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SECURING THE FUTURE: CLAY-BASED SOLUTIONS FOR A COMPREHENSIVE AND SUSTAINABLE POTABLE-WATER SUPPLY SYSTEM

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Abstract—Today's water-treatment plants combine practices designed to cope individually with various types of purification challenges. In some cases, the solution to one has detrimental effects on others, *e.g.* disinfection by chlorination forming hazardous organic contaminants. Water-treatment plants have large ecological footprints and operational costs, making the availability of high-quality water in developing areas almost impossible, due to lack of resources and infrastructure. Indeed, >2 billion people are exposed to diseases caused by contaminated water. Clearly, bringing safe, clean drinking water to people's homes is essential to a good quality of life. Clay minerals may offer technologies and innovative practices which would help to develop a reliable, low-maintenance device with a small environmental footprint that processes stream, lake, or pond water into high-quality potable water. The basis for such technologies has already been established and improved approaches are being introduced on an ongoing basis by clay scientists: nanocomposite pre-treatment and disinfection, photodegradation of organic pollutants using clay-based catalysts, polishing of inorganic contaminants, and removal of biological pathogens by adsorption or deactivation onto specifically designed clay-based filters, *etc*. This short review presents a vision for combining those technologies in a tandem system for the delivery of high-quality water that is low-maintenance, affordable, and environmentally sustainable for the benefit of mankind.

Key Words—Nanocomposite, Pathogens, Photodegradation, Potable Water, Water-processing.

INTRODUCTION

Water should be considered "a public good and a human right, not a commodity" (right2water, 2015), and is at the core of sustainable development due to its potential influence on poverty reduction, economic growth, and environmental sustainability, affecting the livelihoods of billions (UN-Water, 2015). On the other hand, freshwater resources clearly cannot meet all requirements and water should not be considered a self-renewable, low-cost resource (Semiat, 2000).

European directives concerning the quality of water intended for human consumption aim to protect humans from the adverse health effects of contaminated water (European Parliament and Council, 2013). Yet, >2 billion people worldwide lack an adequate supply of safe drinking water and ~15 million babies die every year due to waterborne, diarrheal diseases (Weiner, 2008). In Colombia, >3 million inhabitants (28% of the rural population) use untreated water, and are exposed to pollution and illnesses (Jimenez, 2015). In Nepal (Suwal, 2015), the available drinking water is usually polluted with groundwater contaminated by arsenic or untreated sewage discharge. Colombia and Nepal are presented as examples only; due to a lack of resources and infrastructure, these problems are particularly widespread in the developing world, where 80% of diseases are caused by contaminated water (Zia, 2013).

Several challenges must be met in terms of drinking-water treatment, and these can be divided into three groups:

(1) Removal of undissolved and particulate matter: This includes material from soil erosion or construction runoff, algae developing on nutrients, or bacteria and other pathogens, all of which may originate from domestic sewage, livestock, industry, and even natural sources (UNESCO, 2006).

(2) Removal of dissolved organic pollutants: Hundreds of organic pollutants have been reported in water, some of them highly toxic, carcinogenic, or with long residence times in the environment (Unuabonah and Taubert, 2014). Some of these are included in the Persistent Organic Pollutants (POPs) list, and their use is restricted by the 2001 Stockholm Convention (El-Shahawi *et al.*, 2010). Due to their persistence, however, pesticides, polynuclear aromatic hydrocarbons (PAHs), plasticizers, phenols, personal care products, hormones, antibiotics, and drug residues can still be found in water sources. The latter four are included in the ever-lengthening list of "emerging contaminants," which are chemicals discovered recently in natural streams (Grassi *et al.*, 2012) that may accumulate to biologically hazardous levels (Di Credico

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et al., 2015). Indeed, the presence of low concentrations of pharmaceuticals and personal care products (PPCPs) is becoming a source of concern due to their inherent ability to induce physiological effects in humans at low doses (Ebele *et al.*, 2017). Such products have already been found in streams, rivers, lakes (Sui *et al.*, 2015), and even in soils (Chefetz *et al.*, 2008; Grossberger *et al.*, 2014) and crops (Shenker *et al.*, 2011) irrigated with reused water. For example, a recent study showed that traces of carbamazepine (an anti-epilepsy medication) were found in the urine of consumers of such crops, even though those users had never consumed such medicine (Paltiel *et al.*, 2016).

(3) Removal of inorganic contaminants and pollutants: Inorganic substances, present as a consequence of either natural processes or anthropogenic activities, constitute a large proportion of the chemical contaminants in drinking water (Fawell, 1993). These include major-element compounds such as carbonates, sulfate, and nitrate; and minor, but in some cases hazardous, constituents such as As, Se, Mn, and Pb.

Today's drinking-water plants (Figure 1) are designed to deliver high-quality water *via* a series of processes or stages, often specific to a particular type of contamination in the water. Some of them may have direct detrimental effects on other types of contamination, however. For example, disinfection by chlorination, which is applied for pathogen removal, causes the direct release of hazardous disinfection by-products, such as trihalomethame, chloroform, and bromate (Weiner, 2008; Boal *et al.*, 2015). Furthermore, some of the processes are only needed to make other processes effective: for example, the use of Fe or Al compounds for the removal of suspended materials demands a very narrow and specific pH range, in some cases requiring the addition of strong acids or bases to achieve efficient results (Edzwald and Haarhoff, 2011; Mazille and Spuhler, 2012). Obviously, such practices are far from sustainable, and represent more of a 'patchwork' approach that solves one specific problem in each step, without considering the influence on other water-quality parameters. As a result, water-treatment plants are costly, require a cumbersome infrastructure, and have a large environmental footprint, making their implementation very difficult in underdeveloped and rural areas.

A according to Geldreich (2005):"Ignoring system problems or applying patchwork remedies will eventually lead to unsafe water quality if the current state of affairs is not recognized as a dangerous public health risk." Based on today's practices, UNESCO estimates that food demand, rapid urbanization, and climate change are increasing pressure significantly on global water supplies (UNESCO, 2012), whereas the European Report on Development (ERD) calls for a radical rethinking of the global approach to water and natural resources (ERD, 2011). A study by Columbia University calls for US authorities to rethink what the water utility of the future should look like, and to examine their operations for improvements in efficiency, chemical costs, and energy usage (Growing Blue, 2013). Water treatment demands innovative approaches.

The concept proposed here is the introduction of several developments, based on clays, organoclays, or nanocomposites, to the treatment process. As an ultimate vision, such developments might even be combined into a single, comprehensive water-treatment system: *e.g.* such a system (Figure 2) might be based on three modules in accordance with the three challenges mentioned previously: (1) the removal of suspended particles and pathogens can be based on nanocomposite coago-flocculation and disinfection (Rytwo, 2012, 2016, 2017b; Rytwo *et al.*, 2013, 2014; Litaor *et al.*, 2015); (2) removal of organic pollutants and PPCPs might be based on full mineralization *via* their photocatalytic degradation based on flow-through devices (Rytwo, 2015; Rytwo and Daskal, 2016), with improved clay-

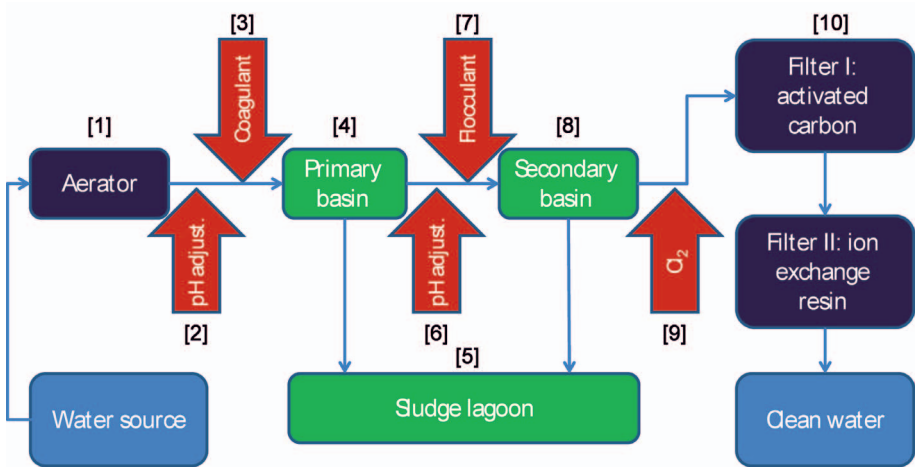


Figure 1. Schematic diagram of a regular drinking-water plant.

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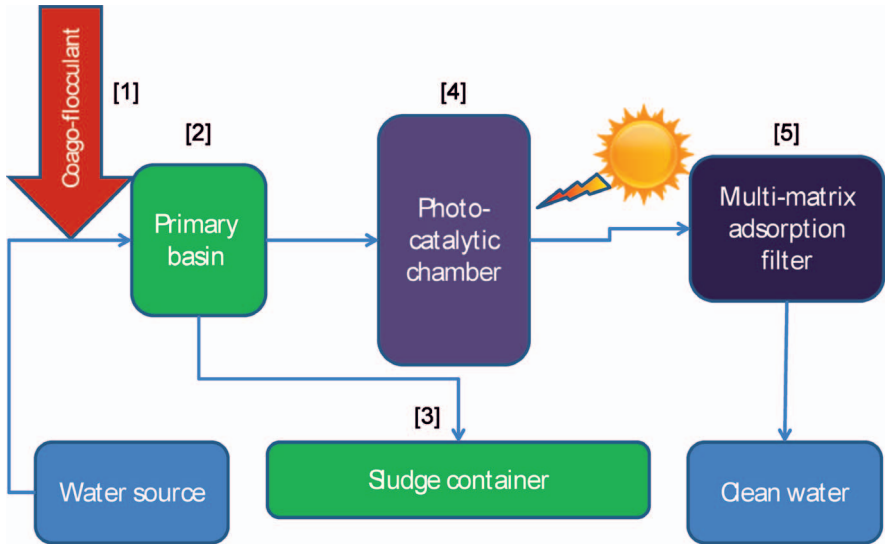


Figure 2. Schematic diagram of the system proposed in the present study.

based photo-catalysts (Miyamoto *et al.*, 2000; Ogawa *et al.*, 2011; Drozd *et al.*, 2014; Stöter *et al.*, 2014, 2015); and (3) removal of the remaining pathogens, organic by-products, and inorganic pollutants can be achieved by combining adsorption on a multi-matrix filter prepared from specifically designed sorbents (Rytwo, 2004; Rytwo and Gonen, 2006; Rytwo *et al.*, 2007; Bleiman and Mishael, 2010; Ganigar *et al.*, 2010; Shtarker-Sasi *et al.*, 2013; Unuabonah *et al.*, 2013; Rytwo and Margalit, 2014; Unuabonah and Taubert, 2014; Kalfa *et al.*, 2017).

The implementation of such a vision requires additional research to cover a range of other aspects, including: (1) theoretical studies of fractal theory-based models for floc formation; (2) full kinetic analysis; (3) optimization of photocatalysts aimed at achieving sun-light-based processes; (4) confirming full mineralization of pollutants to avoid the presence of hazardous photodegradation by-products; (5) modeling of adsorption occurring during flow through a porous medium of combined filtering matrices; and (6) studies of the synergy between the modules and sustainability of the whole system. Research on those aspects could accelerate the coming-to-fruition of a clay-based water purification device, by elucidating processes and enabling estimations of the best combination of purification strategies for each ecosystem, according to the specific problems in each area.

The following sections deliver details on each of the proposed modules, and the ways in which those may be combined to create a comprehensive water-treatment process.

CLARIFICATION: REMOVAL OF ALGAE, SUSPENDED MATERIALS, AND PATHOGENS

The removal of suspended materials by a regular drinking-water plant includes several separate steps (Figure 1) performed in pre-treatments (Sutzkover-Gutman and Hasson, 2010) that include, in most cases, coagulation (‘3’ in Figure 1) and flocculation (Edzwald and Haarhoff, 2011) (‘7’ in Figure 1) steps. Coagulation involves the reduction of electrostatic repulsion so that colloidal materials can aggregate. Flocculation uses bridging compounds to form chemically bonded links between colloidal particles, enmeshing the particles in relatively large masses. The combination of both processes usually increases the size of the particle from 0.2 to ~50 μm (Voutchkov, 2010). Separation of the large aggregates is performed by sedimentation, decantation, or filtration, and the resulting sludge is usually accumulated in a tank or lagoon (‘5’ in Figure 1), and disposed of as waste. The process, in general, is time consuming (Mazille and Spuhler, 2012), requires several different and consecutive tanks (Choi and Yun, 2002) denoted ‘4’ and ‘8’, respectively, in Figure 1, and may also require, *a priori*, aeration to remove volatile compounds (‘1’ in Figure 1), and the addition of acid or base (‘2’ and ‘6’ in Figure 1) to adjust the pH of the water to the very narrow range suitable for the action of the different chemicals added (Edzwald and Haarhoff, 2011; Mazille and Spuhler, 2012). Bacteria and pathogens are usually not removed in this process, but require a separate treatment (‘9’ in Figure 1). Several technologies, such as ozonation (Wang and Shammas, 2007) or irradiation (Wang *et al.*, 2007) are available for that task, but the most widely used method for potable water is chlorination (Weiner, 2008). The possible formation of harmful by-products is considered to be a severe drawback for all disinfection procedures (Unuabonah and Taubert, 2014). Thus, the final module (‘10’ in Figure 1) is, in most cases, a series of filters designed to remove dead biological material, remaining undesired organic chemicals, particles, and in some cases unwanted or hazardous inorganic compounds and metals.

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Since 2011, the concept of nanocomposite use for the removal of colloidal suspended solids has been applied. The term "nanocomposite" is used to define a multiphase hybrid material in which one of the components has at least one dimension of <100 nm (Palmero, 2015). Specific clay-polymer nanocomposites can be prepared and designed by combining clay minerals with organic polymers *via* molecular-level interactions (Ruiz-Hitzky, 2001). Nanocomposites based on clay minerals with relatively high density bound to ionic polymers with a charge opposite that of the effluent's colloids have been shown to perform one-step coago-flocculation in waste water from several sources (Rytwo *et al.*, 2013; Litaor *et al.*, 2015; Rytwo, 2016, 2017b), stream water, and sea water intended for desalination processes (Rytwo, 2017a). In most cases nanocomposite treatment has proven to be an order of magnitude faster and considerably more efficient than using regular mineral or organic coagulants (Rytwo *et al.*, 2014), including bioflocculants. Remaining sludge, which, due to the hybrid composition and the efficacy of the coago-flocculation, is >95% organic, can be used for compost preparation.

Even though in some of those studies an additional bridging agent was added simultaneously with the nanocomposites ('1' in Figure 2) to increase the size of the flocs and the sedimentation velocity (Rytwo, 2017b), in all cases the rapid treatment is achieved under a broad range of conditions, in a single tank ('2' in Figure 2), without the need for pH adjustments. The rationale behind the use of clay–polymer nanocomposites lies in the following assumption: considering that the difference in density between the flocs formed and the water might be very small (at least for organic colloids, algae, bacteria, *etc.*), even if large aggregates are formed, the limiting factor for separation time will be the density difference. Accordingly, increasing the density by preparing a hybrid composite based on a denser clay mineral (2.6-fold greater density than water and most organic compounds) and a neutralizing charged polymer should shorten sedimentation time considerably. A sketch of a needle-like clay (such as sepiolite or palygorskite) bound to a cationic polymer (*e.g.* polyDADMAC or even biopolymers such as chitosan), forming a nanocomposite with a denser core and long cationic branches is shown in Figure 3. Such a nanoparticle would be able to bind electrostatically to negatively charged colloids, forming large and neutralized aggregates that might also connect to neutral colloids by Van der Waals interactions, while the clay mineral 'nuclei' increase the overall density, speeding up sedimentation. The combination of all three mechanisms (neutralization, aggregation, and increased density) is termed "coago-flocculation" (Rytwo, 2012). The specific charge of the nanocomposites, based on the type of polymer (or biopolymer) and polymer-to-clay ratio, may need to be adjusted to the specific type of effluent, depending on colloidal charge. Natural clay minerals are negatively charged so they do not tend to interact with anionic polymers. Acicular clays can also bind non-cationic (Rytwo *et al.*, 1998) and even anionic compounds; negative nanocomposites can, thus, also be prepared within a broad range of charge (Rytwo *et al.*, 2016).

Efficient treatment depends heavily on specific conditions. Efficient removal of algae can only be achieved within a specific concentration range of the coagulant added (Figure 4). Previous studies revealed that the charge of the suspended material has a critical influence on the type and dose of coagulant required for efficient treatment (Rytwo *et al.*, 2014); therefore, clarification is achieved only at a coagulant level that is close to neutralization of the colloid. The overall process and kinetics of floc formation and separation are far from fully understood, however (Thomas *et al.*, 1999). In several cases, discrepancies have been found between tests, as well as unexpected results (more or less successful flocculation) at apparently identical conditions. Such effects could be related to aggregate structure, density, or their interactions with the surrounding solution. In recent decades, a new approach (*e.g.* Vahedi and Gorczyca, 2010, 2012) to flocculation and floc sedimentation velocity has been introduced, based on the concept of fractal geometry (Pfeifer, 1984; Avnir *et al.*, 1985). Fractal geometry suggests that flocs have a non-Euclidian shape and, therefore, the density of the aggregate becomes smaller as the aggregate becomes larger according to the power law: $\rho \approx l^{(D-d)}$, and $\rho \approx M^{(D-d)}/D$, where ρ is the aggregate's average density, l is the aggregate's length, M is the mass, and D and d are the fractal and Euclidean dimensions, respectively. Principles of fractal geometry

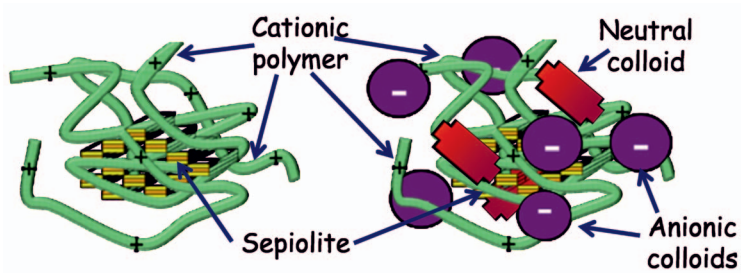


Figure 3. Sketch of a sepiolite-chitosan bionanocomposite used for water clarification (based on Rytwo, 2017a).

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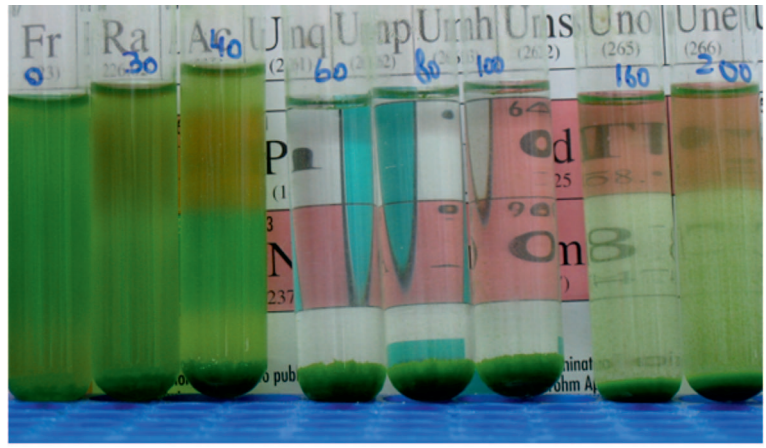


Figure 4. Algae removal and water clarification with various doses (in μL/L of water) of clay-polymer nanocomposite suspension.

can be used to explain the effects of different parameters, such as mixing rates or coagulant type, structure, and concentration, on aggregation, floc structure (Chakraborti *et al.*, 2003), and floc-settling velocities (Vahedi and Gorczyca, 2012). This, in turn, allows the development of models (Tang and Raper, 2002; Tang *et al.*, 2002) that might be further elaborated, adapted, and tested to improve understanding and optimization of such nanocomposite-induced clarification processes.

Even though methods for removal of biological pathogens (bacteria and viruses) *via* adsorption are elaborated below, another important contribution of clay-based removal of suspended particles may be in reducing the disinfection doses: a negative charge on bacterial cells can result in cation binding by nonspecific electrostatic interactions (Cuevas *et al.*, 2011). This may explain why layered double hydroxides (LDH), which have a structure similar to clay minerals but are positively charged, exhibit effective activity in removing pathogens from water (Jin *et al.*, 2007). Accordingly, quaternary ammonium-based organoclays (Alther, 2000), positively charged micelle-clay (Shtarker-Sasi *et al.*, 2013), or polymer-clay nanocomposites (Rytwo, 2017a) were found to be efficient at adsorption or elimination of bacteria. For bacteria or viruses with positively charged membranes (Jucker *et al.*, 1996), negative nanocomposites consisting of anionic polymers bound to neutral-site acicular minerals or even raw clay minerals might be used. Removal of pathogens at this initial stage of the treatment may allow reduction of the required disinfection doses, leaving only the dose needed for residual treatment.

PHOTODEGRADATION OF POLLUTANTS WITH CLAY-BASED CATALYSTS

The increasing detection of many organic compounds in surface water, groundwater, and drinking water has created great concern among scientists (Calamari *et al.*, 2003; Hlavinek *et al.*, 2008; Ebele *et al.*, 2017) due to their high toxicity and persistence in the environment. Moreover, the removal of such pollutants from water is a growing environmental problem. European directives have determined environmental quality standards for >40 priority substances and pollutants (European Parliament and Council, 2013; EU Environment Directorate-General, 2016), most of them persistent organic compounds or organic pesticides. Furthermore, worldwide use of personal care products, steroid hormones, antibiotics, drugs, and flame retardants, classified as the so-called 'emerging micropollutants,' show increased presence in water discharges and water sources (Grossberger *et al.*, 2014; Scotti *et al.*, 2014). Pharmaceuticals (World Health Organization, 2011) and antibiotics (Wang *et al.*, 2016) at levels of ng L^{-1} have been reported in rivers, lakes, and groundwater. Even though concentrations of such contaminants might be very low, most of these pollutants are not removed completely by regular treatment processes (Chefetz *et al.*, 2008; Rytwo and Margalit, 2014). Standard removal techniques, such as adsorption on activated carbon (AC), generally have slow kinetics (Rytwo and Gonen, 2006), and require periodic replacement of the sorbent.

Clay-based materials can contribute to this stage as heterogeneous catalysts in photodegradation processes, sorbents (see next section), or supports for 'bioreactive organoclays' (Sarkar *et al.*, 2012). The last includes complexes of clays with fungi (Acevedo *et al.*, 2010), bacteria (Masaphy *et al.*, 2014), or adsorbed enzymes (Chang *et al.*, 2015; Olshansky *et al.*, 2018), offering a new remediation approach that combines sorption and biodegradation/biotransformation.

Another remediation option is the use of photocatalysis, an advanced oxidation process (AOP), that has demonstrated efficiency in degrading a wide range of refractory organics into biodegradable compounds, in some cases even yielding complete mineralization to carbon dioxide and water (Rajamanickam and Shanthi,

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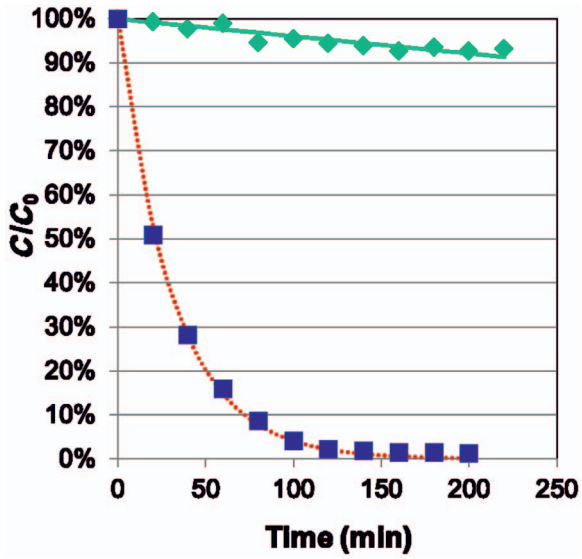


Figure 5. Photodegradation of a 40 mg/L solution of carbamazepine without catalyst (diamonds), or with 0.1 g/L mineral catalyst (squares). Points are measured values and lines represent processes evaluated with a first-order model.

2012; Irawaty *et al.*, 2014). For example, the aforementioned carbamazepine is considered to be a very persistent pharmaceutical (Shenker *et al.*, 2011; Paltiel *et al.*, 2016) found in drinking water sources and treated wastewater (Cabeza *et al.*, 2012). Ultraviolet C (UVC) photolysis without a catalyst (Figure 5) yielded very modest degradation ($t_{1/2}$ = 1270 min). Addition of 0.1 g/L of a mineral catalyst using a 'slurry type' photocatalytic device (Rytwo and Daskal, 2016) yields complete degradation ($t_{1/2}$ = 15.1 min), exhibiting a two orders of magnitude improvement over the non-catalyzed process.

Such heterogeneous photocatalytic processes are usually explained by five independent steps (Herrmann, 1999): (1) transfer of the reactants in the fluid phase to the surface; (2) adsorption of at least one of these reactants; (3) reaction in the adsorbed phase; (4) desorption of the product(s); and (5) removal of the products from the interface region. Stages 2–4 of the photocatalytic process (adsorption–reaction–desorption) are determined directly by very specific interactions between the pollutant, the catalyst, and the photons (Figure 6). The photon energy (hυ) should be greater than or equal to the band gap energy, causing a lone electron to be photo-excited to an empty conduction band over a period of femtoseconds. The photonic excitation leaves behind an unfilled valence band ('hole'), thus creating the electron-hole pair. Oxidative–reductive chain reactions yield the *in situ* generation of highly reactive transitory species (*i.e.* H_2O_2, $OH^{\cdot}$, O_3, $O_2^{-\cdot}$, *etc.*) (Chong *et al.*, 2010), which efficiently degrade a wide range of refractory organics, yielding in some cases complete mineralization to carbon dioxide and water. Several studies on this issue have been reported extensively (Uyguner and Bekbolet, 2009; Chong *et al.*, 2010; Schneider *et al.*, 2014; Fan *et al.*, 2015).

In the widely used commercial photocatalyst "P25" TiO_2 (Benotti *et al.*, 2009; Schneider *et al.*, 2014), the band gap energy is 3.2 eV for anatase or 3.0 eV for rutile, equivalent to wavelengths of 387 and 412 nm, respectively. Taking this into consideration, ultraviolet A (UVA) light should, theoretically, be sufficient to activate the process. Efficient photocatalytic activity is

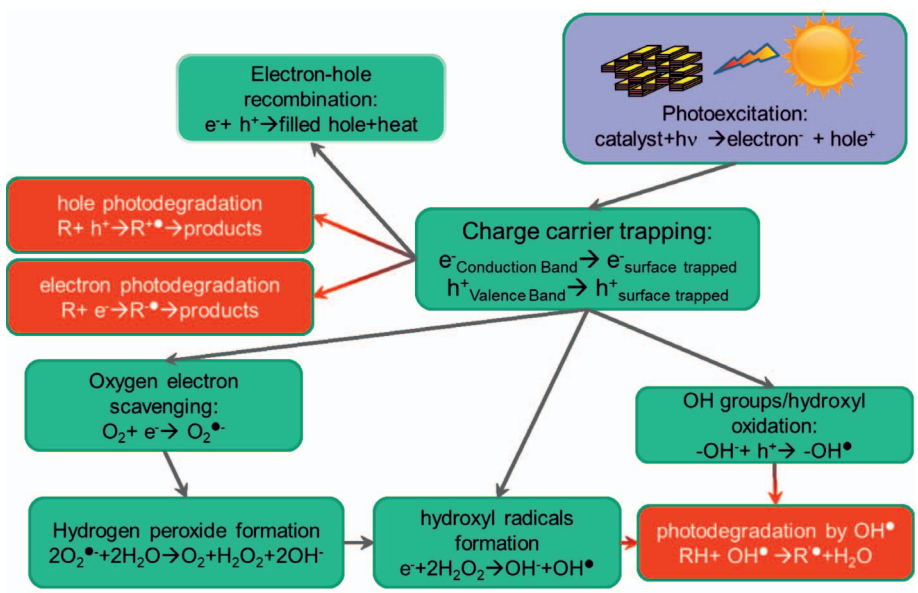


Figure 6. General scheme of the photocatalyzed processes.

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only observed, however, with UVC light (Abd El-Rady *et al.*, 2013), and improving the solar conversion efficiency remains a challenge (Ning *et al.*, 2016). Thousands of studies have aimed to prepare efficient catalysts, active with photons with lower energy or direct solar light. Several of those studies present combinations of metal oxides or other semiconductors (ZnO, Fe_2O_3, Fe_3O_4, CdS, GaP, and ZnS) with clay minerals (Ahn *et al.*, 2006; Ramirez *et al.*, 2007; Iurascu *et al.*, 2009; Werner *et al.*, 2009; Xu *et al.*, 2014), zeolites (Centi *et al.*, 2000), pillared clays (Herney-Ramirez *et al.*, 2010), and even pillared clays based on TiO_2 pillars (Chen *et al.*, 2013; Bel Hadjltaief *et al.*, 2014). A promising approach is the specific engineering of synthetic clay particles based on regular heterostructures with two alternating types of interlayers (Stöter *et al.*, 2014, 2015) which combine two distinct 'micro-reactor' spaces separated by a ~1 nm thick silicate lamella: one reactor optimized for adsorption of the pollutant (stage 2) and the other for photoexcitation (stage 3). Another approach is the development of photocatalysts based on suitable photosensitizers (Hashimoto *et al.*, 2005) that should enhance the production of active photodegrading species such as singlet oxygen (Derosa and Crutchley, 2002). Cationic photosensitizers (organic cationic dyes such as pseudo-isocyanine) may be added directly to clay minerals by cation exchange (Miyamoto *et al.*, 2000; Ogawa *et al.*, 2011), whereas non-cationic photosensitizers are combined with other organocations (Drozd *et al.*, 2014). Such novel photocatalytic materials could broaden efficient excitation energy allowing the use of other lamps (visible light, UVA, UVB, UVC, or even direct solar irradiation), other auxiliary compounds (H_2O_2, O_3, O_2, air injection), and other conditions.

In order to achieve efficient photodegradation, the contact between effluent, catalyst, and light must be optimized. Photocatalytic reactors are usually classified into two main configurations: (1) reactors with suspended photocatalyst particles ('slurry type'); and (2) reactors with photocatalyst immobilized on an inert carrier (Pozzo *et al.*, 2000). The latter configuration allows relatively simpler continuous operation, whereas the first configuration might yield greater rates, although separation of the photocatalyst particles limits this process. A slurry-type photocatalytic reactor in which light is supplied to a vast volume of effluent + large-specific-surface-area catalyst might improve transfer of the reactants to and from the catalyst, yielding an efficient solution to stages 1 and 4 of the photocatalytic process. Such slurry reactors require a cleaning process to avoid membrane fouling. A commercial device known as 'Photo-Cat' (manufactured by Purifics Inc., London, Ontario, Canada) recovers the catalyst by short back-pulses of air (Benotti *et al.*, 2009; Chong *et al.*, 2010). Another device (Rytwo *et al.*, 2015) allows continuous photodegradation, where fouling of the membrane is avoided by a device based on continuous brushing and suction (Rytwo and Daskal, 2016). Thus, slurry-type photocatalysis devices, in which light is supplied to a vast volume of effluent + large-specific-surface-area catalyst, enables improved transfer of the reactants to and from the catalyst, yielding an efficient answer to stages 1 and 5 of the photocatalytic process.

Extensive research in the area has led to hope that, in the near future, specifically engineered clay-based materials combined in membrane-type or slurry-type photocatalytic devices may help "to gain insights into the future development of photocatalysis and into the use of solar energy for environmental remediation and other useful systems and processes" (Schneider *et al.*, 2014).

ADSORPTION ON CLAY-BASED MULTI-MATRIX FILTERS

Following the nanocomposite coago-flocculation that should remove most pathogens and all suspended material, and the photocatalysis process which should mineralize most organic pollutants, a requirement remains for a polishing procedure aimed at removing inorganic pollutants, any remaining bacteria/viruses, organic residues, and possible degradation by-products. A filtering process based on a combination of specifically tailored clays, organoclays, or nanocomposite sorbents can be used for such remaining contaminants. The use of clays, organoclays, and nanocomposites for the adsorption of pollutants and environmental remediation has been studied widely (Churchman *et al.*, 2006; Theng *et al.*, 2008; Unuabonah *et al.*, 2013; Yuan *et al.*, 2013; Nafees and Waseem, 2014; Unuabonah and Taubert, 2014). Clays are characterized by excellent sorption capabilities for cations: hundreds of studies since the middle of the 20th Century have discussed the utility of 'raw' or mildly treated clays in the removal of heavy metals. Extensive reviews summarizing the adsorption of Pb, Cu, Hg, Zn, As, Ni, and other hazardous metals have been published (Ismadji *et al.*, 2015; Uddin, 2017). The clays and clay minerals used for the studies were, in most cases, kaolinite/kaolin or smectitic clays (bentonite, montmorillonite) but studies were also carried out with vermicullites, illites, and several needle-like (palygorskite, sepiolite) or tubular (halloysite) clays. In some cases, the influences of additional conditions were tested, *e.g.* the pH (Farrah and Pickering, 1979; Lukman *et al.*, 2013) or organic substances (Abollino *et al.*, 2003). Adsorption of organic cations was also reported widely with several studies carried out on the removal of 'basic' (cationic) dyes such as methylene blue or rhodamine B, antibiotics such as ciprofloxacin, or quaternary ammonium components such as benzalkonium or triclosan (Ismadji *et al.*, 2015).

Unlike the situation for cations, raw clays are generally ineffective sorbents for anionic, hydrophobic, or non-polar pollutants (Sheng *et al.*, 2001; Shen, 2004),

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but their sorptive capabilities can be modified substantially by replacing the natural inorganic interlayer cations with organic cations such as alkyl ammonium compounds (Mortland, 1986; Koh and Dixon, 2001), monovalent dyes (Borisover *et al.*, 2001; Rytwo *et al.*, 2007), or polymers (Han *et al.*, 2010; Ruiz-Hitzky *et al.*, 2010; Li *et al.*, 2017). For example, adsorption of 2,3,5 trichlorophenol (TCP) and picric acid (PA) on raw SWy-1 montmorillonite is very limited. SWy-1 modified with crystal violet (CV) adsorbed at 80% of the cation exchange capacity (CEC) (referred to as M80) adsorbs TCP and PA to similar levels, 0.2 moles kg^{-1} (Figure 7, based on work by Gonen and Rytwo, 2006). When a sorbent with CV up to 125% of the CEC was used, however, adsorption of PA increased slightly, and adsorption of TCP exhibited a completely different behavior: very high affinity (H-type) allowed complete removal at low concentrations, whereas partition behavior (C-type) allowed a large sorption capacity at high concentrations. Thus, very specific properties of the modified clay surface influenced the adsorption depending on the specific character of both adsorbent and adsorbate. Indeed such organophilic matrices adsorb several organic compounds efficiently (Xu and Boyd, 1994; Beall, 2003; Shen, 2004; Sarkar *et al.*, 2010), and have been proposed for environmental applications such as water treatment (Zhu *et al.*, 2000) or remediation (Zhao and Vance, 1998).

Excellent water quality demands complete removal of biological pathogens (even if dead or inactive), *e.g.* bacteria, viruses, fungi, *etc*. Even though part of this task will be performed by the modules mentioned above (separation of suspended material and photocatalytic processes), adsorption of the remaining pathogens can be achieved using raw clays (Unuabonah *et al.*, 2018), Fe^{3+} clay (Qin *et al.*, 2018), chitosan-modified nanocomposites (Unuabonah *et al.*, 2017), micelle-clays (Shtarker-Sasi *et al.*, 2013; Kalfa *et al.*, 2017), and other clay-based materials. Efficient removal by adsorption of hazardous oxyanions such as chromate, selenate, arsenate, *etc.* can be achieved by similarly prepared, positively charged materials (Churchman *et al.*, 2006; Bleiman and Mishael, 2010; Buzetzky *et al.*, 2017; Ezzatahmadi *et al.*, 2017), but also using layered double hydroxides (LDH) (Goh *et al.*, 2008) or pillared clays (Mohan and Pittman Jr., 2007).

When studying adsorption efficiency of new clay-based sorbents, researchers usually compare the results with those for activated carbon (AC). Carbon in its activated form has been used to adsorb contaminants since the late 1800s (U.S. Army Corps of Engineers, 2001). Activation is achieved by exposing coal, lignite, wood, coconut shell, *etc.* to activating agents, such as steam, yielding a porous graphite lattice structure, very effective for the adsorption of large organic molecules but not for small and polar compounds (Monser and Adhoum, 2002). The capacity of adsorption of organoclays may reach the same order of magnitude as those measured for high-quality AC (Rytwo *et al.*, 2007). Two major differences are observed between the sorbents, however: first, the adsorption to organoclays proceeds in seconds, whereas for AC it takes tens of minutes (Rytwo and Gonen, 2006). This is a great advantage favoring organoclays, considering that the size of an adsorption filter depends to a great extent on the kinetics of removal of the pollutant. Fast kinetics might allow the use of smaller filters. The second difference is that clay-based materials have a very low hydraulic conductivity; thus, the flow rate through an organoclay column is very low. This severe limitation led researchers to mix the

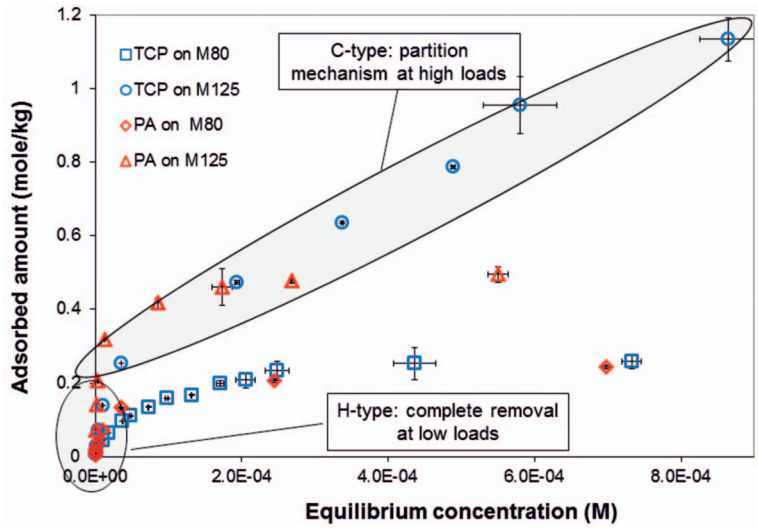


Figure 7. Adsorption isotherm of 2,4,5 trichlorophenol (TCP) or picric acid (PA) on SWy-1 modified with crystal violet up to 80% or 125% of the CEC (M80 and M125, respectively) (based on Gonen and Rytwo, 2006).

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effective organoclays with inactive sand, quartz, or other materials with good hydraulic properties (Zadaka *et al.*, 2007; Radian *et al.*, 2011). The disadvantage of such an approach is that the percentage of active ingredients is reduced, amounting to <5% in most studies.

Several possible solutions may be adopted to overcome the low hydraulic conductivity. For example, the use of 'slurry'-based devices similar to those presented in the previous section for photocatalysis (Rytwo and Daskal, 2016) may enable the fast kinetic advantage without being influenced by the low hydraulic conductivity due to the flow-through filtering column. The 'slurry'-based approach might be applied further in a series of slurry tanks referred to as "sequential batches," where the pollutant passes from one "pseudo-batch" experiment to the other (Rytwo *et al.*, 2007). The disadvantage of such procedures is that they require separation between the adsorbent solids and the treated water, based on filtration, sedimentation, or centrifugation. Solid-phase column filters, on the other hand, are considerably easier to prepare and apply. An improvement to the approach of mixing organoclays with sand can be applied, using AC instead of sand (Ruiz-Hitzky *et al.*, 2010; König, 2011), thus combining a sorbent that has large hydraulic conductivity and sorption capacity but low kinetics (granular AC) with one that has low hydraulic conductivity, medium sorption capacity, and very fast sorption kinetics (organoclay) might allow for optimal pollutant control. Another option is the preparation of granules based on organoclays (Alther, 1999, 2001; Nir and Ryskin, 2016). A combination of both approaches, by mixing organoclay granules with anthracite as a filtering material for suspended solids, has led to a series of commercial products (CETCO, 2016), in most cases used to protect AC from clogging by preliminary sorption of oils and humic substances (Alther, 1995; Beall, 2003).

Additional interesting adsorbing clay-based matrices could be based on zero-valent iron (ZVI) or carbon clay-supported nanoparticles. ZVI has been used for environmental remediation since the early 1990s (Li *et al.*, 2006) in permeable reactive barriers. The efficacy of ZVI is handicapped by aggregation, leading to a need for supporting materials to which such nanoparticles are attached. Clay minerals have been used extensively for that purpose (Ezzatahmadi *et al.*, 2017) leading to successful removal of heavy metals (Petala *et al.*, 2013) or organic pollutants (Li *et al.*, 2016). Carbon-based nanocomposites prepared by hydrothermal processes on clay minerals such as montmorillonite (Zhu *et al.*, 2017) or palygorskite (Chen *et al.*, 2011) had proven effective for removal of heavy metals, whereas combination of a clay binder with a commercially available activated carbon yielded a very effective sorbent for volatile organic compounds (Yates *et al.*, 2012).

Other problems still need to be solved, of course. The regeneration of the polluted adsorbents requires extensive study, and even though several biological, thermal, and chemical approaches have been proposed (Zhu *et al.*, 2009) and in some cases efficient adsorption on regenerated sorbents was observed (Ruiz-Hitzky *et al.*, 2010), research is still required and adaptation of methods used for the regeneration of exhausted AC (Salvador *et al.*, 2015a, 2015b) should be examined and tested on exhausted organoclays.

To conclude, a multi-matrix adsorbing column might be prepared by combining layers of all or part of the following: (1) natural zeolites or other stable granular clays (sepiolite, stevensite) for the adsorption of cations; (2) granular, specifically tailored, organophilic organoclays for the adsorption of non-polar pollutants; (3) positively charged nanocomposite granules for the removal of anionic pollutants and negatively charged oxyanion contaminants (arsenate, chromate, nitrate, selenate, *etc*.); (4) multi-purpose sorbents such as ZVI-clay particles or carbon-clay composites, or (5) micelle-clays or similar hybrid or natural materials for the adsorption of pathogens. This combination might lead to water-treatment columns which provide an affordable and effective system that might be applied at industrial-scale water-treatment plants and even at the domestic scale.

SUMMARY AND CONCLUSIONS

One of the greatest challenges of our time is the provision of clean water using less energy and resources. Improved, simple, and safe processes for water supply are in great demand. This is not a straightforward objective: water purification depends on the interactions of physico-chemical processes on a variety of scales, influencing biological aspects such as removal of pathogens.

This study has described the versatile capabilities of clay-based materials in water treatment. Clearly, covering all of the aspects involved in a single review would be impossible. Health, environmental, and economic aspects of the application of clay-based materials should be addressed in detail. Nanoparticles in general (including clay) can have an "adverse effect on human health when they are inhaled over a very long period" (Carretero *et al.*, 2013), and studies of possible toxicity to biota have also been carried out (Exbrayat *et al.*, 2015). The general perception, however, is that clays and organoclays "are also available commercially at relatively low cost," "are not harmful to human health" (Bergaya *et al.*, 2012), and "do not pose much risk either to the physical environment or to human health" (Yuan, 2004). As for the economic aspects, "establishing cost data for innovative remediation technologies can be difficult, especially for 'in situ' processes" (National Research Council, 1997). In a few cases, very rough preliminary evaluations were made (Rytwo *et al.*, 2013; Ben Moshe and Rytwo, 2018). Hopefully, changes in the

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prices of raw materials due to local mining or mass manufacture may change the financial estimates, making the proposed techniques more cost effective. For now, unfortunately, synthetic, commercial polymers (for example) for the preparation of nanocomposite coagoflocculants are at least an order of magnitude cheaper than biopolymers.

The approach outlined in Figure 2 is considerably more compact than a regular water-treatment plant (Figure 1). The future vision of the system suggested could make aerators, extensive chlorination, secondary sludge basins, or pH adjustments unnecessary. Removal of all suspended particles, including most pathogens and silt, will be performed in a single step. Photocatalytic degradation of fully mineralizing organic contaminants to CO_2 and H_2O may be performed in the future with improved catalysts working with visible or UVA light. A multi-matrix filter based on specifically tailored, modified and raw clays, might remove the inorganic contaminants, possible photodegradation of by-products, or remaining pathogens and organic pollutants. Such a system could be modular, and each module could be treated and regenerated separately, allowing high flexibility. The order of the modules could then be modified as required, *e.g.* by interchanging the adsorption module with the photocatalytic module. Thus, compared to modern treatment, the overall system presented would be considerably simpler, would have a 'footprint' which is an order of magnitude smaller, and could be based entirely on relatively low-maintenance components and low-energy requirements, enabling water to be treated in a sustainable and cost-effective manner that could be applied in remote places or areas with lower levels of infrastructure.

Of course, no specific reason exists to focus only on clay-based materials in real devices but note that clays may offer a comprehensive solution to all the challenges in water treatment.

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REFERENCES

Abd El-Rady, A.A., Abd El-Sadek, M.S., El-Sayed Breky, M.M., and Assaf, F.H. (2013) Characterization and photocatalytic efficiency of palladium doped-TiO_2 nanoparticles. *Advances in Nanoparticles*, **2**, 372–377.

Abollino, O., Aceto, M., Malandrino, M., Sarzanini, C., and Mentasti, E. (2003) Adsorption of heavy metals on Na-montmorillonite. Effect of pH and organic substances. *Water Research*, **37**, 1619–1627.

Acevedo, F., Pizzul, L., Castillo, M., González, M.E., Cea, M., Gianfreda, L., and Diez, M.C. (2010) Degradation of polycyclic aromatic hydrocarbons by free and nanoclay-immobilized manganese peroxidase from anthracophyllum discolor. *Chemosphere*, **80**, 271–278..

Ahn, M.Y., Filley, T.R., and Jafvert, C.T. (2006) Photodegradation of decabromodiphenyl ether adsorbed onto clay minerals, metal oxides, and sediment. *Environmental Science & Technology*, **40**, 215–220.

Alther, G.R. (1995) Organically modified clay removes oil from water. *Waste Management*, **15**, 623–628.

Alther, G.R. (1999) *Granular organoclay for high temperature applications*. US Patent Grant US6093241A, Google Patents.

Alther, G. (2000) *Biocidal organoclay*. US Patent Grant US6165485A, Google Patents.

Alther, G.R. (2001) How to remove emulsified oil from wastewater with organoclays: Water quality products. *Water Quality Publications*. <http://www.wqpmag.com/how-remove-emulsified-oil-wastewater-organoclays> (accessed 21 May 2016).

Avnir, D., Farin, D., and Pfeifer, P. (1985) Surface geometric irregularity of particulate materials: The fractal approach. *Journal of Colloid and Interface Science*, **103**, 112–123.

Beall, G.W. (2003) The use of organo-clays in water treatment. *Applied Clay Science*, **24**, 11–20.

Bel Hadjltaief, H., Galvez, M.E., Ben Zina, M., and Da Costa, P. (2014) TiO_2/clay as a heterogeneous catalyst in photocatalytic/photochemical oxidation of anionic reactive blue 19. *Arabian Journal of Chemistry*. https://doi.org/10.1016/j.arabjc.2014.11.006.

Ben Moshe, S. and Rytwo, G. (2018) Thiamine-based organoclay for phenol removal from water. *Applied Clay Science*, **155**, 50–56.

Benotti, M.J., Stanford, B.D., Wert, E.C., and Snyder, S.A. (2009) Evaluation of a photocatalytic reactor membrane pilot system for the removal of pharmaceuticals and endocrine disrupting compounds from water. *Water Research*, **43**, 1513–1522.

Bergaya, F., Jaber, M., and Lambert, J.-F. (2012) Clays and clay minerals as layered nanofillers for (bio)polymers. Pp. 41–75 in: *Environmental Silicate Nano-Biocomposites* (L. Avérous and E. Pollet, editors). Springer, Berlin.

Bleiman, N. and Mishael, Y.G. (2010) Selenium removal from drinking water by adsorption to chitosan–clay composites and oxides: Batch and columns tests. *Journal of Hazardous Materials*, **183**, 590–595.

Boal, A.K., Rhodes, C., and Garcia, S. (2015) Pump-and-treat groundwater remediation using chlorine/ultraviolet advanced oxidation processes. *Groundwater Monitoring and Remediation*, **35**, 93–100.

Borisover, M., Graber, E.R., Bercovich, F., and Gerstl, Z. (2001) Suitability of dye–clay complexes for removal of non-ionic organic compounds from aqueous solutions. *Chemosphere*, **44**, 1033–1040.

Buzetzky, D., Nagy, N.M., and Kónya, J. (2017) Use of La-, Ce-, Y-, Fe- bentonites for removing phosphate ions from aqueous media. *Periodica Polytechnica Chemical Engineering*, **61**, 27–32.

Cabeza, Y., Candela, L., Ronen, D., and Teijon, G. (2012) Monitoring the occurrence of emerging contaminants in treated wastewater and groundwater between 2008 and 2010. The Baix Llobregat (Barcelona, Spain). *Journal of Hazardous Materials*, **239–240**, 32–39.

Calamari, D., Zuccato, E., Castiglioni, S., Bagnati, R., and Fanelli, R. (2003) Strategic survey of therapeutic drugs in the Rivers Po and Lambro in northern Italy. *Environmental Science & Technology*, **37**, 1241–1248.

Carretero, M.I., Gomes, C.S.F., and Tateo, F. (2013) Clays, drugs, and human health. Pp. 711–764 in: *Handbook of Clay Science* (F. Bergaya and G. Lagaly, editors). Developments in Clay Science. Elsevier, Amsterdam.

Centi, G., Perathoner, S., Torre, T., and Verduna, M.G. (2000) Catalytic wet oxidation with H_2O_2 of carboxylic acids on homogeneous and heterogeneous Fenton-type catalysts. *Catalysis Today*, **55**, 61–69.

https://doi.org/10.1346/CCMN.2018.064114 Published online by Cambridge University Press

CETCO (2016) Products, Environmental Products; Organoclays. https://www.mineralstech.com/business-segments/performance-materials/cetco/products/environmental-products/organoclays.

Chakraborti, R.K., Gardner, K.H., Atkinson, J.F., and Van Benschoten, J.E. (2003) Changes in fractal dimension during aggregation. *Water Research*, **37**, 873–883.

Chang, Y.-T., Lee, J.-F., Liu, K.-H., Liao, Y.-F., and Yang, V. (2015) Immobilization of fungal laccase onto a nonionic surfactant-modified clay material: application to PAH degradation. *Environmental Science and Pollution Research*, **23**, 4024–4035.

Chefetz, B., Mualem, T., and Ben-Ari, J. (2008) Sorption and mobility of pharmaceutical compounds in soil irrigated with reclaimed wastewater. *Chemosphere*, **73**, 1335–1343.

Chen, D., Du, G., Zhu, Q., and Zhou, F. (2013) Synthesis and characterization of TiO_2 pillared montmorillonites: Application for methylene blue degradation. *Journal of Colloid and Interface Science*, **409**, 151–157.

Chen, L.-F., Liang, H.-W., Lu, Y., Cui, C.-H., and Yu, S.-H. (2011) Synthesis of an attapulgite Clay@Carbon nanocomposite adsorbent by a hydrothermal carbonization process and their application in the removal of toxic metal ions from water. *Langmuir*, **27**, 8998–9004.

Choi, C.S. and Yun, T. Il. (2002) *Rapid coagulation-flocculation and sedimentation type waste water treatment method*. US Patent Grant US6447686B1, Google Patents.

Chong, M.N., Jin, B., Chow, C.W.K., and Saint, C. (2010) Recent developments in photocatalytic water treatment technology: A review. *Water Research*, **44**, 2997–3027.

Churchman, G.J., Gates, W.P., Theng, B.K.G., and Yuan, G. (2006) Clays and clay minerals for pollution control. Pp. 625–675 in: *Handbook of Clay Science* (F. Bergaya, B.K.G. Theng, and G. Lagaly, editors). Developments in Clay Science, Elsevier, Amsterdam.

Di Credico, B., Bellobono, I.R., D'Arienzo, M., Fumagalli, D., Redaelli, M., Scotti, R., and Morazzoni, F. (2015) Efficacy of the reactive oxygen species generated by immobilized TiO_2 in the photocatalytic degradation of diclofenac. *International Journal of Photoenergy*, **2015**, 1–13.

Cuevas, J., Leguey, S., and Ruiz, A.I. (2011) Evidence for the biogenic origin of sepiolite. Pp. 219–238 in: *Developments in Palygorskite-Sepiolite Research* (E. Gálan and A. Singer, editors). Developments in Clay Science, **3**, Elsevier, Amsterdam.

Derosa, M.C. and Crutchley, R.J. (2002) Photosensitized singlet oxygen and its applications. *Coordination Chemistry Reviews*, **234**, 351–371.

Drozd, D., Szczubiałka, K., Skiba, M., Kepczynski, M., and Nowakowska, M. (2014) Porphyrin–nanoclay photosensitizers for visible light induced oxidation of phenol in aqueous media. *The Journal of Physical Chemistry C*, **118**, 9196–9202.

Ebele, A.J., Abou-Elwafa Abdallah, M., and Harrad, S. (2017) Pharmaceuticals and personal care products (PPCPs) in the freshwater aquatic environment. *Emerging Contaminants*, **3**, 1–16.

Edzwald, J.K. and Haarhoff, J. (2011) Seawater pretreatment for reverse osmosis: Chemistry, contaminants, and coagulation. *Water Research*, **45**, 5428–5440.

El-Shahawi, M.S., Hamza, A., Bashammakh, A.S., and Al-Saggaf, W.T. (2010) An overview on the accumulation, distribution, transformations, toxicity and analytical methods for the monitoring of persistent organic pollutants. *Talanta*, **80**, 1587–1597.

ERD (2011) Water, energy and land... a radical rethink. *European Report on Development*. https://ec.europa.eu/europeaid/sites/devco/files/erd-consca-we-a-radical-rethink-20110101_en.pdf.

EU Environment Directorate General (2016) Drinking Water Directive – Environment – European Commission. <http://ec.europa.eu/environment/water/water-drink/legislation_en.html>.

European Parliament and Council (2013) *DIRECTIVE 2013/39/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy*. 17 pp. (https://eur-lex.europa.eu/legal-content/en/ALL/?uri=CELEX%3A32013L0039).

Exbrayat, J.-M., Moudilou, E.N., and Lapied, E. (2015) Harmful effects of nanoparticles on animals. *Journal of Nanotechnology*, **2015**, 1–10.

Ezzatahmadi, N., Ayoko, G.A., Millar, G.J., Speight, R., Yan, C., Li, J., Li, S., Zhu, J., and Xi, Y. (2017) Clay-supported nanoscale zero-valent iron composite materials for the remediation of contaminated aqueous solutions: A review. *Chemical Engineering Journal*, **312**, 336–350.

Fan, Y., Ma, W., Han, D., Gan, S., Dong, X., and Niu, L. (2015) Convenient recycling of 3D AgX/graphene aerogels (X = Br, Cl) for efficient photocatalytic degradation of water pollutants. *Advanced Materials*, **27**, 3767–73.

Farrah, H. and Pickering, W.F. (1979) pH effects in the adsorption of heavy metal ions by clays. *Chemical Geology*, **25**, 317–326.

Fawell, J.K. (1993) The impact of inorganic chemicals on water quality and health. *Annali dell'Istituto Superiore di Sanita*, **29**, 293–303.

Ganigar, R., Rytwo, G., Gonen, Y., Radian, A., and Mishael, Y.G. (2010) Polymer-clay nanocomposites for the removal of trichlorophenol and trinitrophenol from water. *Applied Clay Science*, **49**, 311–316.

Geldreich, E.E. (2005) Better intervention strategies are needed to reduce the risk of waterborne outbreaks. *Journal of Water and Health*, **3**, 197–208.

Goh, K.-H., Lim, T.-T., and Dong, Z. (2008) Application of layered double hydroxides for removal of oxyanions: A review. *Water Research*, **42**, 1343–1368.

Gonen, Y. and Rytwo, G. (2006) Using the dual-mode model to describe adsorption of organic pollutants onto an organoclay. *Journal of Colloid and Interface Science*, **299**, 95–101.

Grassi, M., Kaykioglu, G., Belgiorno, V., and Lofrano, G. (2012) *Removal of Emerging Contaminants from Water and Wastewater by Adsorption Process*, pp. 15–37, Springer, Berlin.

Grossberger, A., Hadar, Y., Borch, T., and Chefetz, B. (2014) Biodegradability of pharmaceutical compounds in agricultural soils irrigated with treated wastewater. *Environmental Pollution*, **185**, 168–177.

Growing Blue (2013) U.S. Water Infrastructure and Debt | Water Cost Increasing. http://www.digitaljournal.com/pr/1523282.

Han, Y.-S., Lee, S.-H., Choi, K.H., and Park, I. (2010) Preparation and characterization of chitosan–clay nanocomposites with antimicrobial activity. *Journal of Physics and Chemistry of Solids*, **71**, 464–467.

Hashimoto, K., Irie, H., and Fujishima, A. (2005) TiO_2 photocatalysis: A historical overview and future prospects. *Japanese Journal of Applied Physics*, **44**, 8269–8285.

Herney-Ramirez, J., Vicente, M.A., and Madeira, L.M. (2010) Heterogeneous photo-Fenton oxidation with pillared clay-based catalysts for wastewater treatment: A review. *Applied Catalysis B: Environmental*, **98**, 10–26.

Herrmann, J.-M. (1999) Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants. *Catalysis Today*, **53**, 115–129.

Hlavinek, P., Bonacci, O., Marsalek, J., and Mahrikova, I., editors (2008) *Dangerous Pollutants (Xenobiotics) in Urban*

https://doi.org/10.1346/CCMN.2018.064114 Published online by Cambridge University Press

Water Cycle. 343 pp., Springer, Berlin.
Irawaty, W., Soetaredjo, F.E., and Ayucitra, A. (2014) Understanding the relationship between organic structure and mineralization rate of TiO_2-mediated photocatalysis. *Procedia Chemistry*, **9**, 131–138.
Ismadji, S., Soetaredjo, F.E., and Ayucitra, A. (2015) Natural clay minerals as environmental cleaning agents. Pp. 5–37 in: *Clay Materials for Environmental Remediation* (S. Ismadji, F. Edi Soetaredjo, and A. Ayucitra, editors). Springer, Berlin.
Iurascu, B., Siminiceanu, I., Vione, D., Vicente, M.A., and Gil, A. (2009) Phenol degradation in water through a heterogeneous photo-Fenton process catalyzed by Fe-treated Laponite. *Water Research*, **43**, 1313–1322.
Jimenez, C.Á. (2015) *Cómo es el avance en la cobertura de acueducto en Colombia? ELTIEMPO.COM*. <http://www.eltiempo.com/colombia/otras-ciudades/agua-potable-en-colombia-/15445939> (accessed 29 July 2015) (in Spanish).
Jin, S., Fallgren, P.H., Morris, J.M., and Chen, Q. (2007) Removal of bacteria and viruses from waters using layered double hydroxide nanocomposites. *Science and Technology of Advanced Materials*, **8**, 67–70.
Jucker, B.A., Harms, H., and Zehnder, A.J. (1996) Adhesion of the positively charged bacterium Stenotrophomonas (Xanthomonas) maltophilia 70401 to glass and Teflon. *Journal of Bacteriology*, **178**, 5472–5479.
Kalfa, A., Rakovitsky, N., Tavassi, M., Ryskin, M., Ben-Ari, J., Etkin, H., Shuali, U., and Nir, S. (2017) Removal of Escherichia coli and total bacteria from water by granulated micelle-clay complexes: Filter regeneration and modeling of filtration kinetics. *Applied Clay Science*, **147**, 63–68.
Koh, S.-M. and Dixon, J.B. (2001) Preparation and application of organo-minerals as sorbents of phenol, benzene and toluene. *Applied Clay Science*, **18**, 111–122.
König, T.N. (2011) Clays and organoclays for the removal of humic acid from water. Doctoral thesis, Tel Hai College, Isral.
Li, W., Zuo, P., Xu, D., Xu, Y., Wang, K., Bai, Y., and Ma, H. (2017) Tunable adsorption properties of bentonite/carboxymethyl cellulose-g-poly(2-(dimethylamino) ethyl methacrylate) composites toward anionic dyes. *Chemical Engineering Research and Design*, **124**, 260–270.
Li, X., Zhao, Y., Xi, B., Mao, X., Gong, B., Li, R., Peng, X., and Liu, H. (2016) Removal of nitrobenzene by immobilized nanoscale zero-valent iron: Effect of clay support and efficiency optimization. *Applied Surface Science*, **370**, 260–269.
Li, X.Q., Elliott, D.W., and Zhang, W.X. (2006) Zero-valent iron nanoparticles for abatement of environmental pollutants: Materials and engineering aspects. *Critical Reviews in Solid State and Materials Sciences*, **31**, 111–122.
Litaor, M.I.I., Meir-Dinar, N., Castro, B., Azaizeh, H., Rytwo, G., Levi, N., Levi, M., and MarChaim, U. (2015) Treatment of winery wastewater with aerated cells mobile system. *Environmental Nanotechnology, Monitoring & Management*, **4**, 17–26.
Lukman, S., Essa, M.H., D. Mu'azu, N., Bukhari, A., and Basheer, C. (2013) Adsorption and desorption of heavy metals onto natural clay material: Influence of initial pH. *Journal of Environmental Science and Technology*, **6**, 1–15.
Masaphy, S., Zohar, S., and Jander-Shagug, G. (2014) Biodegradation of p-nitrophenol sorbed onto crystal violet-modified organoclay by Arthrobacter sp. 4Hβ. *Applied Microbiology and Biotechnology*, **98**, 1321–1327.
Mazille, F. and Spuhler, D. (2012) Coagulation-Flocculation. *The SSWM Toolbox. Basel: seecon international GmBh.* <http://www.sswm.info/content/coagulation-flocculation> (Accessed 22 March 2016).
Miyamoto, N., Kawai, R., Kuroda, K., and Ogawa, M. (2000) Adsorption and aggregation of a cationic cyanine dye on layered clay minerals. *Applied Clay Science*, **16**, 161–170.
Mohan, D. and Pittman Jr., C.U. (2007) Arsenic removal from water/wastewater using adsorbents – A critical review. *Journal of Hazardous Materials*, **142**, 1–53.
Monser, L. and Adhoum, N. (2002) Modified activated carbon for the removal of copper, zinc, chromium and cyanide from wastewater. *Separation and Purification Technology*, **26**, 137–146.
Mortland, M.M. (1986) Clay–organic complexes as adsorbents for phenol and chlorophenols1. *Clays and Clay Minerals*, **34**, 581–585.
Nafees, M. and Waseem, A. (2014) Organoclays as sorbent material for phenolic compounds: A review. *CLEAN – Soil, Air, Water*, **42**, 1500–1508.
National Research Council (1997) Comparing costs of remediation technologies. P. 310 in: *Innovations in Ground Water and Soil Cleanup*. National Academies Press, Washington, D.C.
Ning, F., Shao, M., Xu, S., Fu, Y., Zhang, R., Wei, M., Evans, D.G., and Duan, X. (2016) TiO_2/graphene/NiFe-layered double hydroxide nanorod array photoanodes for efficient photoelectrochemical water splitting. *Energy & Environmental Science*, **9**, 2633–2643.
Nir, S. and Ryskin, M. (2016) Method of production of granulated micelle-clay complexes: application for removal of organic, inorganic anionic pollutants and microorganisms from contaminated water. US 2016-0002068, US.
Ogawa, M., Sohmiya, M., and Watase, Y. (2011) Stabilization of photosensitizing dyes by complexation with clay. *Chemical Communications*, **47**, 8602–8604.
Olshansky, Y., Masaphy, S., Root, R.A., and Rytwo, G. (2018) Immobilization of Rhus vernicifera laccase on sepiolite; effect of chitosan and copper modification on laccase adsorption and activity. *Applied Clay Science*, **152**, 143–147.
Palmero, P. (2015) Structural ceramic nanocomposites: A review of properties and powders' synthesis methods. *Nanomaterials*, **5**, 656–696.
Paltiel, O., Fedorova, G., Tadmor, G., Kleinstern, G., Maor, Y., and Chefetz, B. (2016) Human exposure to wastewater-derived pharmaceuticals in fresh produce: A randomized controlled trial focusing on carbamazepine. *Environmental Science & Technology*, **50**, 4476–4482.
Petala, E., Dimos, K., Douvalis, A., Bakas, T., Tucek, J., Zbořil, R., and Karakassides, M.A. (2013) Nanoscale zero-valent iron supported on mesoporous silica: Characterization and reactivity for Cr(VI) removal from aqueous solution. *Journal of Hazardous Materials*, **261**, 295–306. Elsevier.
Pfeifer, P. (1984) Fractal dimension as working tool for surface-roughness problems. *Applications of Surface Science*, **18**, 146–164.
Pozzo, R.L., Giombi, J.L., Baltanás, M.A., and Cassano, A.E. (2000) The performance in a fluidized bed reactor of photocatalysts immobilized onto inert supports. *Catalysis Today*, **62**, 175–187.
Qin, C., Chen, C., Shang, C., and Xia, K. (2018) Fe^{3+}-saturated montmorillonite effectively deactivates bacteria in wastewater. *Science of The Total Environment*, **622–623**, 88–95.
Radian, A., Carmeli, M., Zadaka-Amir, D., Nir, S., Wakshal, E., and Mishael, Y.G. (2011) Enhanced removal of humic acid from water by micelle-montmorillonite composites: Comparison to granulated activated carbon. *Applied Clay Science*, **54**, 258–263.
Rajamanickam, D. and Shanthi, M. (2012) Photocatalytic degradation of an organic pollutant by zinc oxide – solar process. *Arabian Journal of Chemistry*, **9** (supplement 2),

https://doi.org/10.1346/CCMN.2018.064114 Published online by Cambridge University Press

S1858–S1868.
Ramirez, J.H., Costa, C.A., Madeira, L.M., Mata, G., Vicente, M.A., Rojas-Cervantes, M.L., López-Peinado, A.J., and Martín-Aranda, R.M. (2007) Fenton-like oxidation of Orange II solutions using heterogeneous catalysts based on saponite clay. *Applied Catalysis B: Environmental*, **71**, 44–56.
right2water (2015) Water campaign | Water and sanitation are a human right! <http://www.right2water.eu/>.
Ruiz-Hitzky, E. (2001) Molecular access to intracrystalline tunnels of sepiolite. *Journal of Materials Chemistry*, **11**, 86–91.
Ruiz-Hitzky, E., Aranda, P., Darder, M., and Rytwo, G. (2010) Hybrid materials based on clays for environmental and biomedical applications. *Journal of Materials Chemistry*, **20**, 9306–9321.
Rytwo, G. (2004) Applying a Gouy-Chapman-Stern model for adsorption of organic cations to soils. *Applied Clay Science*, **24**, 137–147.
Rytwo, G. (2012) The use of clay-polymer nanocomposites in wastewater pretreatment. *The Scientific World Journal*, **2012**, 1–7.
Rytwo, G. (2015) A continuous-flow device for photocatalytic degradation and full mineralization of priority pollutants in water. *American Chemical Society National Meeting & Exposition*, **57**, 16424–16434.
Rytwo, G. (2016) Methods for Production of Potable Water. PCT/IL2016/050700, WO2017158581 A1.
Rytwo, G. (2017a) Hybrid Clay-Polymer Nanocomposites for the Clarification of Water and Effluents. *Recent Patents on Nanotechnology*, **11**, 181–193.
Rytwo, G. (2017b) Method for pretreatment of wastewater and recreational water with nanocomposites. USPTO US9546102.
Rytwo, G. and Daskal, G. (2016) A system for treatment of polluted effluents. PCT/IL2015/050944, WO2016042558 A1.
Rytwo, G. and Gonen, Y. (2006) Very fast sorbent for organic dyes and pollutants. *Colloid & Polymer Science*, **284**, 817–820.
Rytwo, G. and Margalit, S. (2014) A worksheet based model for adsorption of pollutants on sorbents with multiple sites and sorption mechanisms. *International Journal of Science and Research*, **3**, paper ID OCT1445.
Rytwo, G., Nir, S., Margulies, L., Casal, B., Merino, J., Ruiz-Hitzky, E., and Serratosa, J.M. (1998) Adsorption of monovalent organic cations on sepiolite; experimental results and model calculations. *Clays and Clay Minerals*, **46**, 340–348.
Rytwo, G., Kohavi, Y., Botnick, I., and Gonen, Y. (2007) Use of CV- and TPP-montmorillonite for the removal of priority pollutants from water. *Applied Clay Science*, **36**, 182–190.
Rytwo, G., Lavi, R., Rytwo, Y., Monchase, H., Dultz, S., and König, T.N. (2013) Clarification of olive mill and winery wastewater by means of clay-polymer nanocomposites. *Science of the Total Environment*, **442**, 134–142.
Rytwo, G., Lavi, R., König, T.N., and Avidan, L. (2014) Direct relationship between electrokinetic surface-charge measurement of effluents and coagulant type and dose. *Colloids and Interface Science Communications*, **1**, 27–30.
Rytwo, G., Klein, T., Margalit, S., Mor, O., Naftaly, A., and Daskal, G. (2015) A continuous-flow device for photocatalytic degradation and full mineralization of priority pollutants in water. *Desalination and Water Treatment*, **57**, 16424–16434.
Rytwo, G., Chorsheed, L.L., Avidan, L., and Lavi, R. (2016) Three unusual techniques for the analysis of surface modification of clays and nanocomposites. Pp.73–86 in: *Surface Modification of Clays and Nanocomposites* (G. Beall, editor). CMS Workshop Lectures Series, **20**, The Clay Minerals Society, Chantilly, Virginia, USA.
Salvador, F., Martin-Sanchez, N., Sanchez-Hernandez, R., Sanchez-Montero, M.J., and Izquierdo, C. (2015a) Regeneration of carbonaceous adsorbents. Part I: Thermal Regeneration. *Microporous and Mesoporous Materials*, **202**, 259–276.
Salvador, F., Martin-Sanchez, N., Sanchez-Hernandez, R., Sanchez-Montero, M.J., and Izquierdo, C. (2015b) Regeneration of carbonaceous adsorbents. Part II: Chemical, Microbiological and Vacuum Regeneration. *Microporous and Mesoporous Materials*, **202**, 277–296.
Sarkar, B., Xi, Y., Megharaj, M., Krishnamurti, G.S.R., and Naidu, R. (2010) Synthesis and characterisation of novel organopalygorskites for removal of p-nitrophenol from aqueous solution: Isothermal studies. *Journal of Colloid and Interface Science*, **350**, 295–304.
Sarkar, B., Xi, Y., Megharaj, M., Krishnamurti, G.S.R., Bowman, M., Rose, H., and Naidu, R. (2012) Bioreactive organoclay: A new technology for environmental remediation. *Critical Reviews in Environmental Science and Technology*, **42**, 435–488.
Schneider, J., Matsuoka, M., Takeuchi, M., Zhang, J., Horiuchi, Y., Anpo, M., and Bahnemann, D.W. (2014) Understanding TiO_2 photocatalysis: Mechanisms and materials. *Chemical Reviews*, **114**, 140919080959008.
Scotti, R., Conzatti, L., D'Arienzo, M., Di Credico, B., Giannini, L., Hanel, T., Stagnaro, P., Susanna, A., Tadiello, L., and Morazzoni, F. (2014) Shape controlled spherical (0D) and rod-like (1D) silica nanoparticles in silica/styrene butadiene rubber nanocomposites: Role of the particle morphology on the filler reinforcing effect. *Polymer*, **55**, 1497–1506.
Semiat, R. (2000) Present and future. *Water International*, **25**, 54–65.
Shen, Y.-H. (2004) Phenol sorption by organoclays having different charge characteristics. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **232**, 143–149.
Sheng, G., Johnston, C.T., Teppen, B.J., and Boyd, S.A. (2001) Potential contributions of smectite clays and organic matter to pesticide retention in soils. *Journal of Agricultural and Food Chemistry*, **49**, 2899–2907.
Shenker, M., Harush, D., Ben-Ari, J., and Chefetz, B. (2011) Uptake of carbamazepine by cucumber plants – a case study related to irrigation with reclaimed wastewater. *Chemosphere*, **82**, 905–10.
Shtarker-Sasi, A., Castro-Sowinski, S., Matan, O., Kagan, T., Nir, S., Okon, Y., and Nasser, A.M. (2013) Removal of bacteria and cryptosporidium from water by micelle–montmorillonite complexes. *Desalination and Water Treatment*, **51**, 7672–7680.
Stöter, M., Biersack, B., Reimer, N., Herling, M., Stock, N., Schobert, R., and Breu, J. (2014) Ordered heterostructures of two strictly alternating types of nanoreactors. *Chemistry of Materials*, **26**, 5412–5419.
Stöter, M., Biersack, B., Rosenfeldt, S., Leitl, M.J., Kalo, H., Schobert, R., Yersin, H., Ozin, G.A., Förster, S., and Breu, J. (2015) Encapsulation of functional organic compounds in nanoglass for optically anisotropic coatings. *Angewandte Chemie (International ed. in English)*, **54**, 4963–4967.
Sui, Q., Cao, X., Lu, S., Zhao, W., Qiu, Z., and Yu, G. (2015) Occurrence, sources and fate of pharmaceuticals and personal care products in the groundwater: A review. *Emerging Contaminants*, **1**, 14–24.
Sutzkover-Gutman, I. and Hasson, D. (2010) Feed water pretreatment for desalination plants. *Desalination*, **264**, 289–296.
Suwal, S. (2015) Water In Crisis – Spotlight Nepal. *The Water Project*. <http://thewaterproject.org/water-in-crisis-nepal>

https://doi.org/10.1346/CCMN.2018.064114 Published online by Cambridge University Press

(accessed 30 July 2015).
Tang, P. and Raper, J. (2002) Modelling the settling behaviour of fractal aggregates – A review. *Powder Technology*, **123**, 114–125.
Tang, P., Greenwood, J., and Raper, J.A. (2002) A model to describe the settling behavior of fractal aggregates. *Journal of Colloid and Interface Science*, **247**, 210–219.
Theng, B.K.G., Churchman, G.J., Gates, W.P., and Yuan, G. (2008) Organically modified clays for pollutant uptake and environmental protection. Pp. 145–174 in: *Soil Mineral Microbe–Organic Interactions*. Springer, Berlin-Heidelberg.
Thomas, D.N.N., Judd, S.J.J., and Fawcett, N. (1999) Flocculation modelling: a review. *Water Research*, **33**, 1579–1592.
Uddin, M.K. (2017) A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade. *Chemical Engineering Journal*, **308**, 438–462.
UN World Water Development Report (2015) *Water for a Sustainable World*. http://unesdoc.unesco.org/images/0023/002318/231823E.pdf
UNESCO (2006) *Section 2: Changing Natural Systems, Chapter 4 – The State of the Resource, Part 4: Matching Demands to Supply, p.146*. 119–157 pp. https://www.mendeley.com/research-papers/section-2-changing-natural-systems-chapter-4-state-resource-part-4-matching-demands-supply-p146/?utm_source=desktop&utm_medium=1.19.2&utm_campaign=open_catalog&userDocumentId=%7B5d525714-fb15-4208-a384-b2166a75fac8%7D.
UNESCO (2012) Increasing demand and climate change threatening world water resources says new UN World Water Development Report | United Nations Educational, Scientific and Cultural Organization. *UNESCO Press Service*. https://news.un.org/en/story/2012/03/406062-increasing-demand-and-climate-change-threaten-global-water-supplies-un-report (accessed 16 August 2016).
Unuabonah, E.I. and Taubert, A. (2014) Clay–polymer nanocomposites (CPNs): Adsorbents of the future for water treatment. *Applied Clay Science*, **99**, 83–92.
Unuabonah, E.I., Günter, C., Weber, J., Lubahn, S., and Taubert, A. (2013) Hybrid Clay: A New Highly Efficient Adsorbent for Water Treatment. *ACS Sustainable Chemistry & Engineering*, **1**, 966–973.
Unuabonah, E.I., Adewuyi, A., Kolawole, M.O., Omorogie, M.O., Olatunde, O.C., Fayemi, S.O., Günter, C., Okoli, C.P., Agunbiade, F.O., and Taubert, A. (2017) Disinfection of water with new chitosan-modified hybrid clay composite adsorbent. *Heliyon*, **3**, e00379.
Unuabonah, E.I., Ugwuja, C.G., Omorogie, M.O., Adewuyi, A., and Oladoja, N.A. (2018) Clays for efficient disinfection of bacteria in water. *Applied Clay Science*, **151**, 211–223.
USACE. (2001) Engineering and Design ADSORPTION DESIGN GUIDE DG. P. in: Design Guide 1110-1-2. US Army Corps of Engineers. http://www.dtic.mil/dtic/tr/fulltext/u2/a403095.pdf
Uyguner, C.S. and Bekbolet, M. (2009) Application of photocatalysis for the removal of natural organic matter in simulated surface and ground waters. *Journal of Advanced Oxidation Technologies*, **12**, 87–92.
Vahedi, A. and Gorczyca, B. (2010) Application of fractal dimensions to study the structure of flocs formed in lime softening process. *Water Research*, **45**, 545–556.
Vahedi, A. and Gorczyca, B. (2012) Predicting the settling velocity of flocs formed in water treatment using multiple fractal dimensions. *Water Research*, **46**, 4188–4194.
Voutchkov, N. (2010) Considerations for selection of seawater filtration pretreatment system. *Desalination*, **261**, 354–364.
Wang, H., Wang, N., Wang, B., Zhao, Q., Fang, H., Fu, C., Tang, C., Jiang, F., Zhou, Y., Chen, Y., and Jiang, Q. (2016) Antibiotics in drinking water in Shanghai and their contribution to antibiotic exposure of school children. *Environmental Science & Technology*, **50**, 2692–2699.
Wang, L.K. and Shammas, N.K. (2007) Pressurized ozonation. Pp. 1–55 in: *Advanced Physicochemical Treatment Technologies*. Humana Press, Totowa, New Jersey, USA.
Wang, L.K., Chen, J.P., and Ziegler, R.C. (2007) Irradiation. Pp. 107–134 in: *Advanced Physicochemical Treatment Technologies*. Humana Press, Totowa, New Jersey, USA.
Weiner, E.R. (2008) *Applications of Environmental Aquatic Chemistry: A Practical Guide*. CRC Press, Boca Raton, Florida, USA, 436 pp.
Werner, J.J., McNeill, K., and Arnold, W.A. (2009) Photolysis of chlortetracycline on a clay surface. *Journal of Agricultural and Food Chemistry*, **57**, 6932–6937.
World Health Organization (2011) *Pharmaceuticals in Drinking-water*. Information Sheet WHO, Generva, Switzerland (http://www.who.int/water_sanitation_health/diseases-risks/risks/info_sheet_pharmaceuticals/en/).
Xu, S. and Boyd, S.A. (1994) Cation exchange chemistry of hexadecyltrimethylammonium in a subsoil containing vermiculite. *Soil Science Society of America Journal*, **58**, 1382–1391.
Xu, S., Lu, H., Chen, L., and Wang, X. (2014) Molecularly imprinted TiO_2 hybridized magnetic Fe_3O_4 nanoparticles for selective photocatalytic degradation and removal of estrone. *RSC Advances*, **4**, 45266–45274.
Yates, M., Martín-Luengo, M.A., Argomaniz, L.V., and Velasco, S.N. (2012) Design of activated carbon–clay composites for effluent decontamination. *Microporous and Mesoporous Materials*, **154**, 87–92.
Yuan, G. (2004) Natural and modified nanomaterials as sorbents of environmental contaminants. *Journal of Environmental Science and Health, Part A*, **39**, 2661–2670.
Yuan, G.D., Theng, B.K.G., Churchman, G.J., Gates, W.P., Theng, B.K.G., and Yuan, G.D. (2013) Clays and clay minerals for pollution control. Pp. 587–644 in: *Handbook of Clay Science* (F. Bergaya and G. Lagaly, editors). Developments in Clay Science, Elsevier, Amsterdam.
Zadaka, D., Mishael, Y.G., Polubesova, T., Serban, C., and Nir, S. (2007) Modified silicates and porous glass as adsorbents for removal of organic pollutants from water and comparison with activated carbons. *Applied Clay Science*, **36**, 174–181.
Zhao, H. and Vance, G.F. (1998) Sorption of trichloroethylene by organo-clays in the presence of humic substances. *Water Research*, **32**, 3710–3716.
Zhu, K., Jia, H., Wang, F., Zhu, Y., Wang, C., and Ma, C. (2017) Efficient removal of Pb(II) from aqueous solution by modified montmorillonite/carbon composite: Equilibrium, kinetics, and thermodynamics. *Journal of Chemical & Engineering Data*, **62**, 333–340.
Zhu, L., Chen, B., and Shen, X. (2000) Sorption of phenol, p-nitrophenol, and aniline to dual-cation organobentonites from water. *Environmental Science & Technology*, **34**, 468–475.
Zhu, R., Zhu, J., Ge, F., and Yuan, P. (2009) Regeneration of spent organoclays after the sorption of organic pollutants: A review. *Journal of Environmental Management*, **90**, 3212–3216
Zia, A. (2013) "80% of diseases are waterborne". *The Express Tribune*. Pakistan.

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