficient for their removal [95].

Khamis et al. [96] demonstrated that the sequential treatment at the Al-Quds WWTP removed 100% of paracetamol and p-aminophenol. Removal of paracetamol from RO brine was investigated by using photo-catalytic processes [95]; optimal conditions were found to be acidic- or basic-pH. Toxicity studies indicated that the effluent and brine were not toxic except for using extra low energy (XLE) membrane.

3.5. Removal of Inorganic Anions—Perchlorate

Perchlorate (ClO_4^-), is used as an oxidizer in military and civilian pyrotechnics, explosives, and rocket propellants. Perchlorate is a groundwater pollutant. In the US alone, perchlorate contamination of drinking water from groundwater and rivers is currently affecting more than 20 million consumers. In Israel, the central part of the sea shore aquifer is already contaminated. When present in the soil solution perchlorate is not adsorbed by the soil particles and moves into ground water. It can concentrate in underground water reservoirs above a clay layer which stops water penetration. The major health problem is due to perchlorate displacing iodine from the thyroid gland, which results in a decrease in thyroid hormone output in humans and animals. The main routes of exposure to perchlorate are via drinking of contaminated water, contaminated milk and consuming vegetables irrigated by contaminated water. Bacteria that can transform perchlorate are abundant in nature [97]. Microbial degradation of perchlorate occurs mostly under anaerobic conditions [98]. Since 1998, perchlorate was declared a major inorganic contaminant in drinking water sources and was added by USEPA to the Contaminants Candidate List (CCL). USEPA [99] reported an MCL level of 15 μg L^{-1}. Regulations also apply to irrigation of certain plants. The chemistry, toxicology, and ecotoxicology of perchlorate were intensively investigated [100–102]. Treatment techniques (chemical, electrical, and biological reduction, membrane technologies, and adsorption technologies) were reviewed [103]. Adsorption techniques are mainly based on ion exchange resins (e. g., [103,104]) and adsorbents modified by quaternary amines, such as GAC, zeolites, and clays [105]. The ion exchange membrane bioreactor (IEMB) [106], which combines a continuous Donnan dialysis with biodegradation of perchlorate, has been recently applied for a treatment of groundwater contaminated with high perchlorate concentrations [107].

ODTMA release from a powdered complex during filtration.

We only present LC-MS/MS analysis of ODTMA in water**.** A newly developed efficient procedure for determination of the released ODTMA, can detect the cation with a precision of 0.5 ppb.

3.5.1. Perchlorate Removal: Laboratory and Pilot Experiments

Results of removal of perchlorate by laboratory column filters filled with powdered ODTMA- clay complexes mixed with excess sand at perchlorate concentrations between 50 ppb and 10 ppm were determined and modeled, which enabled predictions and consequently a planning of a pilot ([71]; see Figure 6 below)

Figure 6. Pilot in a Yashresh well.

The experimental and calculated values for a pilot at a well (Yashresh, Israel) are shown in Table 6 below. The length of the active layer which was a mixture of ODTMA-montmorillonite with excess sand at 1:19 w/w was 110 cm and the diameter was 60cm.

One of the aims was to test the capacity of the filter to operate under a flow velocity of about 10 m h^{-1}. A flow rate of 3 $m^3 h^{-1}$ amounts in the case of the pilot filter to a flow velocity of 10.6 m h^{-1}. A continuous operation at a flow rate of 3 $m^3 h^{-1}$ would imply four days of operation, or two weeks for 8 h day^{-1}. Since the plan required a test for two months, the flow rates were set to 3, 2, and 1 $m^3 h^{-1}$ during weeks 1–3, respectively, and later a flow rate of 0.5 $m^3 h^{-1}$ was applied. During 16 h per day, in the absence of an operator, the flow rate was reduced to 0.1 $m^3 h^{-1}$, with average flow rate of 0.8 $m^3 h^{-1}$.

As is shown in Table 6 the perchlorate concentration in the inlet well water varied during the experiment. Consequently, the calculations assumed a perchlorate concentration of 850 ppb or (in parenthesis) 800 ppb. It should be noted that the calculated values are predictions based on laboratory experiments.

Table 6. Summary of a pilot experiment for perchlorate removal from. Water at a closed well in Yashresh [a].

Cumulative Volume Passed (m^3).	Perchlorate Conc. at Filter Inlet (ppb)	Perchlorate Conc. in Water Emerging from Filter (ppb)	Calculated Emerging Perchlorate Conc. (ppb)
164	858	0–4	0.3
182.2		0–4	1
189.6		6	2 (1.6)
211		12	10 (6)
211.7		12	10 (7)
220	787	16	14 (10)
231	806	22	23 (19)
235	832	25	30 (25)
239.5	911	32	32 (27)
244.5	898	44	44 (42)
252	763	46	58 (48)

[a]: Flow rate was 0.5 $m^3 h^{-1}$ from day 26. The calculations employed the same parameters as in a laboratory experiment. The length of the active layer which was a mixture of ODTMA-montmorillonite with excess sand at 1:19 w/w was 110 cm and the diameter was 60 cm. Calculations assumed a perchlorate concentration of 850 ppb or (in parenthesis) 800 ppb. Experimental errors were less than 4 ppb for perchlorate concentrations below 100 ppb, whereas for the other cases the relative error was estimated at 2%. The calculations according to Equation (3.1) employed the following values of parameters: R_0= 0.0266 M; C_1 = 60 $M^{-1} min^{-1}$; D_1 = 0.0018 min^{-1}.

Other Modifications of the Well Water by The Pilot Filter

Values of pH (7.5–8.14) and electrical conductivity (0.96–0.98 mS cm^{-1}) were not modified. Turbidity values of the filtered water were 0.11–0.15 NTU, corresponding to good drinking water. TSS values were below 5 ppm. More than 100 chemicals tested, including metals were in the allowed range. The concentrations of oil and fats were below 1 mg L^{-1} and cyanides were below 0.002 mg L^{-1}. The concentration of trichloroethylene in the well water was initially 0.02 mg L^{-1}; it dropped later to 0.011 mg L^{-1}, and after filtration it was 0.008 mg L^{-1}. The results demonstrated an efficient removal of pathogenic bacteria.

A Pilot Experiment with Granulated Complex

The pilot filter was a cylindrical column filled with granules of the complex based on ODTMA at a height of 170 cm and diameter of 10 cm. The filter included 10.6 kg of granules whose diameters varied between 0.5 and 2 mm. The filter was preceded by a prefilter filled with quartz sand for removing abundant rust particles from the tap water. A peristaltic pump fed the water from a 1 m^3 container, which was covered on its external sides by a reflective paper-metal to prevent growth of algae. The water contained an average of 1170 ppb of perchlorate and the average flow rate was 540 mL min^{-1}, corresponding to a flow velocity of 4.2 m h^{-1}. This perchlorate concentration exceeded by 40% the concentration of perchlorate in the water filtered by the pilot with powdered complex (Table 5). The overall volume passed was 103 m^3. The experimental and calculated values of perchlorate concentrations are given in [20,71]. The parameters used were deduced from analysis of previous laboratory studies in which the granulated complex was mixed with sand for shortening the needed time of the experiment. The calculations could yield a good prediction. It follows that the capacity of the micelle-clay granules to reduce the concentration of perchlorate by filtration to less than 4 ppb amounts to at least 10 m^3 kg^{-1} of the complex. For an emerging perchlorate concentration of 15 ppb the capacity is 11 m^3 1 kg^{-1} of the complex. The concentrations of released ODTMA during filtration were between 25 and 49 ppb, which were below the allowed limit of 100 ppb set by the Israeli Ministry of Health. The production of a granulated complex enables to increase the content of the active material in the filter by more than 10-fold, and consequently to reduce the frequency of filter replacements.

Removal of perchlorate from water in the range of concentrations under 100 ppb is most efficient by application of an anion exchanger, such as purolite, which is widely used commercially. The capacity of the anion exchanger drops about linearly with perchlorate concentrations. In Gu et al. [108] who used purolite A520E, the emerging water included 20 μg L^{-1} of perchlorate after the passage of 17,000 or 100 BV, when the initial perchlorate concentrations were 50, or 1100 μg L^{-1}, respectively. In this case the ratio between corresponding bed volumes (170) was even larger than the ratio between perchlorate concentrations, due to a better geometry of the filter used for the less concentrated solution. A similar pattern was observed in [109] who employed purolite D3696 for initial perchlorate solutions of 10 mg L^{-1} and 50 μg L^{-1}. Hence, it appears likely that the micelle-clay filter may be relatively more efficient and economical in purifying water from perchlorate in the range of several hundred μg L^{-1} to several mg L^{-1}. For larger perchlorate concentrations (e.g., several hundred mg L^{-1}) it might be of interest to consider a sequential treatment by a membrane reactor [106,107] followed by the micelle-clay filter. An added value of the micelle-clay filter is its capability to remove simultaneously perchlorate and pathogenic bacteria.

3.5.2. Removal of Ferricyanide

Cyanide is used in mining industry in extracting metals, such as gold, by employing the Ferricyanide complex, $(Fe(CN)_6)^3$. Guideline value for cyanide in drinking water is 0.04 mg/L [77]; see more details in [20]. A most noted spill occurred in 2000 in Baia Mare, Romania, which was considered the worst environmental disaster in Europe since the Chernobyl blow-up of a nuclear reactor. After the spill, the Somes river had cyanide concentrations 700-fold larger than the permitted levels. A cyanide plume reached the Tisza river and through it the Danube river, eventually reaching, in a largely diluted form, the black sea.

We reported on efficient removal from water of Ferricyanide by filtering its solutions through laboratory columns. which included 6.5 g of powdered ODTMA-bentonite mixed with excess sand at a w/w ratio of 100:1; the initial concentrations of cyanide were 2680 (Table 4.4.1) and 114 ppb (Table 4.4.2) [20]). By using the granulated complex a large filter can be operated.

3.6. Removal of Bacteria from Water

Earlier studies have employed powdered micelle–clay complexes based on ODTMA and BDMHDA [19] in removal in dispersion and by filtration. All the studied bacteria were removed efficiently, including the Gram-negative: *Escherichia coli (**E.coli**)*, (K-12 and S-17 strains), Azospirillum brasilense, coliforms and fecal coliforms; Gram-positive: Bacillus megaterium, *B. subtilis* and fecal streptococci. The bacteria in bold were removed from water during the pilot for perchlorate removal (Section 3.5.1).

Negligible removal was recorded for *E. coli* and *B. megaterium* by loamy soil and montmorillonite, whereas the observed removal by ODTMA micelle–montmorillonite complex was 7 log units for *E. coli*; and 6 log units for *B. megaterium* bacteria in the presence of BDMHDA–clay complex.

Inhibition of bacterial growth could be detected in the supernatant when 10^7, and 10^4 CFU ml^{-1} of *A. brasilense* and *B. megaterium*, respectively, were treated with 0.2 g (in 20 mL, i.e., 10 g L^{-1}) of BDMHDA–montmorillonite complex. A complete removal was recorded for both bacteria strains. After sedimentation of the complex, the upper solution was plated on LB agar and the bacteria were enumerated. No growth was detected for any treatment, suggesting that bacteria which were tightly attached to the complex were not released to the liquid medium or were dead.

Bacterial respiration and the evolved CO_2 were used as indicator for *E. coli* viability. The effect of BDMHDA–montmorillonite complex on respiration activity of *E. coli* was measured by GC as CO_2 accumulation. The results indicate that the micelle–montmorillonite complex possesses bactericidal properties which may result in bacterial death following such interaction.

Quaternary ammonium cations (QACs) are powerful in removal of bacteria and in disinfection [19,110–112]. Polymers bearing also QACs sorbed on montmorillonite were very effective in the removal of *E. coli* but this was affected not only by the surface charge of the complex, with larger biocidal activity as the surface charge increased, but also of polymer conformation on the surface. Complexes with the same surface charge but with a flat layer conformation pose a higher bactericidal effect than those with an extended loops-and-train conformation [27]. We have emphasized the advantage in removal of bacteria by a combination of filtration (adsorption) and biostatic and/or biocidal effects by free organic cations, such as ODTMA and possibly other QACs [20,80,113–115]. Filtration results will be described in detail only for the case of granulated micelle–clay complexes.

3.6.1. Removal of Bacteria from Water by Filtration with Granulated Complex and Effect of Free Cations

Bacteria removed from water by filtration included (a) *Escherichia coli* S-17; (b) Total bacteria count (TBC); and (c) Cyanobacteria (*Microcistis* and *Aphanizomenon).* In these studies regeneration of the used filter material was demonstrated to enhance its capacity 2-fold at least by (i) passing a dilute solution of NaOCl (0.01%; 2 L per filter volume of 0.4 L), or HCl (0.01–0.05 M), followed by washing by 10 filter volumes, or by (ii) heating in a furnace at 105 °C for 2.5 h. Recently [116,117], we have established a regeneration procedure based on microwave (MW) heating. In comparison with ordinary oven, regeneration of used micelle–clay complexes (after removal of total bacteria count (TBC)) by MW heating needed 20- and 5-fold less energy and time, respectively.

(a) **Filtration of water solutions of *Escherichia coli* S-17 [80]**

The initial bacteria concentrations were from 6.4×10^5 to 5×10^6 mL^{-1}. Flow rates were between 3 and 50 mL^{-1} min, corresponding in the upper case to a flow velocity of 1.53 m h^{-1}, or 7.6 mh^{-1} if a filter length of 1 m rather than 0.2 m would be used. The filters included between 3 and 27 g of granulated micelle–clay complexes per single filter.

We focus on a main experiment. The granules based on BDMHDA were mixed with 640 g of sand, which implies a w/w ratio of 24 of sand to complex. The mixing with sand was not for the purpose of facilitating the flow, but rather to shorten the duration of the experiments for adsorbing a large number of bacteria per unit weight of the complex. The experiment involved filtration of two such filters in a series. The concentration of bacteria was 3.3×10^6 mL^{-1}. No bacteria emerged through the first column for the first 88 L passed, which corresponds to 3.3 L g^{-1} of complex. The total number of bacteria captured by the first column after the passage of 136 L (45 h) was 4.47×10^{11}, or 1.66×10^{13} kg^{-1}, which amounted to 99.6% of the filtered bacteria. The issue of capacity is elaborated later.

After first regeneration of the columns no emerging bacteria were detected during the passage of 76 L. The same parameters used for the fresh complex could fit the results with the regenerated one up to 127 L. The results of the second regeneration of the same system showed that no bacteria emerged through the first filter in series during the first 50 L. Thus, the first two regenerations enabled to increase the capacity of the filter by 86% and 57%, respectively, i.e., more than double the capacity. Clearly, regeneration makes filtration by the micelle-clay quite economical.

Modeling and estimates of capacity

The number of adsorbing sites was fixed at the values for the powdered complex. The calculations (Tables 1, 2, and 1S in [80]) provided 22 data points. As stated in this section, the experiments included variations of amounts of complex per filter, flow rates, and bacteria concentrations, whereas the total volumes passed varied between 4.2 and 136 L.

The values chosen for the parameters were $C_1 = 9.5 \times 10^{11}$ $M^{-1}min^{-1}$; $D_1 = 10^{-4}$ min^{-1}, are largely similar to the values $C_1 = 9 \times 10^{11}$ M^{-1} min^{-1}; $D_1 = 2 \times 10^{-4}$ min^{-1} obtained for the powdered complex which employed a different strain of *E. coli* [19]. The estimated uncertainty in these parameters is 20 to 40%. The same parameters were employed in other calculations (or predictions). The values obtained for the statistical criteria of the fits were: $R^2 = 0.898$ and RMSE=15,500 (bacteria mL^{-1}) (Equation (3.7)). The value of RMSE is less than 1% of the sum of emerging bacteria, 2.4×10^6 mL^{-1}.

In comparison with removal of molecular pollutants from water [71,73,89], the values of R_0, the molar concentration of adsorption sites and C_1, the forward rate constant of bacterial adsorption, were 10^{10}- to 10^{11}-fold smaller and larger, respectively, which reflects the different pollutant sizes. D_1, the rate constant of desorption is 10–1000 smaller than in the case of molecular pollutants, which reflects the fact that bacterial detachment from the adsorbing surface requires breaking many more bonds simultaneously than for a detachment of a molecule of a pollutant. Indeed, [19] reported on the apparent irreversibility in the attachment of bacteria to micelle–clay complexes. The estimated capacity is quite significant, for water including 10^6 bacteria mL^{-1} or less.

(**b**) **Filtration of TBC**

Bacteria in this category are not considered harmful, but regulations set some limits on their numbers per volume, and situations exist, as in the case of water provided for dialysis where the water should not include bacteria. Extensive experiments were conducted by using filters, (1.6 × 20 cm) which included 32 g of granules of ODTMA-, or BDMHDA-clay for filtering tap water from TBC. This led to a proposal of constructing domestic filters which rely solely on filtration, i.e., do not include inactivation of bacteria by radiation, e.g., by a UV lamp. [80,115,116].

The TBC numbers in the tap water were between 0 and 600 CFU mL^{-1}, but occasionally values exceeding 1000 CFU mL^{-1} were recorded. The capacities recorded were between 2 and 4.5 L g^{-1} of ODTMA–clay complex, and 3.7 to 8.3 g L^{-1} when first regeneration was considered. For BDMHDA-clay granules the values were larger, but significantly below the capacities in Table 7 for indicator bacteria. Tap water from a very clean source was incubated for 3 d in a glass vessel. After the first day the number of TBC was of the order of 10 CFU mL^{-1}, but after 3 d large values were measured, above 55,000. CFU mL^{-1}. Tests (according to [118] required that the numbers of bacteria counted should not exceed 5000 mL^{-1} after a halt of filtration for 72 h and residence of water without disinfectants, such as chlorine, in the filter. When such halt occurred after the passage of about 30 L or less through a filter, which included 32 g of ODTMA, the numbers of emerging bacteria after resumption of filtration were close to 1 CFU mL^{-1}, but when the halt occurred after 64 L the measurements of emerging bacteria from ODTMA-clay filters were in the range of 1000 to 60,000 CFU mL^{-1}. For filters including BDMHDA the results were somewhat better.

Table 7. Capacities of filters (1m long) filled with granulated BDMHDA-clay for removal of *E. coli* bacteria at a flow velocity of 10 m/h. [a].

Number of Bacteria mL^{-1} in Initial Solution	Number of m^3 Water Purified to Less Than 1 Emerging Bacterium 100 mL^{-1} $1kg^{-1}$ of Granulated Complex, and after First Regeneration (in Parenthesis).
10,000	74 (137)
100,000	55 (104)
1,000,000	22 (41)
5,000,000	5 (9)

[a] The values of the parameters used in the calculations were: $R_0 = 6.5 \times 10^{-11}$ M (for a filter filled with a granulated complex only), $C_1 = 9.5 \times 10^{11}$ $M^{-1}min^{-1}$; $D_1 = 10^{-4}$ min^{-1}.

The explanation of these results is that after a decrease of the chlorine concentration in the water, the bacteria in the glass vessel could feed on organic residues and minerals and reproduce. If the halt in flow occurs when the filter is unsaturated, then most of the bacteria within the water pores in the filter and in water above the active layer will be further removed from water. When the filter is close to saturation, then bacteria at concentrations beyond the saturation capacity would not be retained by the filter, when filtration is resumed after the halt. The issue of developing a domestic filter based on ODTMA-clay granules, which does not need UV radiation is still under study as will be elaborated later.

(c) Role of released cations during filtration

The Israeli Ministry of Health gave a conditional permission to employ the micelle-clay technology for treatment of water for drinking and irrigation provided that the concentration of released ODTMA would not exceed 100 µg/L. Zadaka et al. [79] reported small values of cation release from ODTMA–clay powdered complex, whereas much larger release was observed from BDMHDA–clay complexes. The concentrations of released ODTMA during filtration of 100 m^3 by a pilot filter with granulated complex ODTMA–clay were between 25 and 50 µg/L [71]. Using a small column (1.6 cm × 20 cm) filled with granulated complexes followed by a similar one filled with activated carbon, indicated that after 64 L the concentrations of released ODTMA and BDMHDA were 82 and 1817 µg/L, respectively, whereas after passing through the second (GAC) filter the corresponding values were reduced to 1.6 and 0.9 µg/L [80]. This study reported that numbers of bacteria captured by granulated micelle-clay filters were the same for ODTMA or BDMHDA complexes, and were independent of regeneration for two rounds. On the other hand the BDMHDA–clay complex had an advantage over the complex based on ODTMA in reducing the number of emerging bacteria. A hypothesis was tested that the advantage of BDMHDA– over ODTMA–clay complexes in removal of bacteria from water was due to larger concentrations of released BDMHDA than ODTMA cations during filtration, which may affect bacteria reproduction. In this context the removal of TBC from water which included more than 57,000 bacteria per mL by several concentrations of free cations of ODTMA or BDMHDA was tested. At 6–15 mg/L of free cations, all or most of the bacteria were removed (0 to 3/mL remained), whereas at 80 mg/L of either cation, complete removal was achieved. Hence, when the cations were added at equal concentrations as monomers, the removal of the bacteria was similar. Hence, it was suggested that the relatively larger fraction of released BDMHDA during filtration exerts a much larger biocidal, or biostatic effect on the emerging bacteria than in the case of ODTMA. This effect was seen both with *E. coli* or TBC.

Ferreira et al. [111] demonstrated the biocidal effect of a quaternary cation similar to BDMHDA, but with an alkyl chain C_{12}, rather than C_{16}. Maillard [110] and Ferreira et al. [111] demonstrated and proposed explanations for the biocidal action of free QAC. Inacio et al. [112] demonstrated three modes of antibacterial action by QAC; at low concentrations impairment of cell reproduction; membrane permeabilization at intermediate doses, and disruption of bacterial membranes at higher concentrations. They also demonstrated that toxicity to mammalian cells occurred at higher cation concentrations and results primarily from mitochondrial dysfunction and apoptotic cell death.

Shtarker-Sasi et al. [19] reported that (i) BDMHDA at both 0.6 and 0.15 mM exhibited toxicity against *B. megaterium* and *E. coli*. This indicates that the toxic effect was due to the free cations. (ii) In abolishing bacterial respiration in dispersion the effect was presented as due to a biocidal activity of the BDMHDA–clay complex. We suggest that the mentioned effect might be due to the activity of free cations which are released from the complex according to a mode of dynamic adsorption, which includes events of adsorption and desorption. We note that removal of perchlorate [71] and sulfentrazone [78] from water was much more efficient by the use of a complex based on ODTMA, rather than by a complex based on BDMHDA. In the case of BDMHDA the released cations could form dimers or oligomers with the pollutant molecules, which were not retained in the filter.

We have proposed [2] to prepare an enriched granulated complex obtained by adding the salt of ODTMA at a larger ratio to bentonite than in the ordinary complex during preparation of the complex, since such a complex is expected to release more ODTMA cations during filtration. Preliminary results (D. Margalit and S. Nir, personal communication, available upon request) indicated that, the granulated micelle-(ODTMA)–clay complex with 10% excess of ODTMA during preparation yielded significantly better removal from water of total bacteria count (TBC) than the current, or ordinary complex.

3.6.2. Removal of Cyanobacteria and Their Toxins from Water

We focus on the removal from drinking water of two cyanobacteria: filamentous *Aphanizomenon ovalisporum* (Nostocales) and the single cells *Microcystis aeruginosa* (Chroococcales). Photosynthesis is a main metabolic activity of these cyanobacteria, which are present in Lake Kinneret, Israel. These cyanobacteria produce toxins, which are harmful to humans and animals. Drinking water should include less than 1 $\mu g\ L^{-1}$ of cyanobacterial toxins. The biovolumes of cells of *Aphanizomenon* filament and a *Microcystis* cell are 4500 and 14 μm^3, respectively, i.e., significantly larger than that of *E. coli*, which is less than 1 μm^3. Due to eutrophication and climatic changes, cyanobacterial blooms are increasing in freshwater ecosystems all around the world, Paerl and Paul [119]. Over the last two decades, more than 60% of the lakes in China have undergone harmful cyanobacteria blooms (HCBs), in which the toxin producer, *M. aeruginosa*, is a dominant cyanobacteria species, Song et al. [120].

Chlorination has been the main strategy for disinfecting drinking water, but it has minor effect on the removal of cyanotoxins of the microcystin contingent. Adsorption by granulated activated carbon and advanced oxidation processes (AOP) are currently the preferred processes to remove cyanotoxins from water, Szlag et al. [121]. Sukenik et al. [113] presented removal of these cyanobacteria by filtration with granules of ODTMA–clay and by free ODTMA cations, and removal of their toxins.

Removal of cyanobacteria by filtration with ODTMA–clay granulated complex.

Filtration experiments employed columns of 40 cm length and 5 cm diameter, which contained 40 g of granulated ODTMA–clay complex mixed with 1200 g of sand, and the flow rate was 40 mL min^{-1}. Samples were analyzed for chlorophyll fluorescence intensity ($\mathbf{F_t}$) and photosynthetic activity ($\mathbf{Q_y}$). In addition, the total number and mass (cell or filament number) of cyanobacteria was estimated by microscopic counts. An efficient removal of both cyanobacteria was demonstrated. More than 32 L of *Microcystis* culture (an overall load of $5.6 \cdot \times 10^{10}$ cells with a cell density of 4.0×10^5 cells mL^{-1} in the first 10 L and 2.4×10^6 cells mL^{-1} in the next 22 L) passed the column, leaving the effluent fluorescence signal (F_t) practically zero. Additional load with higher cell density (1.4×10^7 cells mL^{-1}) caused a substantial increase of the fluorescence signal of the effluent, indicating saturation of the filtration column. The filtration of *Aphanizomenon* culture through a column packed with ODTMA-clay granulated complex demonstrated somewhat higher efficiency than the filtration of *Microcystis* cells. The parameters which describe the kinetics of filtration are given in Table 8. The value of R_0 is 32-fold larger for *Microcystis* cells than for filaments of *Aphanizomenon*, and 7-fold smaller than for *E. coli*, in line with the corresponding sizes and applied numbers of the cells.

Table 8. Parameter values for convection and adsorption/desorption model which best describe the results of the filtration experiments for laboratory cultures of *Microcystis, Aphanizomenon,* and *E. coli* S-17.

Bacteria	Volume (μm^3)	Molecular R_0 (M)	C_1 (M^{-1} min^{-1})	D_1 (min^{-1})
E. coli S-17	1	5.8×10^{-12}	9.5×10^{11}	1.0×10^{-4}
Microcystis	14	7.94×10^{-13}	2×10^{12}	1.0×10^{-4}
Aphanizomenon	4500	$>2.5 \times 10^{-14}$	6×10^{13}	1.5×10^{-5}

The parameters which describe the kinetics of filtration are given in Table 8. The value of R_0 is 32-fold larger for *Microcystis* cells, than for filaments of *Aphanizomenon*, and 7-fold smaller, than for *E. coli*, in line with the corresponding sizes and applied numbers of the cells. The results in Table 8 indicate that the value of C_1, the forward rate constant of adsorption is 30- fold larger, and the value of D_1, the rate constant of dissociation is 6-fold smaller for *Aphanizomenon* filaments than for *Microcystis* cells. This outcome can be rationalized, since the value of C_1 is expected to increase with the area of contact between a single cell and the complex, and the dissociation of a cell from the complex requires simultaneous breakage of bonds whose number is expected to be larger for *Aphanizomenon*.

Effect of free ODTMA cations on cyanobacteria in dispersion [113].

Addition of 0.1 mM or 0.3 mM ODTMA to cultures of *A. ovalisporum* (3.5×10^3 mL^{-1}), or *M. aeruginosa (*4.5×10^6 mL^{-1}), respectively, yielded full inhibition of the photosynthetic activity within 5 min. The gradual reduction in the photosynthetic activity was accompanied by a steady increase in fluorescence to a maximal value, indicating degradation of the cells. Exposure of cyanobacteria to much lower concentrations of ODTMA (0.25 μM and 20 μM for *Aphanizomenon* and *Microcystis* cultures, respectively) imposed full inhibition of the photosynthetic activity and enhanced fluorescence within 20–40 min.

Removal of toxins by the granulated complex.

In the presence of 1 g L^{-1} of granulated complex in dispersion, a complete removal of microcystins (toxins of *Microcystis)* was observed at concentrations lower than 100 μg/L [113]. Lesser efficiency of removal of CYN, the toxin of *Aphanizomenon* was observed. Recently larger efficiency of removal was observed by filtration (personal communication, A. Sukenik, Y. Vinner-Mozzin, A. Benitez, and S. Nir).

A small filter filled with GAC used for purifying water from a treatment plant supplemented by 5 μg/L of microcystins [122]. The water also included between 6 and 8 mg L^{-1} of DOC. The filter which included unsterilized GAC removed microcystins both by filtration and degradation; complete removal was observed for more than six months. The authors concluded that an active biofilm formed at the surface of the GAC. In this context we add that a successful modeling of the kinetics of filtration followed by degradation was developed has been recently described for removal of bacteria by dipeptides immobilized by beads [123].

Filtration modeling, coagulation of cyanobacteria and capacity.

Gerchman et al. [124] demonstrated an efficient procedure for coagulation-sediments of microalgae. It was shown that the addition of 5 mg L^{-1} of the positively charged polymer polydiallyldimethylammonium chloride (PDADMAC) flocculated 90% of the algae within 60min. Application of this procedure to samples of cyanobacteria (*Aphanizomenon* and *Microcystis*) yielded similar results (A. Sukenik; personal communication). Studies

[125,126] employed a composite, produced by 2 g L^{-1} of sepiolite, which interacted with 3.6 g L^{-1} of PDADMAC. When this nano-composite was added at 0.5 to 1.5 mL L^{-1}, the outcome was sedimentation of cells of *Aphanizomenon* or *Microcystis* within several minutes (G. Rytwo and A. Sukenik, personal communication). Hence, a first stage of coagulation-sedimentation, will yield a 10-fold reduction in the number of cells remaining in dispersion before filtration.

The capacity of a filter to remove cyanobacteria was estimated by employing the filtration model and the restriction that the filtered water should satisfy the threshold criterion of less than 1μg L^{-1} of cyanobacterial toxins (MC-LR). The MCs content in a *Microcystis* cell varies between 110 and 400 fg microcystin $cell^{-1}$ depending on growth conditions [127]. Taking an average value of $2 \cdot 10^{-13}$ g microcystin $cell^{-1}$, it is calculated that the treated water should contain no more than $5 \cdot 10^{3}$ *Microcystis* cells mL^{-1}. The length and the flow velocity of the commercial filter were chosen as 1m and 6.1 m h^{-1}, respectively. In the case of purification of water from *Microcystis* cells, the value of R_0 for a filter which was filled exclusively with granules was $9.5 \cdot 10^{-12}$ M. For water including $1 \cdot 10^{5}$ *Microcystis* cells mL^{-1}, the use of this value of R_0 and the kinetic parameters in Table 8 in the calculations gave the capacities in Table 9.

Table 9. Calculated capacities for removal of *Microcystis* cells by coagulation/sedimentation followed by filtration, assuming that the final numbers of cells in the treated water is limited by 5 × 10^{3} cells mL^{-1}.

Initial Number of Cells mL^{-1}	Number of Cell mL^{-1} after Coagulation/Sedimentation	Capacity of the Filter:Volume (m^3) of Water Which Can Be Purified from *Microcystis* Cells Removed kg^{-1} of Complex
10^{7}	10^{6}	3
10^{6}	10^{5}	22
2×10^{5}	2×10^{4}	45
10^{5}	10^{4}	67

3.7. Collaboration of Technologies: Purification of Greywater

A main purpose is to demonstrate the advantage of the combined operation of filtration by the micelle–clay granulated complex and a moving bed biological reactor. A brief survey of relatively recent studies is presented.

Reuse of grey water (GW) from sinks, showers, and baths amounts to 150–300 L per household day^{-1} [128]. Use of inadequately treated GW can be a potential health hazard [129]. Several studies provided risk assessment of GW due to presence of pathogens [130–132]. Rotating biological contactor combined with sand filtration and ultra-filtration membranes [133] combined with UV disinfection [134] were tested for GW treatment. Constructed wetlands have been employed for GW treatment, e.g., [135] employed a recirculating Vertical Flow Constructed Wetland (RVFCW), whereas [136] examined the use of an anaerobic pretreatment stage before treatment of GW by RVFCW.

For filtration results of water from showers and sinks outside the kitchen [137] used two columns (5 × 20 cm) in a series including powdered micelle (ODTMA)–montmorillonite complex mixed with quartz sand at a 1:100 w/w ratio. The raw GW included large numbers of indicator and pathogenic bacteria per 100 mL, e.g., 10^{7} of fecal coliforms and 20,000 of fecal streptococci, whereas the allowed numbers for irrigation vary between 10 to 1000 per 100 mL [138]. The use of such water for irrigation without treatment poses a health hazard. The results demonstrated that after passing 15 L, no fecal coliforms or fecal streptococci were detected even in the water emerging from the first filter. The results indicated that a GAC filter yielded poor removal of bacteria even after the passage of 5 L.

The results indicated that organic materials in GW from showers and sinks were in the range of 30 mg L^{-1} and above, whereas the total mass per liter of 100×10^{6} of such bacteria is about 0.1 mg L^{-1}, or two orders of magnitude less than the mass of the other materials in the grey water. Hence, removal of organic material prior to filtration by the micelle–clay complex might significantly enhance the filter's capacity for removal of bacteria. Consequently, the treatment was extended to a two-stage configuration for GW purification [75], where a moving bed reactor [139] was used to decompose a fraction of the organic matter in the GW prior to filtration. The amount of the active material in the granulated micelle-clay filter could be enhanced at least 10-fold in comparison to previously used filter, by using a granulated complex. The moving bed reactor was also efficient in removing pathogenic bacteria. The values of turbidity in the purified GW ranged between 0.2 and 4.4 NTU with average and median values of 1.8 and 1.5 NTU, respectively. The turbidity values of the raw GW varied between 21.1 and 65.7 NTU with an average of 44.1 NTU. BOD values in the moving bed reactor and in the filtered samples were below 5mg L^{-1} in all cases. Raw GW contained 5, 0.3 and 0.05 mg N/L of nitrate, nitrite and ammonia, respectively, whereas the corresponding values for filtered samples were 4.6, 0.09, and 0.003 mg N/L, respectively. A regeneration stage of the micelle-clay filter was conducted by passing either dilute solutions of Na-hypochlorite (0.5%), or HCl (0.05 mM) or by heating the complex at 120 °C for 3 h. The capacity of the granulated complex to purify grey water from showers, baths, and sinks amounts to 20 m^3 kg^{-1} of the granulated complex, and when two regenerations are considered, the capacity becomes 47 m^3 kg^{-1} of the complex. The two-stage procedure yields a safe and economical reuse of GW, since the plan is to have <1 per 100 mL of fecal coliforms or other indicator, or pathogenic bacteria in the filtered water.

Tertiary treatment by combining filtration with photo-Fenton processes.

Tertiary treatment is an advanced purification process that improves the quality of wastewater after secondary treatment. The treated water can be used for irrigation of plants for food production, or discharged to the environment, e.g., into creeks, or rivers. The treatment can further remove from the water organic compounds, pharmaceuticals, bacteria, and/or inorganic molecules.

In the two cases examined, the secondary treated waste water had characteristics very similar to those of raw GW. Hence, it may be of interest to test tertiary treatment by the procedure described for treatment of GW.

Another procedure for a tertiary treatment of secondary treated waste water was described in [140] who succeeded to remove most of 13 representative emerging contaminants (ECs), and all the bacteria from water, which included 26.3 mg L^{-1} TOC and 10^5 and 10^4 of *E. coli* and *Enterococcus faecalis* mL^{-1}, respectively. The volume treated was 40 L at a flow rate of 10mL min^{-1}. The purification started first due to adsorption by a filter which included 70 g of GAC (2 × 40 cm) followed by a filter, which included 20 g of granulated ODTMA-bentonite mixed with 100 g of sand. Most of the TOC was removed by the GAC to 5.95 mg L^{-1}, and further reduction to 2.22 mg L^{-1} was by the micelle-clay filter. The GAC filter was not efficient in removal of the bacteria, whereas the micelle-clay achieved complete removal. Solar photo-Fenton advanced oxidation processes were efficient in elimination of trace levels of ECs. The final effluent presented an improved sanitary level with acceptable chemical and biological characteristics for irrigation.

Authors Contribution: Conceptualization: T.U., U.S., S.N., B.R.; Methodology: T.U., U.S., S.N., B.R.; Software: Windows 2016; Writing original draft: Section 1 B.R., S.N.; Section 2 T.U., U.S., S.N., B.R.; Section 3 S.N., U.S., T.U.; Writing-review and editing T.U., U.S., S.N., B.R. All authors have read and agreed to the published version of the manuscript.

Funding: T. Undabeytia acknowledges financial support by the Spanish Ministry of Science and Innovation (project CTM2016-77168–R; this project received funding by the European Social Fund). S. Nir acknowledges financial support by the Ministry of Science & Technology, Israel & The Ministry of Science and Technology of the People's Republic of China (grant No. 3-15707). The authors are indebted to Dr. M. Ryskin, the main inventor of the granulation process, for his unique contribution.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Hedlund, J.; Longo, S.B.; York, R. Agriculture, Pesticide Use, and Economic Development: A Global Examination (1990–2014). *Rural. Sociol.* **2019**, *85*, 519–544, doi:10.1111/ruso.12303.
2. Leng, M.L.; Leovey, E.M.; Zubkoff, P.L. *Agrochemical Environmental Fate: State of the Art*; Lewis Publishers: Boca Raton, FL, USA, 1995; p.410.
3. Tominack, R.L. Herbicide Formulations. *J. Toxicol. Clin. Toxicol.* **2000**, *38*, 129–135, doi:10.1081/clt-100100927.
4. Seaman, D. Trends in the formulation of pesticides-an overview. *Pestic. Sci.* **1990**, *29*, 437–449, doi:10.1002/ps.2780290408.
5. Huang, B.; Chen, F.; Shen, Y.; Qian, K.; Wang, Y.; Sun, C.; Zhao, X.; Cui, B.; Gao, F.; Zeng, Z.; et al. Advances in Targeted Pesticides with Environmentally Responsive Controlled Release by Nanotechnology. *Nanomaterials* **2018**, *8*, 102, doi:10.3390/nano8020102.
6. Mishael, Y.G.; Undabeytia, T.; Rabinovitz, O.; Rubin, B.; Nir, S. Slow-Release Formulations of Sulfometuron Incorporated in Micelles Adsorbed on Montmorillonite. *J. Agric. Food Chem.* **2002**, *50*, 2864–2869, doi:10.1021/jf011497e.
7. Mishael, Y.G.; Undabeytia, T.; Rytwo, G.; Papahadjpoulos-Steinberg, B.; Rubin, B.; Nir, S. Sulfometuron adsorption via alkylammonium cations adsorption as monomers and micelles on montmorillonite. *J. Agric. Food Chem.* **2002**, *50*, 2856–2863.
8. Margulies, L.; Stern, T.; Rubin, B.; Ruzo, L.O. Photostabilization of trifluralin adsorbed on a clay matrix. *J. Agric. Food Chem.* **1992**, *40*, 152–155, doi:10.1021/jf00013a030.
9. Undabeytia, T.; Nir, S.; Tel-Or, E.; Rubin, B. Photo-stabilization of the herbicide norflurazon by using organo-clays. *J. Agric. Food Chem*. **2000**, *48*, 4774–4779.
10. Margulies, L.; Stern, T.; Rubin, B. Slow Release of S-Ethyl Dipropylcarbamothioate from Clay Surfaces. *J. Agric. Food Chem.* **1994**, *42*, 1223–1227, doi:10.1021/jf00041a033.
11. El-Nahhal, Y.; Nir, S.; Serban, C.; Rabinovitch, O.; Rubin, B. Montmorillonite-phenyltrimethylammonium yields environmentally improved formulations of hydrophobic herbicides. *J. Agric. Food Chem.* **2000**, *48*, 4791–4801, doi:10.1021/jf000327j.
12. El-Nahhal, Y.; Nir, S.; Serban, C.; Rabinovitz, O.; Rubin, B. Organo-clay formulation of acetochlor for reduced movement in soil. *J. Agric. Food Chem.* **2001**, *49*, 5364–5371, doi:10.1021/jf010561p.
13. Carter, A.D. Herbicide movement in soils: Principles, pathways and processes. *Weed Res.* **2000**, *40*, 113–122, doi:10.1046/j.1365-3180.2000.00157.x.
14. Ternes, T. Occurrence of drugs in German sewage treatment plants and rivers1Dedicated to Professor Dr. Klaus Haberer on the occasion of his 70th birthday.1. *Water Res.* **1998**, *32*, 3245–3260, doi:10.1016/s0043-1354(98)00099-2.
15. Ternes, T.A.; Meisenheimer, M.; McDowell, D.; Sacher, F.; Brauch, H.-J.; Haist-Gulde, B.; Preuss, G.; Wilme, U.; Zulei-Seibert, N. Removal of Pharmaceuticals during Drinking Water Treatment. *Environ. Sci. Technol.* **2002**, *36*, 3855–3863, doi:10.1021/es015757k.
16. Stackelberg, P.E.; Furlong, E.T.; Meyer, M.T.; Zaugg, S.D.; Henderson, A.K.; Reissman, D.B. Persistence of pharmaceutical compounds and other organic wastewater contaminants in a conventional drinking-water-treatment plant. *Sci. Total. Environ.* **2004**, *329*, 99–113, doi:10.1016/j.scitotenv.2004.03.015.
17. Stackelberg, P.E.; Gibs, J.; Furlong, E.T.; Meyer, M.T.; Zaugg, S.D.; Lippincott, R.L. Efficiency of conventional drinking-water-treatment processes in removal of pharmaceuticals and other organic compounds. *Sci. Total. Environ.* **2007**, *377*, 255–272, doi:10.1016/j.scitotenv.2007.01.095.
18. Cirja, M.; Ivashechkin, P.; Schäffer, A.; Corvini, P.F.-X. Factors affecting the removal of organic micropollutants from wastewater in conventional treatment plants (CTP) and membrane bioreactors (MBR). *Rev. Environ. Sci. Bio Technol.* **2007**, *7*, 61–78, doi:10.1007/s11157-007-9121-8.
19. Shtarker-Sasi, A.; Castro Sowinski, A.; Matan, O.; Kagan, T.; Nir, S.; Okon, Y.; Nasser, A.M. Removal of bacteria and cryptosporidium from water by micelle—Montmorillonite complexes. *Desalin. Water Treat*. **2013**, *51*, 7672–7680.
20. Nir, S.; Shuali, U. *Water Purification by Micelle-Clay Nano-Particles*; Nova Science Publishers: New York, NY, USA, 2019.
21. Hwang, B.-F.; Magnus, P.; Jaakkola, M.S. Risk of specific birth defects in relation to chlorination and the amount of natural organic matter in the water supply. *Am. J. Epidemiol.* **2002**, *156*, 374–382, doi:10.1093/aje/kwf038.
22. Charrois, J.W.; Boyd, J.M.; Froese, K.L.E.; Hrudey, S. Occurrence of N-nitrosamines in Alberta public drinking-water distribution systems. *J. Environ. Eng. Sci.* **2007**, *6*, 103–114, doi:10.1139/s06-031.
23. Asami, M.; Oya, M.; Kosaka, K. A nationwide survey of NDMA in raw and drinking water in Japan. *Sci. Total. Environ.* **2009**, *407*, 3540–3545, doi:10.1016/j.scitotenv.2009.02.014.
24. Bond, T.; Huang, J.; Templeton, M.R.; Graham, N. Occurrence and control of nitrogenous disinfection by-products in drinking water—A review. *Water Res.* **2011**, *45*, 4341–4354, doi:10.1016/j.watres.2011.05.034.
25. Lukasik, J.; Cheng, Y.-F.; Lu, F.; Tamplin, M.; Farrah, S.R. Removal of microorganisms from water by columns containing sand coated with ferric and aluminum hydroxides. *Water Res.* **1999**, *33*, 769–777, doi:10.1016/s0043-1354(98)00279-6.
26. Torkelson, A.; Da Silva, A.; Love, D.; Kim, J.; Alper, J.; Coox, B.; Dahm, J.; Kozodoy, P.; Maboudian, R.; Nelson, K.L. Investigation of quaternary ammonium silane-coated sand filter for the removal of bacteria and viruses from drinking water. *J. Appl. Microbiol.* **2012**, *113*, 1196–1207, doi:10.1111/j.1365-2672.2012.05411.x.

27. Undabeytia, T.; Posada, R.; Nir, S.; Galindo, I.; Laiz, L.; Saiz-Jimenez, C.; Morillo, E. Removal of waterborne microorganisms by filtration using clay–polymer complexes. *J. Hazard. Mater.* **2014**, *279*, 190–196, doi:10.1016/j.jhazmat.2014.07.006.
28. Nir, S. Cation adsorption to clay particles: Specific and nonspecific adsorption and associated changes in solution concentrations and surface potentials. *Soil Sci. Soc. Am. J.* **1986**, *50*, 52–57.
29. Margulies, L.; Rozen, H.; Nir, S. A model for competitive adsorption of organic cations and clays. *Clays Clay Miner.* **1988**, *36*, 270–276.
30. Rytwo, G.; Nir, S.; Margulies, L. Interactions of Monovalent Organic Cations with Montmorillonite: Adsorption Studies and Model Calculations. *Soil Sci. Soc. Am. J.* **1995**, *59*, 554–564, doi:10.2136/sssaj1995.03615995005900020041x.
31. Rytwo, G.; Nir, S.; Margulies, L. Adsorption and interaction studies of the divalent cationic herbicides diquat and paraquat with montmorillonite. *Soil Sci. Soc. Am. J.* **1996**, *60*, 601–610.
32. Rytwo, G.; Nir, S.; Margulies, L. A Model for Adsorption of Divalent Organic Cations to Montmorillonite. *J. Colloid Interface Sci.* **1996**, *181*, 551–560, doi:10.1006/jcis.1996.0412.
33. Cruz-Guzmán, M.; Celis, R.; Hermosín, M.C.; Cornejo, J. Adsorption of the Herbicide Simazine by Montmorillonite Modified with Natural Organic Cations. *Environ. Sci. Technol.* **2004**, *38*, 180–186, doi:10.1021/es030057w.
34. Dutta, A.; Singh, N. Surfactant-modified bentonite clays: Preparation, characterization, and atrazine removal. *Environ. Sci. Pollut. Res.* **2015**, *22*, 3876–3885, doi:10.1007/s11356-014-3656-3.
35. Polubesova, T. Adsorption of Benzyltrimethylammonium and Benzyltriethylammonium on Montmorillonite: Experimental Studies and Model Calculations. *Clays Clay Miner.* **1997**, *45*, 834–841, doi:10.1346/ccmn.1997.0450607.
36. Nir, S.; Undabeytia, T.; Yaron-Marcovich, D.; El-Nahhal, Y.; Polubesova, T.; Serban, C.; Rytwo, G.; Lagaly, G.; Rubin, B. Optimization of Adsorption of Hydrophobic Herbicides on Montmorillonite Preadsorbed by Monovalent Organic Cations: Interaction between Phenyl Rings. *Environ. Sci. Technol.* **2000**, *34*, 1269–1274, doi:10.1021/es9903781.
37. Huang, A.; Huang, Z.; Dong, Y.; Chen, L.; Fu, L.; Li, L.; Ma, L. Controlled release of phoxim from organobentonite based formulation. *Appl. Clay Sci.* **2013**, 63–68, doi:10.1016/j.clay.2013.06.010.
38. Zhu, L.; Zhu, R.; Xu, L.; Ruan, X. Influence of clay charge densities and surfactant loading amount on the microstructure of CTMA–montmorillonite hybrids. *Colloids Surfaces A Physicochem. Eng. Asp.* **2007**, *304*, 41–48, doi:10.1016/j.colsurfa.2007.04.019.
39. Cornejo, J.; Celis, R.; Pavlovic, I.; Ulibarri, M.A. Interactions of pesticides with clays and layered double hydroxides: A review. *Clay Miner.* **2008**, *43*, 155–175, doi:10.1180/claymin.2008.043.2.01.
40. Carrizosa, M.; Calderón, M.; Hermosín, M.C.; Cornejo, J. Organosmectites as sorbent and carrier of the herbicide bentazone. *Sci. Total. Environ.* **2000**, *247*, 285–293, doi:10.1016/s0048-9697(99)00498-2.
41. Celis, R.; Hermosín, C.; Cornejo, L.; Carrizosa, J.; Cornejo, J.; Hermosín, M.C. Clay-Herbicide Complexes to Retard Picloram Leaching in Soil. *Int. J. Environ. Anal. Chem.* **2002**, *82*, 503–517, doi:10.1080/03067310290018785.
42. Celis, R.; Facenda, G.; Hermosín, M.C.; Cornejo, J. Assessing factors influencing the release of hexazinone from clay-based formulations. *Int. J. Environ. Anal. Chem.* **2007**, *85*, 1153–1164, doi:10.1080/03067310500273302.
43. Celis, R.; Trigo, C.; Facenda, G.; Hermosín, M.D.C.; Cornejo, J. Selective Modification of Clay Minerals for the Adsorption of Herbicides Widely Used in Olive Groves. *J. Agric. Food Chem.* **2007**, *55*, 6650–6658, doi:10.1021/jf070709q.
44. Cornejo, C.D.; Celis, R.; Domínguez, C.; Hermosín, L.C. Use of modified montmorillonites to reduce herbicide leaching in sports turf surfaces: Laboratory and field experiments. *Appl. Clay Sci.* **2008**, *42*, 284–291, doi:10.1016/j.clay.2008.01.008.
45. Trigo, C.; Koskinen, W.C.; Celis, R.; Sadowsky, M.J.; Hermosín, M.C.; Cornejo, J. Bioavailability of Organoclay Formulations of Atrazine in Soil. *J. Agric. Food Chem.* **2010**, *58*, 11857–11863, doi:10.1021/jf102909y.
46. Chevillard, A.; Angellier-Cpoussy, H.; Peyron, S.; Gontard, N.; Gastaldi, E. Investigating ethofumeste-clay interactions for pesticide-controlled release. *Soil Sci. Soc. Am. J.* **2012**, *76*, 420–430.
47. Pool, C.F.; Du-Toit, D. Leaching depth of imazamethabenz methyl and chlorsulfuron and metsulfuron methyl in different soils. *Appl. Plant. Sci.* **1995**, *9*, 43–47.
48. Sarmah, A.K.; Kookana, R.S.; Alston, A.M. Fate and behavior of trisulfusulfuron, metsulfuron-methyl, and chlorsulfuron in Australian soil environment: A review. *Aust. J. Agric. Res.* **1998**, *49*, 775–790.
49. Undabeytia, T.; Mishael, Y.G.; Nir, S.; Papahadjopoulos-Sternberg, B.; Rubin, B.; Morillo, E.; Maqueda, C. A Novel System for Reducing Leaching from Formulations of Anionic Herbicides: Clay-Liposomes. *Environ. Sci. Technol.* **2003**, *37*, 4475–4480, doi:10.1021/es0343508.
50. Mishael, Y.G.; Undabeytia, T.; Rabinovitz, O.; Rubin, A.B.; Nir, S. Sulfosulfuron Incorporated in Micelles Adsorbed on Montmorillonite for Slow Release Formulations. *J. Agric. Food Chem.* **2003**, *51*, 2253–2259, doi:10.1021/jf0261497.
51. Polubesova, T.; Nir, S.; Rabinovitz, O.; Borisover, A.M.; Rubin, B. Sulfentrazone Adsorbed on Micelle−Montmorillonite Complexes for Slow Release in Soil. *J. Agric. Food Chem.* **2003**, *51*, 3410–3414, doi:10.1021/jf030002d.
52. Ziv, D.; Mishael, Y.G. Herbicide solubilization in micelle-clay composites as a basis for controlled release formulations. *J. Agric. Food Chem.* **2008**, *56*, 9159–9165.
53. Galán-Jiménez, M.D.C.; Mishael, Y.-G.; Nir, S.; Morillo, E.; Undabeytia, T. Factors Affecting the Design of Slow Release Formulations of Herbicides Based on Clay-Surfactant Systems. A Methodological Approach. *PLoS ONE* **2013**, *8*, e59060, doi:10.1371/journal.pone.0059060.
54. Galán-Jiménez, M.D.C.; Morillo, E.; Bonnemoy, F.; Mallet, C.; Undabeytia, T. A sepiolite-based formulation for slow release of the herbicide mesotrione. *Appl. Clay Sci.* **2020**, *189*, 105503, doi:10.1016/j.clay.2020.105503.

55. Galán-Jiménez, M.; Gómez-Pantoja, E.; Morillo, E.; Undabeytia, T. Solubilization of herbicides by single and mixed commercial surfactants. *Sci. Total. Environ.* **2015**, *538*, 262–269, doi:10.1016/j.scitotenv.2015.08.008.
56. Undabeytia, T.; Nir, S.; Gómara, M.J. Clay−Vesicle Interactions: Fluorescence Measurements and Structural Implications for Slow Release Formulations of Herbicides. *Langmuir* **2004**, *20*, 6605–6610, doi:10.1021/la0494472.
57. Undabeytia, T.; Nir, S.; Sánchez-Verdejo, T.; Villaverde, J.; Maqueda, C.; Morillo, E. A clay–vesicle system for water purification from organic pollutants. *Water Res.* **2008**, *42*, 1211–1219, doi:10.1016/j.watres.2007.09.004.
58. Sánchez-Verdejo, T.; Undabeytia, T.; Nir, S.; Maqueda, C.; Morillo, E. Environmentally Friendly Slow Release Formulations of Alachlor Based on Clay-Phosphatidylcholine. *Environ. Sci. Technol.* **2008**, *42*, 5779–5784, doi:10.1021/es800743p.
59. Sánchez-Verdejo, T.; Undabeytia, T.; Nir, S.; Villaverde, J.; Maqueda, C.; Morillo, E. Environmentally Friendly Formulations of Alachlor and Atrazine: Preparation, Characterization, and Reduced Leaching. *J. Agric. Food Chem.* **2008**, *56*, 10192–10199, doi:10.1021/jf8018408.
60. Undabeytia, T.; Sopeña, F.; Sánchez-Verdejo, T.; Villaverde, J.; Nir, S.; Morillo, E.; Maqueda, C. Performance of Slow-Release Formulations of Alachlor. *Soil Sci. Soc. Am. J.* **2010**, *74*, 898–905, doi:10.2136/sssaj2009.0133.
61. Undabeytia, T.; Recio, E.; Maqueda, C.; Morillo, E.; Gómez-Pantoja, E.; Sánchez-Verdejo, T. Reduced metribuzin pollution with phosphatidylcholine-clay formulations. *Pest. Manag. Sci.* **2010**, *67*, 271–278, doi:10.1002/ps.2060.
62. Undabeytia, T.; Recio, E.; Maqueda, C.; Sánchez-Verdejo, T.; Balek, V. Slow diuron release formulations based on clay–phosphatidylcholine complexes. *Appl. Clay Sci.* **2012**, *55*, 53–61, doi:10.1016/j.clay.2011.10.005.
63. EFSA (European Food Safety Authority. Document 4982). Guidance document for predicting environmental concentrations of active substances of plant protection products and transformation products of these active substances in soil. *EFSA J.* **2017**, *15*, 1–115.
64. Celis, R.; Hermosín, M.C.; Carrizosa, M.J.; Cornejo, J. Inorganic and Organic Clays as Carriers for Controlled Release of the Herbicide Hexazinone. *J. Agric. Food Chem.* **2002**, *50*, 2324–2330, doi:10.1021/jf011360o.
65. Kaluđerović, L.M.; Tomić, Z.P.; Đurović-Pejčev, R.D.; Vulić, P.J.; Asanin, D. Influence of the organic complex concentration on adsorption of herbicide in organic modified montmorillonite. *J. Environ. Sci. Health Part. B* **2017**, *52*, 291–297, doi:10.1080/03601234.2017.1281636.
66. Wu, C.; Lou, X.; Xu, X.; Huang, A.; Zhang, M.; Ma, L. Thermodynamics and Kinetics of Pretilachlor Adsorption on Organobentonites for Controlled Release. *ACS Omega* **2020**, *5*, 4191–4199, doi:10.1021/acsomega.9b04025.
67. Shirvani, M.; Farajollahi, E.; Bakhtiari, S.; Ogunseitan, O.A. Mobility and efficacy of 2,4-D herbicide from slow-release delivery systems based on organo-zeolite and organo-bentonite complexes. *J. Environ. Sci. Health Part. B* **2014**, *49*, 255–262, doi:10.1080/03601234.2014.868275.
68. Hermosín, M.; Celis, R.; Facenda, G.; Carrizosa, M.; Ortega-Calvo, J.; Cornejo, J. Bioavailability of the herbicide 2,4-D formulated with organoclays. *Soil Biol. Biochem.* **2006**, *38*, 2117–2124, doi:10.1016/j.soilbio.2006.01.032.
69. Tejada, M.; Morillo, E.; Gómez, I.; Madrid, F.; Undabeytia, T. Effect of controlled release formulations of diuron and alachlor herbicides on the biochemical activity of agricultural soils. *J. Hazard. Mater.* **2017**, *322*, 334–347, doi:10.1016/j.jhazmat.2016.10.002.
70. Polubesova, T.; Nir, S.; Zadaka, D.; Rabinovitz, O.; Serban, C.; Groisman, A.L.; Rubin, B. Water Purification from Organic Pollutants by Optimized Micelle−Clay Systems. *Environ. Sci. Technol.* **2005**, *39*, 2343–2348, doi:10.1021/es049251o.
71. Nir, S.; Brook, I.; Anavi, Y.; Ben-Ari, J.; Sheveky-Huterer, R.; Etkin, H.; Zadaka-Amir, D.; Shuali, U. Water purification from perchlorate micelle-clay complex. Laboratory and pilot experiments. *Appl. Clay Sci.* **2015**, *114*, 151–156.
72. Nir, S.; Ryskin, M. Method of Production of Granulated Micelle-Clay Complexes: Application for Removal of Organic, Inorganic Anionic Pollutants and Microorganisms from Contaminated Water. U.S. Patent 10,384,959, 20 August 2019.
73. Nir, S.; Zadaka-Amir, D.; Kartaginer, A.; Gonen, Y. Simulation of adsorption and flow of pollutants in a column filter: Application to Micelle-clay mixtures with sand. *Appl. Clay Sci.* **2012**, *67–68*, 134–140.
74. Simunek, J.; Van Genuchten, M.T.; Sejna, M.; Toride, N.; Leij, F.J. *The STANMOD Computer Software for Evaluating Solute Transport. In Porous Media Using Analytical Solutions of Convection-Dispersion Equation*; U.S. Salinity Laboratory Agricultural Research Service: Riverside, CA, USA, 1999.
75. Rakovitsky, N.; Brook, I.; Van Rijn, J.; Ryskin, M.; Mkhweli, Z.; Etkin, H.; Nir, S. Purification of greywater by a moving bed reactor followed by a filter including a granulated micelle-clay composite. *Appl. Clay Sci.* **2016**, *132*, 267–272, doi:10.1016/j.clay.2016.06.012.
76. US EPA (United States Environmental Protection Agency). *Exposure Factors Handbook: 2011 Edition*; Office of Research and Development, United States Environmental Protection Agency: Washington, DC, USA, 2011.
77. WHO. *Guidelines for Drinking-Water Quality*, 4th ed.; WHO: Geneva, Switzerland, 2017.
78. Lelario, F.; Gardi, I.; Mishael, Y.; Dolev, N.; Undabeytia, T.; Nir, S.; Scrano, L.; Bufo, S.A. Pairing micropollutants and clay-composite sorbents for efficient water treatment: Filtration and modeling at a pilot scale. *Appl. Clay Sci.* **2017**, *137*, 225–232, doi:10.1016/j.clay.2016.12.029.
79. Zadaka, D.; Polubesova, T.; Mishael, Y.; Spitzy, A.; Koehler, H.; Wakshal, E.; Rabinovitz, O.; Nir, S. Determination of release of organic cations from micelle–clay complexes and their re-adsorption in sand/clay columns. *Appl. Clay Sci.* **2005**, *29*, 282–286, doi:10.1016/j.clay.2005.01.007.
80. Kalfa, A.; Rakovitsky, N.; Tavassi, M.; Ryskin, M.; Ben-Ari, J.; Etkin, H.; Shuali, U.; Nir, S. Removal of Escherichia coli and total bacteria from water by granulated micelle-clay complexes: Filter regeneration and modeling of filtration kinetics. *Appl. Clay Sci.* **2017**, *147*, 63–68, doi:10.1016/j.clay.2017.06.023.

81. Radian, A.; Carmeli, M.; Zadaka-Amir, D.; Nir, S.; Wakshal, E.; Mishael, Y.G. Enhanced removal of humic acid from water by micelle-montmorillonite composites: Comparison to granulated activated carbon. *Appl. Clay Sci.* **2011**, *54*, 258–263, doi:10.1016/j.clay.2011.09.008.
82. Schaumann, G.E. Soil organic matter beyond molecular structure Part I: Macromolecular and supramolecular characteristics. *J. Plant. Nutr. Soil Sci.* **2006**, *169*, 145–156, doi:10.1002/jpln.200521785.
83. Polubesova, T.; Zadaka, D.; Groisman, L.; Nir, S. Water remediation by micelle–clay system: Case study for tetracycline and sulfonamide antibiotics. *Water Res.* **2006**, *40*, 2369–2374, doi:10.1016/j.watres.2006.04.008.
84. Joss, A.; Keller, E.; Alder, A.C.; Göbel, A.; McArdell, C.S.; Ternes, T.; Siegrist, H. Removal of pharmaceuticals and fragrances in biological wastewater treatment. *Water Res.* **2005**, *39*, 3139–3152, doi:10.1016/j.watres.2005.05.031.
85. Pérez, S.; Eichhorn, P.; Aga, D.S. Evaluating the biodegradability of sulfamethazine, sulfamethoxazole, sulfathiazole, and trimethoprim at different stages of sewage treatment. *Environ. Toxicol. Chem.* **2005**, *24*, 1361–1367, doi:10.1897/04-211r.1.
86. Awwad, M.; Al-Rimawi, F.; Dajani, K.J.K.; Khamis, M.; Nir, S.; Karaman, R. Removal of amoxicillin and cefuroxime axetil by advanced membranes technology, activated carbon and micelle–clay complex. *Environ. Technol.* **2015**, *36*, 2069–2078, doi:10.1080/09593330.2015.1019935.
87. Karaman, R.; Khamis, M.; Quried, M.; Halabieh, R.; Makharzeh, I.; Manassra, A.; Abbadi, J.; Qtait, A.; Bufo, S.A.; Nasser, A.; et al. Removal of diclofenac potassium from wastewater using clay-micelle complex. *Environ. Technol.* **2012**, *33*, 1279–1287, doi:10.1080/09593330.2011.619582.
88. Lozano-Morales, V.; Gardi, I.; Nir, S.; Undabeytia, T. Removal of pharmaceuticals from water by clay-cationic starch sorbents. *J. Clean. Prod.* **2018**, *190*, 703–711, doi:10.1016/j.jclepro.2018.04.174.
89. Khalaf, S.; Al-Rimawi, F.; Khamis, M.; Zimmerman, D.; Shuali, U.; Nir, S.; Scrano, L.; Bufo, S.A.; Karaman, R. Efficiency of advanced wastewater treatment plant system and laboratory-scale micelle-clay filtration for the removal of ibuprofen residues. *J. Environ. Sci. Health Part. B* **2013**, *48*, 814–821, doi:10.1080/03601234.2013.781372.
90. Zimmerman, D. Removal of Micropollutants from Water Using Clay and Micelle-Clay Complexes Packed in Adsorption Columns. Master’s Thesis, The Robert, H. Smith Faculty of Agriculture, Food and Environment of Rehovot, The Hebrew University of Jerusalem, Jerusalem, Israel, 2020.
91. Khalaf, S.; Al-Rimawi, F.; Khamis, M.; Nir, S.; Bufo, S.A.; Scrano, L.; Mecca, G.; Karaman, R. Efficiency of membrane technology, activated charcoal, and a micelle-clay complex for removal of the acidic pharmaceutical mefenamic acid. *J. Environ. Sci. Health Part A* **2013**, *48*, 1655–1662, doi:10.1080/10934529.2013.815475.
92. Qurie, M.; Khamis, M.; Malek, F.; Nir, S.; Bufo, S.A.; Abbadi, J.; Scrano, L.; Karaman, R. Stability and Removal of Naproxen and Its Metabolite by Advanced Membrane Wastewater Treatment Plant and Micelle-Clay Complex. *CLEAN Soil Air Water* **2013**, *42*, 594–600, doi:10.1002/clen.201300179.
93. Sulaiman, S.; Khamis, M.; Nir, S.; Lelario, F.; Scrano, L.; Bufo, S.A.; Mecca, G.; Karaman, R. Stability and removal of atorvastatin, rosuvastatin and simvastatin from wastewater. *Environ. Technol.* **2015**, *36*, 3232–3242, doi:10.1080/09593330.2015.1058422.
94. Sulaiman, S.; Khamis, M.; Nir, S.; Lelario, F.; Scrano, L.; Bufo, S.A.; Karaman, R. Stability and removal of spironolactone from wastewater. *J. Environ. Sci. Health Part A* **2015**, *50*, 1127–1135, doi:10.1080/10934529.2015.1047668.
95. Karaman, R.; Khamis, M.; Abbadi, J.; Amro, A.; Qurie, M.; Ayyad, I.; Ayyash, F.; Hamarsheh, O.; Yaqmour, R.; Nir, S.; et al. Paracetamol biodegradation by activated sludge and photocatalysis and its removal by a micelle–clay complex, activated charcoal, and reverse osmosis membranes. *Environ. Technol.* **2016**, *37*, 2414–2427, doi:10.1080/09593330.2016.1150355.
96. Khamis, M.; Karaman, R.; Ayyash, F.; Qtait, A.; Deeb, O.; Manssra, A. Efficiency of advanced membrane wastewater treatment plant towards removal of aspirin, salicylic acid, paracetamol and p-aminophenol. *J. Environ. Sci. Eng.* **2011**, *5*, 121–137.
97. Coates, J.D.; Michaelidou, U.; O’Connor, S.M.; Bruce, R.A.; Achenbach, L.A. The Diverse Microbiology of (Per)Chlorate Reduction. In *Perchlorate in the Environment*; Springer Science and Business Media LLC: Berlin, Germany, 2000; pp. 257–270.
98. Tan, K.; Anderson, T.A.; Jones, M.W.; Smith, P.N.; Jackson, W.A. Accumulation of Perchlorate in Aquatic and Terrestrial Plants at a Field Scale. *J. Environ. Qual.* **2004**, *33*, 1638–1646, doi:10.2134/jeq2004.1638.
99. USEPA. *Drinking Water. Regulatory Determination on Perchlorate*; Federal Register: Washington DC, USA 2011.
100. Urbansky, E.T. Perchlorate as an environmental contaminant. *Environ. Sci. Pollut. Res.* **2002**, *9*, 187–192, doi:10.1007/bf02987487.
101. McLaughlin, C.L.; Blake, S.; Hall, T.; Harman, M.; Kanda, R.; Hunt, J., Rumsby, P.C. Perchlorate in raw and drinking water in England and Wales. *Water Environ. J.* **2011,** 25, 456–465.
102. Brown, G.M.; Gu, B.; Moyer, B.A.; Bonnensen, P.V. Regeneration of Strong-Base Anion Exchange Resin by Sequential Chemical Displacement. U.S. Patent No. 6,448,229 B1, 10 September 2002.
103. Gu, B.; Coats, D.J.; (Eds.) *Perchlorate: Environmental Occurrence, Interactions and Treatments*; Springer: New York, NY, USA, 2006.
104. Xiong, Z.; Zhao, A.D.; Harper, J.W.F. Sorption and Desorption of Perchlorate with Various Classes of Ion Exchangers: A Comparative Study. *Ind. Eng. Chem. Res.* **2007**, *46*, 9213–9222, doi:10.1021/ie0702025.
105. Lutes, C.C.; Patterson, J.; Goltz, M.; Graham, J. *Tailored Granular Activated Carbon Treatment of Perchlorate in Drinking Water*; Environmental security Technology Program (ESTCP) project ER-200546*;* Department of Defense (DoD): Washington, DC, USA; 2010.
106. Velizarov, S.; Matos, C.T.; Reis, M.A.; Crespo, J.G. Removal of inorganic charged micropollutants in an ion-exchange membrane bioreactor. *Desalination* **2005**, *178*, 203–210, doi:10.1016/j.desal.2004.11.037.
107. Fox, S.; Oren, Y.; Ronen, Z.; Gilron, J. Ion exchange membrane bioreactor for treating groundwater contaminated with high perchlorate concentrations. *J. Hazard. Mater.* **2014**, *264*, 552–559, doi:10.1016/j.jhazmat.2013.10.050.

108. Gu, B.; Brown, G.M.; Alexandratos, S.D.; Ober, R.; Patel, V. *Selective Anion Exchange Resins for the Removal of Perchlorate* ClO_4^-; Publication No. 4863; Oak Ridge National Library, Environmental Sciences Division: Oak Ridge, TN, USA; 1999.
109. Gu, B.; Brown, G.M.; Maya, L.; Lance, M.J.; Moyer, B.A. Regeneration of perchlorate (ClO4-)-loaded anion exchange resins by a novel tetrachloroferrate (FeCl4-) displacement technique. *Environ. Sci. Technol.* **2001**, *35*, 3363–3368, doi:10.1021/es010604i.
110. Maillard, J.-Y. Bacterial target sites for biocide action. *J. Appl. Microbiol.* **2002**, *92*, 16–27.
111. Ferreira, C.; Pereira, A.M.; Pereira, M.C.; Melo, L.F.; Simões, M. Physiological changes induced by the quaternary ammonium compound benzyldimethyldodecylammonium chloride on Pseudomonas fluorescens. *J. Antimicrob. Chemother.* **2011**, *66*, 1036–1043, doi:10.1093/jac/dkr028.
112. Inácio, Â.S.; Domingues, N.S.; Nunes, A.; Martins, P.T.; Moreno, M.J.; Estronca, L.M.; Fernandes, R.; Moreno, A.J.M.; Borrego, M.J.; Gomes, J.P.; et al. Quaternary ammonium surfactant structure determines selective toxicity towards bacteria: Mechanisms of action and clinical implications in antibacterial prophylaxis. *J. Antimicrob. Chemother.* **2015**, *71*, 641–654, doi:10.1093/jac/dkv405.
113. Sukenik, A.; Viner-Mozzini, Y.; Tavassi, M.; Nir, S. Removal of cyanobacteria and cyanotoxins from lake water by composites of bentonite with micelles of the cation octadecyltrimethylammonium (ODTMA). *Water Res.* **2017**, *120*, 165–173.
114. Shuali, U.; Nir, S. Prepublication: Role of micelle-clay complexes and quaternary amine cations in removal of bacteria from water: Adsorption, biostatic and biocidal effects. *Clays Clay Miner.* **2018**, *66*, 485–492, doi:10.1346/ccmn.2018.064116.
115. Nir, S. Water Purification by a Micelle-Clay Composite Alone and its Collaboration with other Technologies. *Open Access, J. Waste Manag. Xenobiotics* **2019**, *2*, doi:10.23880/oajwx–16000118.
116. Kaya, A.U.; Güner, S.; Ryskin, M.; Lameck, A.S.; Benitez, A.R.; Shuali, U.; Nir, S. Effect of Microwave Radiation on Regeneration of a Granulated Micelle–Clay Complex after Adsorption of Bacteria. *Appl. Sci.* **2020**, *10*, 2530, doi:10.3390/app10072530.
117. Benitez, A.R. *Application of Granulated Micelle-Clay Complexes for Removal from Water of (i) Bacteria (ii) Non-Ionic Herbicide: Regeneration and Effects of Organic Cation Loading on Complex. Capacity. M.Sc. Thesis. The Robert, H. Smith Faculty of Agriculture, Food and Environment*; The Hebrew University: Jerusalem, Israel, 2020.
118. APHA; AWWA; WEF. *Standard Methods for the Examination of Water and Waste Water*, 21st ed.; American Public Health Association, American Water Works Association, Water Environment Federation: Washington, DC, USA, 2005.
119. Paerl, H.W.; Paul, V.J. Climate change: Links to global expansion of harmful cyanobacteria. *Water Res.* **2012**, *46*, 1349–1363, doi:10.1016/j.watres.2011.08.002.
120. Song, L.; Chen, W.; Peng, L.; Wan, N.; Gan, N.; Zhang, X. Distribution and bioaccumulation of microcystins in water columns: A systematic investigation into the environmental fate and the risks associated with microcystins in Meiliang Bay, Lake Taihu. *Water Res.* **2007**, *41*, 2853–2864, doi:10.1016/j.watres.2007.02.013.
121. Szlag, D.; Sinclair, J.L.; Southwell, B.; Westrick, J.A. Cyanobacteria and Cyanotoxins Occurrence and Removal from Five High-Risk Conventional Treatment Drinking Water Plants. *Toxins* **2015**, *7*, 2198–2220, doi:10.3390/toxins7062198.
122. Wang, H.; Ho, L.; Lewis, D.M.; Brookes, J.D.; Newcombe, G. Discriminating and assessing adsorption and biodegradation removal mechanisms during granular activated carbon filtration of microcystin toxins. *Water Res.* **2007**, *41*, 4262–4270, doi:10.1016/j.watres.2007.05.057.
123. Cheriker, H.; Bauer, T.S.; Oren, Y.; Nir, S.; Hayouka, Z. Immobilized random peptide mixtures exhibit broad antimicrobial activity with high selectivity. *Chem. Commun.* **2020**, *56*, 11022, doi:10.1039/d0cc04759g.
124. Gerchman, Y.; Vasker, B.; Tavasi, M.; Mishael, Y.; Kinel-Tahan, Y.; Yehoshua, Y. Effective harvesting of microalgae: Comparison of different polymeric flocculants. *Bioresour. Technol.* **2017**, *228*, 141–146, doi:10.1016/j.biortech.2016.12.040.
125. Rytwo, G.; Lavi, R.; Rytwo, Y.; Monchase, H.; Dultz, S.; König, T.N. Clarification of olive mill and winery wastewater by means of clay–polymer nanocomposites. *Sci. Total. Environ.* **2013**, *442*, 134–142, doi:10.1016/j.scitotenv.2012.10.031.
126. Rytwo, G. Hybrid Clay-Polymer Nanocomposites for the Clarification of Water and Effluents. *Recent Patents Nanotechnol.* **2017**, *11*, 181–193, doi:10.2174/1872210511666170125125928.
127. Lyck, S. Simultaneous changes in cell quotas of microcystin, chlorophyll a, protein and carbohydrate during different growth phases of a batch culture experiment with Microcystis aeruginosa. *J. Plankton Res.* **2004**, *26*, 727–736, doi:10.1093/plankt/fbh071.
128. Alfiya, Y.; Damti, O.; Stoler-Katz, A.; Zoubi, A.; Shaviv, A.; Friedler, E. Potential impacts of on-site greywater reuse in landscape irrigation. *Water Sci. Technol.* **2012**, *65*, 757–764, doi:10.2166/wst.2012.903.
129. Gross, A.; Maimon, A.; Alfiya, Y.; Friedler, E. *Greywater Reuse*; CRC Press. Taylor & Francis Group, Inc.: London, UK, 2015; p. 306.
130. Winward, G.P.; Avery, L.M.; Stephenson, T.; Jefferson, B. Chlorine disinfection of grey water for reuse: Effect of organics and particles. *Water Res.* **2008**, *42*, 483–491, doi:10.1016/j.watres.2007.07.042.
131. Winward, G.P.; Avery, L.M.; Frazer-Williams, R.; Pidou, M.; Jeffrey, P.; Stephenson, T.; Jefferson, B. A study of the microbial quality of grey water and an evaluation of treatment technologies for reuse. *Ecol. Eng.* **2008**, *32*, 187–197, doi:10.1016/j.ecoleng.2007.11.001.
132. Maimon, A.; Friedler, E.; Gross, A. Parameters affecting greywater quality and its safety for use. *Sci. Total Environ.* **2014**, *487*, 20–25.
133. Friedler, E.F.; Kovalio, R.; Ben-Zvi, A. Comparative Study of the Microbial Quality of Greywater treated by Three On-Site Treatment Systems. *Environ. Technol.* **2006**, *27*, 653–663, doi:10.1080/09593332708618674.
134. Gilboa, Y.; Friedler, E.F. UV disinfection of RBC-treated light greywater effluent: Kinetics, survival and regrowth of selected microorganisms. *Water Res.* **2008**, *42*, 1043–1050, doi:10.1016/j.watres.2007.09.027.

135. Benami, M.; Gross, A.; Zhang, W.; Orlofsky, E.; Vonshak, A.; Gillor, O. Assessment of pathogenic bacteria in treated graywater and irrigated soils. *Sci. Total. Environ.* **2013**, *458*, 298–302, doi:10.1016/j.scitotenv.2013.04.023.
136. Travis, M.J.; Wiel-Shafran, A.; Weisbrod, N.; Adar, E.; Gross, A. Greywater reuse for irrigation: Effect on soil properties. *Sci. Total. Environ.* **2010**, *408*, 2501–2508, doi:10.1016/j.scitotenv.2010.03.005.
137. Brook, I.; Malchi, T.; Nir, S. Removal of anionic detergents from water and treatment of gray water by micelle–clay composites. *DESALINATION Water Treat.* **2013**, *53*, 2184–2192, doi:10.1080/19443994.2013.860405.
138. WHO. *Overview of Greywater Management, Health Considerations. Regional Office for the Eastern Mediterranean Centre for Environmental Health Activities*; Eco Design Ideal: Amman, Jordan, 2006; Document WHO-EM/CEH/125/E.
139. Biswas, K.; Turner, S.J. Microbial Community Composition and Dynamics of Moving Bed Biofilm Reactor Systems Treating Municipal Sewage. *Appl. Environ. Microbiol.* **2011**, *78*, 855–864, doi:10.1128/aem.06570-11.
140. Brienza, M.; Nir, S.; Plantard, G.; Goetz, V.; Chiron, S. Combining micelle-clay sorption to solar photo-Fenton processes for domestic wastewater treatment. *Environ. Sci. Pollut. Res.* **2018**, *26*, 18971–18978, doi:10.1007/s11356-018-2491-3.