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Raw and modified clays and clay minerals for the removal of pharmaceutical products from aqueous solutions: state of the art and future perspectives

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Abstract

The occurrence of pharmaceutical products (PPs) within environmental compartments challenges the scientific community and water treatment operators to find suitable and practicable removal solutions. Clay minerals are among the oldest and cheapest adsorbents used for the removal of organic and inorganic pollutants. However, despite their significant adsorption properties, little is known about their potential to remove organic contaminants such as pharmaceutical products from wastewater effluents. Hence, based on the latest published articles this review aims to standardize the adsorption properties of clay minerals for the removal of PPs. Specifically, the charge state of PPs appears to play a key role in their adsorption mechanism. In order to overcome the limitations of batch experiments (i.e. idealized solutions, static conditions) and design of a field solution, the impact of external parameters on the adsorption capacities of clay minerals is reviewed. The effect of thermal treatment and acid activation of clay minerals is also assessed in order to better understand the consequences of such modifications on the adsorption properties of clay-based adsorbents. Finally, even if most authors agree on the potential of clay-based adsorbents for the removal of PPs from wastewater, there remain significant gaps in the existing literature that need to be filled, with the aim of forecasting the real potential of clay-based treatment for the removal of pharmaceutical products at industrial scale.

Keywords: Pharmaceutical Products, Clay minerals, Adsorption, Ion exchange, Water treatment, Thermal treatment

Introduction

The extensive use of pharmaceutical products (PPs) since the 1960s significantly increased their occurrence within various environmental compartments such as wastewaters (Halling-Sørensen et al., 1998; Hignite & Azarnoff, 1977; Ternes, 1998), river waters (Burns, Carter, Kolpin, Thomas-Oates, & Boxall, 2018; Loos et al., 2009), sediments (Kerrigan, Sandberg, Engstrom, LaPara, & Arnold, 2018; Thiebault, Chassiot, et al., 2017) and seawaters (Björlenius et al., 2018; Gaw, Thomas, & Hutchinson, 2014). PPs belong to the class of emerging contaminants as they may impact the health of living beings, including humans, even if their precise toxicological effect remains poorly recognized (Arnold, Brown, Ankley, & Sumpter, 2014; Carlsson, Johansson, Alvan, Bergman, & Kühler, 2006; Fent, Weston, & Caminada, 2006; Richmond et al., 2018). However, several disorders have already been observed among fauna such as fish or bacteria at field-relevant concentrations or in real solutions (Brodin, Fick, Jonsson, & Klaminder, 2013; de Jongh, Kooij, de Voogt, & ter Laak, 2012; Godoy & Kummrow, 2017; Guo, Boxall, & Selby, 2015; Saaristo et al., 2018). Contamination by PPs is distinctive in that it is mostly generated by people themselves, *via* the consumption/excretion of PPs (Baker, Barron, & Kasprzyk-Hordern, 2014; Choi et al., 2018; H. E. Jones et al., 2014). The excretion of a significant proportion of consumed PPs in maternal, conjugated or degraded forms causes the transfer of this contamination toward waste-water treatment plants (Coutu, Wyrsch, Wynn, Rossi, & Barry, 2013; Gerrity, Trenholm, & Snyder, 2011; Thiebault, Fougère, Destandau, Réty, & Jacob, 2017). However, these installations are currently inefficient to completely remove PPs, whatever the treatment chain used (Alvarino, Lema, Omil, & Suárez, 2018; Thiebault, Boussafir, & Le Milbeau, 2017; Verlicchi, Al Aukidy, & Zambello, 2012; Verlicchi et al., 2013). PPs continue to be present in wastewater effluents, therefore, and

their transfer within aquatic environments can lead them to enter drinking water intended for human consumption (Bruce, Pleus, & Snyder, 2010; de Jongh et al., 2012; O. A. Jones, Lester, & Voulvoulis, 2005) or to contaminate agricultural soils following spreading of sewage sludge (Hospido et al., 2010; Ivanová et al., 2018; Siemens et al., 2010). Several tertiary treatments have been proposed to improve the removal of PPs from wastewater, in particular adsorption onto activated carbons which present the advantage of a high specific surface area and a good porosity (Guillossou et al., 2019; Mailler et al., 2015; Wong, Ngadi, Inuwa, & Hassan, 2018; Zietzschmann, Altmann, Hannemann, & Jekel, 2015). Some other treatments such as ozonation or biodegradation have demonstrated their potential (Ibáñez et al., 2013; Klavarioti, Mantzavinos, & Kassinos, 2009; Lee & von Gunten, 2016; Rosal et al., 2010). However, the high energy requirement and/or high management costs of these processes can make them too expensive for a field application (Ali, Asim, & Khan, 2012; Grandclément et al., 2017). Hence, the most promising way to reduce the contamination of environmental compartments by PPs would be to limit drug prescriptions (Daughton, 2014; Kümmerer, Dionysiou, Olsson, & Fatta-Kassinos, 2018). Such a restriction appears to be very speculative, however, in view of the current increase in the consumption of PPs worldwide (Van Boeckel et al., 2014; Williams, Gabe, & Davis, 2008).

Novel removal techniques therefore remain necessary and are framed by several constraints: firstly, the cost, which is relatively high as waste-water effluents are not economically valuable and the management of the advanced solution may be costly (e.g. their durability and regeneration). Among these advanced treatment techniques, adsorption appears to be a promising solution due to its moderate cost provided that the material used is cheap and relatively unmodified (Crini, Lichtfouse, Wilson, & Morin-

Crini, 2019; de Andrade, Oliveira, da Silva, & Vieira, 2018; N. Jiang, Shang, Heijman, & Rietveld, 2018; B. Wang et al., 2019). Moreover, the main advantage of adsorption is the retention of contaminants in maternal form (i.e. non-degraded), whereas some other techniques generate unwanted byproducts in the effluents (Andreozzi, Raffaele, & Nicklas, 2003; Cuthbertson et al., 2019; Zietzschmann, Mitchell, & Jekel, 2015).

Because of the need to use materials that are as raw as possible, several adsorbents such as zeolites, muds or agricultural wastes were envisaged (de Gisi, Lofrano, Grassi, & Notarnicola, 2016; Kyzas, Fu, Lazaridis, Bikiaris, & Matis, 2015; Quesada et al., 2019). However, these adsorbents exhibited a limited sorption capacity towards PPs in particular, and their further management cost could be prohibitive. Moreover, the literature on the adsorption capacity of these materials is not sufficient to accurately assess their potential in a field solution.

Clay minerals represent are cheap and highly-available materials, and commonly used in several applications such as PPs (as active compounds or carriers) for humans or cattle, biomedical applications, biosensors and cosmetics (Aguzzi, Cerezo, Viseras, & Caramella, 2007; Carretero, 2002; Ruiz-Hitzky, Aranda, Darder, & Rytwo, 2010; Viseras, Cerezo, Sanchez, Salcedo, & Aguzzi, 2010). The properties of clay minerals such as their high specific surface area (SSA) and cation exchange capacity (CEC) make them particularly suitable for these applications (Bergaya & Lagaly, 2013; Lambert, 2018; Theng, 1982; Uddin, 2017). Moreover, most natural clay minerals are innocuous for the environment and are even pharmaceutically graded (Ghadiri, Chrzanowski, & Rohanizadeh, 2015; López-Galindo, Viseras, & Cerezo, 2007). Their adsorption capacity was for a long time thought to be limited to cationic pollutants and thus to cationic PPs (Gao & Pedersen, 2005; Zhu et al., 2016). However, several studies recently exhibited a significant sorption capacity onto raw clay minerals for neutral and

anionic PPs at field-relevant concentrations (Bonina et al., 2007; Dordio, Carvalho, Teixeira, Dias, & Pinto, 2010; Thiebault, Boussafir, Le Forestier, et al., 2016; W. Zhang, Ding, Boyd, Teppen, & Li, 2010). The adsorption of neutral and anionic PPs was mostly tested on organo-modified clays, due to the affinity of hydrophobic moieties for organic compounds such as surfactants (de Oliveira et al., 2017; de Paiva, Morales, & Valenzuela Díaz, 2008; Guégan, 2019; Y. Park, Ayoko, & Frost, 2011). The potential of organo-clays was not assessed, however, due to significant limitations for environmental purposes (e.g. toxicity of surfactant, stability of organo-clays). Two types of modification have been proposed, acid and thermal activation. These two modifications were not initially designed for the removal of organic compounds but rather for industrial applications as catalysts or filtering media, and mostly result in stable and non-toxic adsorbents (Komadel, 2003; Pentrák, Madejová, & Komadel, 2009).

The main purpose of this review, therefore, is to provide a comprehensive survey of the literature on the adsorption properties of various types of raw and slightly modified clay minerals for various types of PPs. PPs were selected as this group of contaminants of emerging concern displays a wide chemical diversity and also problematic occurrences in several environmental compartments. The literature on PP-clay interactions can be divided in two main parts: Firstly, studies that focused on the potential of clay minerals as carriers for medical applications and second, studies that evaluated the potential of clay minerals as sorbents for the removal of PPs from wastewater effluents. Due to different objectives, each type of study explores the affinity between PPs and clay minerals under various experimental conditions such as starting concentrations, pH, solid/liquid ratio, etc. It is therefore important to note that even if some parameters are remote from wastewater treatment when studying a

medical application, they enable a deeper understanding of the affinity between PPs and clay minerals.

A second objective of this review is to assess the potential of these natural materials for application as a tertiary treatment. This involves understanding the impact of several parameters such as ionic strength, temperature, organic matter, heavy metals, etc. on the adsorption of PPs and their removal efficiency.

Methodology

Prior to writing this review, a comprehensive literature research was conducted on several databases such as Web of Science, ScienceDirect, American Chemical Society, Scopus and the Royal Society of Chemistry based on carefully selected keywords such as adsorption, clay minerals, pharmaceuticals, acid activated clays, thermally modified clays, water treatment, etc. Only peer-reviewed articles were selected (except for one post-graduate student report and one PhD thesis), but no geographical sorting was performed. Preference was given to articles published since 2010 except for highly cited research or particularly relevant articles (especially for the basic characterization of adsorbents) within the scope of this review. The references cited in the present work belong to various scientific areas, such as materials chemistry for the general description of raw and modified clays and clay minerals, and environmental chemistry for the precise evaluation of the adsorption properties of PPs. Depending on the objectives, raw data or general conclusions were extracted from the articles for standardization and comparison purposes.

Throughout the manuscript, the adsorption mechanisms onto clay minerals are divided in two types, cation exchange and physisorption. Whereas cation exchange refers to a specific process, physisorption gathers numerous processes such as cationic

bridges, n-π electron donor-acceptor, hydrophobic interactions, etc. Yet, all these latter processes are considered lower energetic and lower stable than cation exchange. The global term physisorption is therefore use for comparison purpose with cation exchange, whereas specific mechanisms could be pointed out for particular cases.

Clay minerals, basic properties and adsorption capacities of PPs in idealized solutions

Origin, structure and basic properties of clay minerals

Clay minerals are the products of rock weathering or hypothermal action and are therefore common minerals on Earth (Meunier, 2006). They belong to the phyllosilicate group of minerals, and exhibit a wide variety depending on several factors. Clay minerals are basically formed of at least one tetrahedral sheet (T) and one octahedral sheet (O), ideally continuous. Both of them are composed of a cation coordinated with 4 and 6 oxygen atoms, in the tetrahedron and octahedron respectively. Tetrahedral cations are mostly Si^{4+}, Al^{3+} and Fe^{3+}, whereas octahedral cations are mostly Al^{3+}, Fe^{3+} and Mg^{2+}. The latter are important in the classification of clay minerals: depending on the valence of these cations, the layers can be di- or trioctahedral, corresponding to the occupation of those sites, i.e. in trioctahedral clay minerals all octahedral sites are occupied by divalent cations, whereas in dioctahedral clay minerals one site of three is empty due to the trivalent octahedral cations (Bergaya & Lagaly, 2013). Finally some substitutions (e.g. Si^{4+}/Al^{3+}, Al^{3+}/Mg^{2+}) in tetrahedral and/or octahedral sheets affect the global charge equilibrium (Velde & Meunier, 2008). These substitutions create a deficit of positive charge within the layer that is filled by compensating inorganic cations naturally present within the environment (Na^{+}, Ca^{2+}, K^{+}, etc.). The number of isomorphic substitutions determines the charge of the layer, with charges ranging from

~ 0 for the kaolin group to 1 and beyond for true mica (Table 1).

The charge of the layer is an important parameter as it governs the exfoliation potential of the layers. For example, the interlayer space of high-charge clay minerals is difficult to access (even for water molecules) whereas that of low-charge clay minerals is generally easier to reach due to the weak cohesion between the layers (Figure 1). As a result, smectite are swelling clay minerals, whereas illite and vermiculite are theoretically non-swelling (Dazas et al., 2015; Hensen & Smit, 2002).

Moreover, the compensating inorganic cations have different properties (monovalent, divalent) and also various hydration capacities. For example, the hydration potential of Na^+ can be considered as infinite while K^+ allows only one water layer (Ferrage, Lanson, Michot, & Robert, 2010; Ferrage, Lanson, Sakharov, & Drits, 2005). Accordingly, this variety in the hydration potential of each cation generates a swelling potential, an important property for several clay minerals (Saidy, Smernik, Baldock, Kaiser, & Sanderman, 2013; Yu et al., 2013).

Clay minerals are therefore classified according to (i) the layer structure (i.e. 1:1 or TO, 2:1 or TOT and 2:1:1 or TOTO), (ii) the charge density of their layers generated by the isomorphic substitutions, and (iii) their octahedral character.

Table 1 summarizes the main properties of various clay types. For example, the CEC of clay minerals appears to strongly depend on the layer charge, with an increase between kaolinite and vermiculite depending on the increase in the net layer charge, and a decrease between vermiculite and illite due to the higher charge and non-swelling behavior of the latter.

The reactivity of clay minerals is also impacted by the occurrence of unsaturated bonds such as singly coordinated –OH groups, which present an amphoteric charge (Swartzen-Allen & Matijević, 1975; Tombácz & Szekeres, 2004). This type of chemical

group is very significant in kaolinites (Conley & Althoff, 1971; Schroth & Sposito, 1997), which are the only clay groups displaying –OH groups on its surface (Figure 1). Conversely, most of –OH groups in smectites and other 2:1 clay minerals are situated on clay edges (Johnston & Tombacz, 2002; Tournassat, Davis, Chiaberge, Grangeon, & Bourg, 2016). As a result, whereas most of the reactivity of kaolinites is controlled by these amphoteric charges (i.e. charge ~0), the participation of such charges in the whole reactivity of 2:1 clay minerals is less important, but remains significant (Rotenberg et al., 2007; Tertre et al., 2013).

The SSA values are decorrelated from the layer charge. The most important parameter controlling these values appears to be the organization/conformation of the layers. For example, the highest SSA values are found for disk-shaped (i.e. Laponite®) and fibrous clay minerals (i.e. palygorskite and sepiolite). Moreover, significant variations in SSA values can be found for the same clay type: SSA values for smectite range from 23 to 87 $m^2.g^{-1}$, for smectite (Table 1). These variations are generated by the strong impact of the compensating cation on the N_2 BET (Brunauer Emmett Teller) SSA measurements, and the possible structural and chemical heterogeneity of clay minerals, even within one clay type (Kaufhold, Dohrmann, Klinkenberg, Siegesmund, & Ufer, 2010; Tombácz & Szekeres, 2004). It therefore remains difficult to standardize SSA values for a specific clay type.

Adsorption capacities of PPs onto clay minerals in batch experiments

In the literature, batch experiments are conducted with two distinct objectives: (i) to determine the adsorption capacity of organic contaminants onto adsorbents, and (ii) to evaluate the adsorption performance of adsorbents with natural or slightly doped concentrations of adsorbates. These two types of experiments will be discussed jointly,

focusing on the key role of the charge state of PPs on their adsorption onto clay minerals. This section begins with positively charged (i.e. cationic and zwitterionic) PPs and then moves on to neutral and anionic PPs. As a reminder, the charge state of each PP depends on the pH value, and the investigated adsorption capacity of a specific PP onto clay minerals is therefore strongly controlled by the background acidity, as PP can be anionic, cationic, neutral and/or zwitterionic depending on the pH conditions.

Adsorption of cationic and zwitterionic PPs

As previously observed, raw clay minerals are especially renowned for their cation exchange capacities (Murray, 2000). It is therefore not surprising that most of the existing literature focuses on the adsorption of cationic PPs onto clay minerals (Ghadiri et al., 2015; Ruiz-Hitzky et al., 2010). Among the clay minerals studied, smectites are extensively used due to their swelling properties and high CEC (Meier & Kahr, 1999; Zhu et al., 2016).

Mono-molecular interactions between cationic and zwitterionic (i.e. positively charged) PPs and clay minerals have demonstrated that adsorption kinetics are fast and generally performed through a cation exchange mechanism (Table 6). This is especially evidenced by the good fit of adsorption isotherms with the Langmuir equation and the increase in the interlayer space of adsorbents after interaction (e.g. Chang et al., 2014; Hamilton, Roberts, Hutcheon, & Gaskell, 2019). Based on the literature data, the adsorption capacity of cationic and zwitterionic PPs is highly dependent on the CEC of clay minerals, emphasizing the key role of the permanent charges of the adsorbents on this saturation (Figure 2).

This is especially true of high-CEC clay minerals such as vermiculites and smectites, whose adsorption capacity of PPs is close to the CEC values (Figure 1).

However, several adsorption capacities exceed the CEC of clay minerals (Ghadiri, Chrzanowski, & Rohanizadeh, 2014; Hamilton, Hutcheon, Roberts, & Gaskell, 2014). This can be explained by several possible mechanisms. Firstly, the role of amphoteric charges can be significant especially for low CEC clay minerals (kaolinite, illite) and disk-shaped clays such as laponites (i.e. synthetic hectorite) due to their higher (or at least, significant) amount of amphoteric charges than permanent ones (Jozefaciuk & Bowanko, 2002). For laponite, this specific disk shape associated to the small particle diameter (i.e. 25 nm) maximize the number of edge-sites and the exchange capacity of edge-sites is considered to account for half the whole CEC (Negrete Herrera, Letoffe, Putaux, David, & Bourgeat-Lami, 2004). As a result, amphoteric charges on the edge-sites can play an important role in the chemisorption of PPs through edge site ligand exchange depending on the pH conditions (i.e. pH > pH_{ZNPC} for zero net proton charge; (Majzik & Tombácz, 2007; Tombácz, Libor, Illés, Majzik, & Klumpp, 2004)). Depending on the chemical structure of the PPs, electrostatic interactions between PP molecules themselves can also occur, explaining why the quantities adsorbed can exceed the CEC value (Kulshrestha, Giese, & Aga, 2004; Pei, Kong, Shan, & Wen, 2012; Thiebault, Guégan, & Boussafir, 2015). For example, the apparent adsorbed amount of metformin onto Na-Mt was 264.7 $cmol/kg^{-1}$ whereas after a water washing this apparent adsorbed amount decreased to 101.8 $cmol.kg^{-1}$ emphasizing the possible weak electrostatic interactions between PP molecules themselves or with the adsorbent (Rebitski, Aranda, Darder, Carraro, & Ruiz-Hitzky, 2018).

Conversely, the saturation adsorption capacity (i.e. ~ the CEC) of cationic and zwitterionic PPs was not reached in several studies. This can be attributed to the experimental conditions, in which the starting concentrations in the solid to liquid ratio used did not exceed the CEC. This feature is emphasized by the C_{max}/CEC ratio in

Table 2, and when this ratio is below 1, this indicates that the experimental conditions are not optimal to adsorb an amount of PPs equivalent to the CEC of clay minerals, as the starting amount of PPs was too weak. Logically, the maximum adsorbed amount remains far below the CEC values (Antón-Herrero et al., 2018; Lozano-Morales, Gardi, Nir, & Undabeytia, 2018). Conversely, several studies used starting PP amounts up to the CEC value of adsorbents. As a result, the adsorption capacity systematically reached or approached the CEC during such experiments (Table 2).

Unlike the CEC values, the SSA value appears to play a minor role in the adsorption of cationic and zwitterionic PPs onto the adsorbents reviewed here. For example, even if kaolinite and smectite present similar N_2 BET SSA values, their PP adsorption capacities are very different (Table 2). The only exception to this strong dependence on the CEC concerns laponites, due to its specific form as previously mentioned (Figure 2). Although the CEC of laponite is moderate (i.e. ~50 $cmol.kg^{-1}$), its SSA value is very high due to a very small and homogeneous particle size, unlike "natural" clay minerals (Esumi, Takeda, & Koide, 1998; Valencia, Djabourov, Carn, & Sobral, 2018).

From these results, it appears that in standardized conditions, clay minerals are particularly suitable adsorbents for cationic and zwitterionic PPs due to their permanent charges. Among them, smectites have significant adsorption capacities due to their structural properties. Even if most of these experiments are conducted with high starting concentrations (i.e. from $mg.L^{-1}$ to $g.L^{-1}$), much higher than the occurrences of PPs in anthropized and natural environments, the adsorption is generally considered as very favorable, as shown by the adsorption isotherm shapes which are generally H or S types (Limousin et al., 2007). This favorable behavior displays very weak equilibrium concentrations for the lower starting concentrations. The clay/water partition is

therefore very high, indicating that the affinity of cationic PPs for clay minerals within environmental compartments can be very significant.

However, several studies have demonstrated that the experimental setup (e.g. solid/liquid ratio) may be an important factor in the expression of the saturation. For example, whereas the adsorption capacity of venlafaxine onto bentonite is around ~70 % of the CEC of bentonite (Patel, Shah, Shah, & Joshi, 2011), another study, performed with lower starting concentrations also displayed a favorable adsorption behavior onto vermiculite but with a saturation plateau at ~2% of the CEC (Silva et al., 2018). Hence, the cation exchange extent depends on the starting concentration, the solid/liquid ratio and the compensating cation (C. Wang et al., 2009). Moreover, the conformation of adsorbed PPs is also affected by the amount of PPs adsorbed, especially in the interlayer space (Aristilde, Lanson, & Charlet, 2013; Z. Li, Chang, Jiang, & Jean, 2019; Okaikue-Woodi et al., 2018). The transition from a monolayer adsorption to a bilayer or paraffinic adsorption is for example only possible for high starting concentrations on the one hand, and for high adsorbed amounts on the other hand (McLauchlin & Thomas, 2008; Theng, 1982). As a result, even if clay minerals are suitable for the adsorption of cationic PPs, the transfer from batch experiments conducted with high starting concentrations to field experiments at environmental concentrations is not direct, and the contribution of the interlayer space to the adsorption is still debated for concentrations below 1 $mg.L^{-1}$.

Adsorption of neutral and anionic PPs

The adsorption mechanisms of non-positively charged PPs (i.e. neutral and anionic) onto clay minerals are trickier as it is impossible to speak about any theoretical adsorption capacity since adsorption is mostly performed through physisorption. The extent of physisorption depends strongly on experimental conditions such as the

solid/liquid ratio, the temperature, pH value and the properties of the selected PPs. Clay minerals bear few positively charged sites that would be appropriate sites for the adsorption of anionic PPs through anion exchange. As previously described, only the edge-sites of clay minerals (or the octrahedral sheet for 1:1 clay minerals) bear amphoteric charges that can be either protonated or deprotonated depending on the background acidity (Claverie, Garcia, Prevost, Brendlé, & Limousy, 2019). Moreover, amphoteric charges are lower in smectites and vermiculites (Bourg, Sposito, & Bourg, 2007; Tournassat, Bourg, Steefel, & Bergaya, 2015), which were proposed as powerful adsorbents for cationic and zwitterionic PPs.

In order to assess the adsorption of neutral and anionic PPs onto clay minerals, it therefore makes no sense to use the CEC of the adsorbent. Instead, the specific surface area is often used, as well as other parameters such as the solid-liquid distribution coefficient (Log K_d) or the normalized organic carbon to water partition coefficient (Log K_{oc}). The equations for the calculation of these two coefficients are:

$$Log\ K_d = Log\ (\frac{q_s}{C_{eq}}) \qquad (1)$$

$$Log\ K_{oc} = Log\ (\frac{K_d}{OC}) \qquad (2)$$

with K_d and K_{oc}, the solid-liquid distribution coefficient and normalized organic carbon to water partition coefficient respectively, q_s, C_{eq} and OC the equilibrium adsorbed amount in mmol.kg^{-1}, the equilibrium concentration in mmol.L^{-1} and the organic carbon content in % respectively.

Log K_{oc} appears to be particularly relevant to assess the adsorption of hydrophobic organic compounds due to their high affinity for organic rather than inorganic surfaces (Mader, Uwe-Goss, & Eisenreich, 1997; Stein, Ramil, Fink, Sander, & Ternes, 2008). However, the very low carbon content in clay minerals favors the use of Log K_d for the assessment of the adsorption capacity of PPs onto pure adsorbent.

Moreover, the substantial literature on the adsorption of PPs onto soils and sediments is difficult to standardize due to the strong variations between adsorbents and the lack of systematic mineralogical information (Carrasquillo, Bruland, MacKay, & Vasudevan, 2008; Droge & Goss, 2013; Kodešová et al., 2015; Martínez-Hernández, Meffe, Herrera López, & de Bustamante, 2016; Tolls, 2001). Hence, only the studies that assess the adsorption of neutral and anionic PPs onto a well-characterized adsorbent will be discussed in the present review.

In contrast to the previous section on positively charged PPs, the maximum amount of PP adsorbed onto clay minerals cannot be used to compare different studies, as the use of various starting concentrations, particularly when close to environmental concentrations, leads to the underestimation of the saturation adsorption capacity or limits our understanding of the precise affinity between neutral and anionic PPs and clay minerals. Hence, the solid/water partition will be discussed instead because it enables different studies to be compared. Traditionally, the adsorption is considered to be favorable/significant for a Log K_d value > 2.

The adsorption of neutral and anionic PPs onto clay minerals differs greatly depending on the PP investigated and the clay mineral used (Table 3). Moreover, for the same PP and a similar adsorbent, the extent of adsorption can be very different, as exhibited by the wide dispersion of Log K_d values for the adsorption of diclofenac (i.e. anionic) and carbamazepine (i.e. neutral). For the former, the Log K_d values range from 0.82 to 2.51 and for the latter from 0.84 to 3.59 (Khazri, Ghorbel-Abid, Kalfat, & Trabelsi-Ayadi, 2017; Lozano-Morales et al., 2018; Styszko, Nosek, Motak, & Bester, 2015). Systematically, the lowest Log K_d value is found with kaolinite, whereas the highest is observed with smectites or vermiculites (e.g. Behera, Oh, & Park, 2012; Styszko et al., 2015). Kaolins generally present low CEC and SSA. While the latter

appears to be a key property for the adsorption of neutral and anionic PPs, a high SSA is not the sole explanation for the significant adsorption as the adsorbed amount is not proportional to the SSA. For example, the highest SSA values are displayed by palygorskite without a significantly higher adsorbed amount of carbamazepine (Berhane, Levy, Krekeler, Danielson, & Stalcup, 2015). The fibrous shape of this clay type could increase the N_2 BET SSA values, even if the pore size is not necessarily sufficient to host the targeted PP.

Finally, for the same PP, the amount adsorbed is higher in neutral form than in anionic form, exhibiting the repulsion between adsorbate and adsorbent in the latter case (Putra, Pranowo, Sunarso, Indraswati, & Ismadji, 2009; Q. Wu, Li, & Hong, 2013). However, several authors have pointed out the role of divalent compensating cations (e.g. Ca^{2+}, Mg^{2+}) in the formation of cationic bridges between anionic PPs and clay minerals (Aristilde, Lanson, Miéhé-Brendlé, Marichal, & Charlet, 2016; Rowley, Grand, & Verrecchia, 2018; Salihi & Mahramanlıoğlu, 2014; Thiebault, Boussafir, Guégan, Le Milbeau, & Le Forestier, 2016). Yet, this mechanism appears to display a limited impact on the adsorption extent of negatively charged PPs. Finally, looking at all the Log K_d values, no clear trend can be discerned concerning a preferable adsorbent for neutral and anionic PPs, although kaolinites seem to be ineffective (Aleanizy, Alqahtani, Al Gohary, El Tahir, & Al Shalabi, 2015; Rakić, Rajić, Daković, & Auroux, 2013).

Thermally modified and acid-activated clay minerals

This review focuses particularly on the two types of modification that are among the most widely applied in the literature, namely acid activation and thermal modification, detailed below. They provide comprehensive insights into the impact of such

modifications on the structure and properties of modified clay minerals and the specific adsorption of pharmaceuticals.

Structure and basic properties

Acid activation of clay minerals

As detailed in the first section, clay minerals are classically characterized by their high cation exchange capacities and surface area. From a structural point of view and except for kaolinites, clay minerals have few singly coordinated –OH groups, which hinders their applications in industrial catalysis, for example. To counteract this, the acid activation of clay minerals increases the specific surface area of clay minerals by leaching inorganic cations from the structure of the adsorbent (Jozefaciuk, 2002). The impact of acid activation depends on several factors such as the relative amount and nature of the acid. Nevertheless, according to the literature, the nature of the acid only weakly impacts the properties of the resulting activated adsorbent (Chmielarz et al., 2012; Steudel, Batenburg, Fischer, Weidler, & Emmerich, 2009a). Conversely, the amount of acid used during the acid activation strongly impacts the final properties of the acid-activated clays (Hussin, Aroua, & Daud, 2011; Santos et al., 2015). As demonstrated in Table 4, several studies have investigated the acid activation of various clay types. All these studies show that by increasing the amount of inorganic acid, the SSA of clay minerals is strongly improved although the CEC significantly decreases (Christidis, Scott, & Dunham, 1997; Tomić, Logar, Babic, Rogan, & Makreski, 2011). This can be explained by the fact that the leaching of inorganic structural cations such as Al^{3+} and compensating inorganic cations such as Na^{+} and Ca^{2+} significantly modifies the porosity and the charge balance of clay minerals (Komadel & Madejová, 2013; Steudel, Batenburg, Fischer, Weidler, & Emmerich, 2009b). The SSA (especially N_2-

BET) measurement is very sensitive to such leaching, resulting in a pronounced increase in these values during acid activation. Conversely, the replacement of structural and compensating cations by protons leads to opposite results with (i) a reduction in the CEC of the clay minerals due to the leaching of octahedral cations and (ii) a change in the global charge of the layer from negative to positive in the case of proton excess (Komadel, 2016; Krupskaya et al., 2019). Hence, this type of treatment should be preferentially performed if the main purpose is to increase the SSA (Komadel, 2003; Krupskaya et al., 2017).

Several acid-activated clay minerals are currently on the market such as K10, K30 and KSF montmorillonites. These acid-washed or acid-activated materials present a proton excess, leading to their use in catalysis applications (Chmielarz et al., 2012; B. S. Kumar, Dhakshinamoorthy, & Pitchumani, 2014). Other authors have performed the acid activation on raw clay minerals, thereby controlling the original properties of the acid-activated materials (P. Kumar, Jasra, & Bhat, 1995; Q. Wang, Zhang, Zheng, & Wang, 2014).

Thermally modified clay minerals

The thermal treatment of clay minerals can induce several modifications depending on the maximum temperature. Two types of mass losses are expected during the gradual heating of clay minerals. The first one, between 50 and 200 °C is due to the dehydration of clay minerals and is considered as reversible. The dehydration temperature is a function of the clay type and compensating cation (Ferrage, Kirk, Cressey, & Cuadros, 2007). Then, dehydroxylation occurs between 500 and 750°C depending on the clay type and octahedral sheet occupation (Emmerich, Madsen, & Kahr, 1999). Beyond this temperature, the impact on the adsorbent is considered as irreversible and further

thermal treatment could also lead to the formation of other, mostly refractory, crystalline phases, such as metakaolin or pyrophyllite (Heller-Kallai, 2013).

The effect of a gradual heating on the properties of clay minerals is highly dependent on the selected temperature (Table 5). Around the dehydration temperature, both the CEC and SSA values are poorly affected, exhibiting a slight decrease (H. Chen, Zhao, Zhong, & Jin, 2011; Drzal, Rynd, & Fort, 1983; Sarikaya, Önal, Baran, & Alemdaroğlu, 2000). Beyond 200°C, the CEC and SSA values continue to diminish slightly, and a dramatic decrease in both CEC and SSA values occurs beyond the dehydroxylation temperature (Bayram, Önal, Yılmaz, & Sarıkaya, 2010; Gan, Zhou, Wang, Du, & Chen, 2009; Suraj, Iyer, & Lalithambika, 1998). Beyond this temperature, the resulting materials differ greatly from the initial adsorbent as they display very low CEC and SSA values (Table 5), whereas the thermal treatment developed the porosity of the adsorbent leading to very different structures. Among the commercially available thermally activated clays, numerous adsorbents are marketed as "expanded clays", such as LECA (i.e. for Light Expanded Clay Aggregates) and Filtralite®. These adsorbents are very useful in numerous applications such as gardening, building materials, aquaculture or water filtration (Ardakani & Yazdani, 2014; Bartolini, Filippozzi, Princi, Schenone, & Vicini, 2010; Sales, de Souza, dos Santos, Zimer, & do Couto Rosa Almeida, 2010).

Expanded clay minerals are generally produced by flash heating beyond the dehydroxylation temperature (~1000°C), strongly affecting their CEC and SSA (Drizo, Frost, Grace, & Smith, 1999; Machado, Dordio, Fragoso, Leitão, & Duarte, 2017). As a result, their properties are very different from those of raw clay minerals, raising questions about their potential to efficiently adsorb organic contaminants such as PPs.

Adsorption of PPs onto thermally modified and acid-activated clay minerals

The adsorption properties of PPs onto acid-activated and thermally modified clay minerals are presented in Table 6. In the literature, the calculated properties (i.e. CEC and SSA) for the same adsorbent often vary. For example, the CEC of Mt-K10 ranges from 42.9 to 119 $cmol.kg^{-1}$ and the SSA from 183 to 269 $m^2.g^{-1}$ (Calabrese, Gelardi, Merli, Liveri, & Sciascia, 2017; Figueroa, Leonard, & MacKay, 2004; Hamilton et al., 2014; Lawal & Moodley, 2015). Yet, the adsorbent is theoretically the same, raising questions about the methodology employed and the homogeneity of the literature (H. N. Tran, You, Hosseini-Bandegharaei, & Chao, 2017).

Beyond these differences, the adsorption potential of modified clay minerals appears to be close to that of raw clay minerals. Speciation plays a key role, with in general high adsorption capacity and solid/water partition coefficient values for cationic and zwitterionic PPs whereas the opposite pattern is observed with modified clay minerals. As previously described, on increasing the amount of acid, the adsorption of ofloxacin is decreased due to the drop in both CEC and SSA (Q. Wang et al., 2014). However, other studies found an increase in SSA on increasing the acid amount. This increase in SSA appears to be favorable for the adsorption of anionic and neutral PPs such as diclofenac and carbamazepine onto Mt-K10 and Mt-K30 (Styszko et al., 2015). The latter adsorbent has a higher SSA due to a higher amount of acid in comparison to Mt-K10, and the adsorption capacity is therefore higher for such PPs. As a result, the impact of the acid activation of clay minerals on the adsorbent properties varies, favoring the adsorption of neutral and anionic contaminants due to the increase in SSA, and decreasing the adsorption of positively charged PPs due to the drop in CEC.

The thermal treatment of clay minerals is conversely unfavorable for the adsorption of PPs, whatever their charge, especially beyond the dehydroxylation

temperature. For example, the lowest adsorption capacity of carbamazepine, as well as of other PPs such as ibuprofen, is displayed by LECA (Dordio, Estêvão Candeias, Pinto, Teixeira da Costa, & Palace Carvalho, 2009; Dordio, Miranda, Ramalho, & Carvalho, 2017). Only one study found very significant adsorption of a neutral PP (i.e. metronidazole) onto LECA (Kalhori, Al-Musawi, Ghahramani, Kazemian, & Zarrabi, 2017). Similarly, a gradual heating of the adsorbent is considered as unfavorable for the adsorption of ofloxacin onto halloysite (Q. Wang et al., 2014).

Judging from the literature, the modification of clay minerals by acid activation and thermal treatment does not significantly improve the adsorption of PPs. If we except the better adsorption of neutral and anionic PPs onto modified clay minerals in comparison to raw ones (i.e. due to the increase in the SSA), it can even be considered that such modifications are unfavorable for the proper adsorption of PPs due to the dramatic decrease in the CEC of the adsorbent. However, these adsorbents could present other advantages in comparison to raw clay minerals, justifying their use for the removal of organic contaminants despite their limited adsorption properties.

Impact of external parameters on the adsorption of PPs onto clay-based adsorbents

After the assessment of the affinity between PPs and various adsorbents in idealized solutions, the objective of this section is to precisely determine the impact of external parameters on the extent of the adsorption of PPs onto clay and modified clay minerals. Among them, pH, temperature, salinity and competition with organic moieties will be particularly emphasized.

Impact of pH

The pH of the solution is of great concern when designing a removal technology, as it

controls the charge state pf the adsorbate according to its pK_a value and it can strongly impact the reactivity of the adsorbent. While the permanent charges generated by the isomorphic substitutions within the clay layers remain unaffected by the modification in background acidity (except for strongly acidic solutions), the amphoteric charges can be protonated or deprotonated depending on the pH to pH_{ZNPC} ratio (S.-J. Park, Seo, & Lee, 2002; Tournassat et al., 2016). Classically, Si-OH, Al-OH and Mg-OH pH_{ZNPC} are considered to be 4.5-5.5, 4-5 and 10-11, respectively (Ganor, Cama, & Metz, 2003; Kretzschmar, Holthoff, & Sticher, 1998; C. Martin et al., 2002; Rand & Melton, 1975; Tarì, Bobos, Gomes, & Ferreira, 1999; Tawari, Koch, & Cohen, 2001; Tombácz & Szekeres, 2006).

As the pH of classical wastewater and river water is between 6 and 8, it can be considered that Si-OH and Al-OH will be mostly deprotonated and Mg-OH mostly protonated under such pH conditions. Hence, the clay mineral composition in environmental background acidity could have an adverse effect on the adsorption of positively charged PPs in presence of Si-OH edge sites, whereas the adsorption of negatively charged PPs would be enhanced in presence of Mg-OH sites. As these two types of hydroxides are often simultaneously present in the tetrahedral (i.e. mostly Si-OH) and octahedral sheets (i.e. mostly Al-OH and Mg-OH) of clay minerals, it is difficult to determine precisely the full reactivity of clay minerals in such solutions.

Temperature effect

Among the controlling parameters of the extent of the adsorption of organic contaminants onto mineral surfaces, the temperature is a crucial factor. Depending on the adsorption mechanism, the temperature has reverse effects. Physical adsorption is generally considered to be enhanced at lower temperatures due to its exothermic nature,

whereas the impact of temperature of ionic exchange is still debated. Several studies have investigated the impact of temperature on the adsorption capacity of PPs onto clay minerals (Table 7). An aggregation of these results is presented in Figure 3, and clearly shows that physical adsorption (i.e. mostly for the adsorption of neutral and anionic PPs onto clay minerals) is enhanced for lower interaction temperatures as the solid/water partition is higher for lower temperatures, whatever the adsorbent. For example, the solid/water partition of neutral carbamazepine is systematically higher for lower interaction temperatures on raw clay minerals (Berhane et al., 2015; Khazri et al., 2017; Salihi & Mahramanlıoğlu, 2014).

The pattern for the impact of temperature on ion exchange is less clear, however. Several studies have demonstrated that increasing the interaction temperature increases the adsorption capacity of cationic PPs onto clay minerals (Chang et al., 2014; Y. Chen, Zhou, Liu, & Liang, 2010), whereas the opposite results were recorded for the same charge state (W.-T. Jiang, Chang, Tsai, & Li, 2016; Z. Li, Fitzgerald, Jiang, & Lv, 2016). Looking at the general pattern presented in Figure 3, it appears that the impact of temperature on ion exchange is controlled by the solid/water partition. When Log K_d values are higher than 3 (i.e. very favorable adsorption behavior with limited initial concentration), the increase in the interaction temperature appears to be favorable for the adsorption capacity whereas for intermediate Log K_d (i.e. very favorable adsorption behavior with oversaturated initial concentration) the increase in the interaction temperature is generally unfavorable for the adsorption capacity. This distinct pattern seems to depend on the selected starting concentration.

An increasing temperature favors the adsorption process by increasing the diffusive contribution of its mass transfer while it reduces the electrostatic attractions between PPs and the clay mineral surfaces. By increasing the mobility of PPs (i.e.

reducing the mean free path), making adsorption by contact with a surface easier, the adsorption capacity is enhanced in non-saturated conditions, whereas reducing the activation energies of the adsorption process can be unfavorable for the adsorption capacity in over-saturated conditions.

Ionic strength effect

The competition between PPs and other chemicals is highly dependent on the nature of the chemicals. Most interaction studies between PPs and clay minerals were conducted in idealized conditions with no or a very low ionic strength (i.e. 0 or 0.01 mM) in contrast to the general composition of field solutions in which the salinity is generally higher. Hence, modifying the concentration of inorganic cations in the solution could affect the adsorption capacity of PP onto clay minerals. Moreover, within natural environments, the concentration of inorganic cations is expected to be far higher than the concentrations of PPs, impacting the potential competitive effect. It is therefore mandatory to understand how salinity could impact the adsorption capacity of clay minerals.

According to the aggregation of the results presented in Figure 4, the impact of Na^+ concentration can be considered to differ depending on the speciation of the adsorbed PPs. Whatever the compensating cation or the clay minerals, an increase in the Na^+ concentration is unfavorable for the adsorption of cationic and zwitterionic PPs onto clay minerals through ion exchange. This is because the ion exchange reaction is controlled by the amount of chemical in solution (i.e. both PP and competitive inorganic cations). As a result, the higher the Na^+ concentration, the lower the PP amount exchanged onto adsorbents. However, under equivalent interaction experiments and even for very high Na^+/PP ratios, the adsorption generally remains significant or even

slightly lower. This is probably due to a higher selectivity for the ion exchange of organic molecules in comparison with inorganic ones maybe generated by the impact of hydrophobic interactions between organic moieties and clay minerals. As a result, even if the adsorption of positively charged PPs is affected by the competition with a monovalent inorganic cation such as Na^+, the higher selectivity for organic moieties maintains the favorable adsorption behavior.

The results are the same in the case of competition between cationic PPs and a divalent inorganic cation such as Ca^{2+}: the amount of adsorbed PP decreases. However, the pattern is different for zwitterionic PPs, for which the adsorption capacity is higher in presence of Ca^{2+} (Aristilde et al., 2016). This pattern is due to the divalent nature of Ca^{2+} that authorizes the formation of cationic bridges as the main explanation of organo-mineral interaction within the natural environment (Bronick & Lal, 2005; Rowley et al., 2018). However, some zwitterionic PPs are mainly adsorbed through cation exchange onto clay minerals, and the competition with a divalent inorganic salt such as Ca^{2+} could also lead to a decrease in the adsorption capacity (Rivagli et al., 2014). For the same PP, the adsorption of the cationic form is diminished by the presence of Cu^{2+} in the solution, whereas the opposite pattern is observed for the zwitterionic form (Pei, Shan, Kong, Wen, & Owens, 2010; Pei et al., 2011). Consequently, even zwitterionic PPs display a positive charge; the impact of background salinity on their adsorption varies depending on the valence of the inorganic cations added.

Based on these results, the presence of divalent cations such as Ca^{2+} or Cu^{2+} should favor the adsorption of anionic PPs (Pei et al., 2010). However, physical adsorption of both neutral and anionic species is favored when the salt concentration increases, whatever their valence (Table 8). This is especially visible in Figure 4 with a

systematic increase in the solid/water partition for higher NaCl concentrations. From a physical point of view, it can be explained by the Gouy-Chapman theory of the diffuse double layer. The thickness of the double layer is compressed by the increase in ionic strength of the solution, limiting the repulsion between non-cationic PPs and clay surfaces (Rashid, Buckley, & Robertson, 1972). Yet, even if this non-specific interaction is noticeable in batch experiments, its reality for remediation purposes remain speculative.

As a result, it can be considered that the increase in the ionic strength generally decreases the cation exchange mechanism, whereas other mechanisms such as cationic bridges (i.e. for divalent cations only) and surface adsorption are favored on increasing the background salinity. Hence, the adsorption of neutral and anionic PPs is higher in highly saline solutions.

Competition with other organic compounds

Beyond the impact of temperature and salinity on the adsorption capacity, environmental matrices often display significant concentrations of organic compounds (e.g. other PPs, fatty acids, other organic contaminants) which could affect the adsorption of the targeted PPs. In the literature, several studies aimed at improving our understanding of the precise impact of other organic compounds on the adsorption capacity of PPs onto clay minerals. Most of the studies use “humic acids” as competing agents, even if the representativeness of such compounds can be questioned (Lehmann & Kleber, 2015). However, it is clear that commercially available humic acids present a wide diversity of organic moieties and functions that can mimic natural organic matter.

In several environmental compartments such as soils, the interaction between organic matter and clay minerals is known to generate organo-mineral complexes.

These types of complexes are strongly enhanced by the presence of divalent cations such as Ca^{2+}, allowing the formation of cationic bridges between negatively charged organic matter and clay minerals (Droge & Goss, 2012). Hence, this type of interaction favors the stabilization of organic matter and modifies the reactivity of clay minerals (Keil, Montlucon, & Prahli, 1994; Mahamat Ahmat, Thiebault, & Guégan, 2019). Their cation exchange capacity can indeed be significantly hindered by the presence of such organic moieties onto the surface (Y. Zhang et al., 2019). Organic saturated clay minerals therefore display different behaviors with respect to the adsorption of organic contaminants, especially due to the significant hydrophobicity of organic moieties (de Paiva et al., 2008; Guégan, 2019). While the adsorption of positively charged PPs is strongly favored in standard solutions, the presence of organic moieties on the surface or within the layer leads to different adsorption mechanisms favoring the adsorption of hydrophobic contaminants through weak electrostatic interactions (de Oliveira & Guégan, 2016; M. Wu et al., 2019). This type of interaction is the starting point of a substantial body of literature that deals with the use of organo-modified clay minerals for the removal of organic contaminants (Han et al., 2019; Moyo, Tandlich, Wilhelmi, & Balaz, 2014; Zhu et al., 2016). However, for the reasons mentioned in the introduction, such studies are not reviewed in this article.

For example, Behera et al. demonstrated that the adsorption of ibuprofen (i.e. an anionic PP) onto kaolinite and montmorillonite is significantly enhanced with the presence of increasing concentrations of humic acids (Behera et al., 2012). The same type of results were also found by several authors (Gao & Pedersen, 2010; Zhao, Geng, Wang, Gu, & Gao, 2011; Zhao, Gu, Gao, Geng, & Wang, 2012). The adsorption of cationic PPs onto montmorillonite was also considered as favorable for the adsorption of non-cationic organic contaminants (de Oliveira et al., 2018; Pei et al., 2012; M. Wu

et al., 2019). Conversely, other authors have demonstrated that the presence of organic moieties on clay minerals is unfavorable for the adsorption of tetracycline (Pils & Laird, 2007). This was attributed to the locking effect generated by humic acids, hindering the clay interlayer access of the PP. As a result, the presence of organic moieties on clay minerals plays a combined effect, favoring the adsorption of neutral and anionic species through weak electrostatic interactions due to the hydrophobicity of organic fractions, and hindering the cation exchange mechanism by limiting the availability of sorption sites for positively charged PPs.

Potential of clay and modified clay minerals for the removal of PPs in batch experiments

In this section, the impact of external parameters such as pH and temperature, or of the enrichment of the solution (i.e. both inorganic and organic compounds) is assessed. Most studies conclude that clay minerals represent a potential solution for the removal of organic contaminants, even if interaction is performed in standard conditions. In pure water, the adsorption of PPs onto clay minerals is largely affected by their charge state (Figure 5A). Positively charged PPs mostly interact with clay minerals through cation exchange, which is an energetic and stable mechanism even if an increase in the inorganic or organic salts concentration can strongly limit its extent (Figure 5). Neutral and anionic PP adsorption mechanisms onto clay minerals are less clear, and several mechanisms are proposed in the literature. These adsorption mechanisms, such as cationic bridges, hydrogen bindings and van der Waals interaction, are considered as weak electrostatic interactions that can be easily reversible. Some anion exchange can also occur on the edge sites of clay minerals, depending on the solution pH (i.e. mostly if $pH < pH_{ZNPC}$). However, as environmental pH are generally around 7-8, slightly higher than the pH_{ZNPC} of the edge-sites of most clay minerals, neutral and anionic PPs

display limited adsorption capacities onto clay minerals in comparison to cationic ones. Moreover, their adsorption is mostly governed by the solid/water partition and therefore strongly depends on the hydrophobicity and the starting concentration of the selected PP. We can conclude that the affinity of such contaminants is not optimal for clay minerals. However, the presence of inorganic compounds and organic moieties in "natural" solutions systematically enhances the adsorption of neutral and anionic PPs. Several mechanisms are put forward to explain this increase such as hydrophobic interactions with organic moieties and compression of the double-layer surrounding clay particles.

As a result, the enrichment of the solution balances the clay minerals' adsorption properties, favoring the adsorption of neutral and anionic PPs and disfavoring the adsorption of cationic and zwitterionic PPs in general. This pattern indicates that clay minerals could be suitable for the adsorption of a wide range of chemicals, even if the adsorption of cationic and zwitterionic PPs remains higher even in environmental solutions, due to the CEC. Consequently, modified clay minerals do not bring any specific added value to these adsorption properties. It can even be considered that both acid activation (except for the increase in SSA in certain conditions) and thermal treatment are not efficient modification strategies to improve the adsorption properties of organic contaminants onto clay minerals in batch experiments.

High-CEC clay minerals such as smectites and vermiculites therefore appear particularly suitable for the development of a green solution for the removal of PPs from wastewater, due to their significant adsorption properties, availability, cheapness and safety. However, thinking about a field solution requires assessing the adsorption capacity of the adsorbent in dynamic experiments with a continuous flow. Both smectites and vermiculites are swelling clay minerals, and this specific may be an

obstacle for their use in field experiments, where modified clay minerals present better hydrodynamic properties.

Hence, the design of a field solution must take into account the operating constraints, to find a good tradeoff between the adsorption efficiency, cost, availability, safety and practicability of such solutions under continuous flow. The transfer from batch experiments to field solutions is therefore less straightforward than the conclusions of most studies suggest.

Dynamic experiments

Hydraulic conductivity of clay-based adsorbents

Clay minerals, and especially swelling clays, are generally considered as waterproof materials with hydraulic conductivities between 10^{-10} and 10^{-12} $m.s^{-1}$ (Benson & Trast, 1995; Boynton & Daniel, 1985; Le Forestier, Muller, Villieras, & Pelletier, 2010). This specific property allows several applications, such as for example the containment of radioactive wastes (Madsen, 1998; Sellin & Leupin, 2013). However, when seeking a field solution for the removal of organic contaminants from wastewaters, dynamic experiments should be preferred over batch experiments in order to better understand the precise removal efficiency of each adsorbent in realistic operating conditions. Moreover, the filtration technique maximizes the solid/liquid ratio, enhancing the removal performance in comparison to batch experiments if the kinetics are appropriate (de Gisi et al., 2016; Sophia & Lima, 2018; Sotelo, Rodríguez, Álvarez, & García, 2012). However, the very low hydraulic conductivity of clay minerals is a limiting factor, as several authors have reported a severe clogging in column experiments with clay minerals (Cunningham, Anderson, & Bouwer, 1987; Le Forestier et al., 2010; Lozano-Morales et al., 2018).

Among the possible ways to improve the permeability of such materials, the organo-modification of clays improves the hydraulic conductivity; however, it also produces xenobiotic and potentially toxic organic compounds.

Other ways can be explored in order to improve the hydraulic conductivities of clay. One is to use non-swelling clay minerals such as illite that allow a significantly higher hydraulic conductivity than smectites (Alperovitch, Shainberg, Keren, & Singer, 1985). However, this type of clay presents other limitations, especially due to its weak adsorption capacity of the targeted contaminants.

The most widely employed clay types are smectites and vermiculites, which are swelling clay minerals. However, the hydration potential of the compensating cations is a crucial factor in the hydraulic conductivity value (Shainberg & Kemper, 1966; Zheng, Zaoui, & Shahrour, 2011) as it can have a strong impact on the swelling, depending on its hydration potential. For example, Li^+ and Na^+ are small monovalent cations that authorize several water layers in the interlayer spaces, whereas divalent cations such as Ca^{2+} and Mg^{2+} only authorize 2 water layers, and K^+ (as Cs^+) only authorizes one water layer (Bérend et al., 1995; Ferrage et al., 2005; Hensen & Smit, 2002; Teppen & Miller, 2006).

Hence, in order to improve the hydraulic conductivity of swelling clays, the nature of the main compensating cations is very important. Na-compensated clay minerals are unfavorable for such applications due to their very high swelling capacity, leading to potential delamination (Laird, 2006), whereas Ca and K-compensated cations have limited swelling properties. However, K-compensated clay minerals are largely considered as non-swelling clay minerals and K^+ is very hard to exchange (Missana, Benedicto, García-Gutiérrez, & Alonso, 2014; Shainberg, Alperovitch, & Keren, 1987). As a result, Ca-compensated clay minerals may be an appropriate solution. When the

variable swelling properties of smectites were tested in order to verify the impact of compensating cations, it was found that the hydraulic conductivity of Ca-SWy2 was three times as high as that of Na-SWy2, with hydraulic conductivities of 6.0×10^{-13} and 1.9×10^{-12} $m.s^{-1}$ respectively (Thiebault, Boussafir, Guégan, et al., 2016). This difference is generated by the axial swelling strain, which is about 37 % for Na-SWy2 and 1.5 % for Ca-SWy2 (Ghayaza, 2012). Although significant, the hydraulic conductivity of Ca-SWy2 remains far higher than the classical limit of 10^{-9} $m.s^{-1}$ for waterproof materials.

These calculations emphasize the need to mix clay particles with more conductive materials such as sand (i.e. ~10^{-6} $m.s^{-1}$). Several studies have performed such analyses on clays and clay minerals (Nir, Zadaka-Amir, Kartaginer, & Gonen, 2012; Polubesova, Zadaka, Groisman, & Nir, 2006) in order to determine the appropriate clay/sand ratio. Yet again, the compensating cations prove to be important. For Na-compensated clay minerals, the hydraulic conductivity remains very high even for a low clay/sand ratio (i.e. 1.35×10^{-9} $m.s^{-1}$ for 5:95 clay:sand), whereas the decrease in the hydraulic conductivity of Ca-compensated clay minerals appears to be proportional to the increase in the clay/sand ratio (Thiebault, Boussafir, Guégan, et al., 2016). Jolin and Kaminski worked with a much lower clay sand ratio (i.e. 0.25% of clays) allowing both a regular and significant flow rate and a good removal of contaminants (Jolin & Kaminski, 2016).

As a result, the hydrodynamic properties of raw clay minerals represent an obstacle for their use as a filtration media for wastewaters. To overcome this limitation, the mixing with sand appears to be a suitable solution, as well as the modification of clay minerals (by thermal treatment for example) in order to enhance hydrodynamic

properties. However, such solutions could diminish the adsorption potential of the adsorbents, as previously mentioned.

Fixed-bed adsorption of PPs onto raw and modified clay minerals

The experiment in dynamic mode based on a filtrating media (e.g. fixed-bed experiment) maximizes the solid/liquid ratio and limits the contact time between PPs and adsorbent. However, during such experiments, the removal capacity is significant only if the sorption kinetics are fast. This is one of the main advantages of clay minerals in comparison with activated carbons or other waste derived adsorbents(Ahmed & Hameed, 2018; Putra et al., 2009; H. N. Tran et al., 2019). The weak porosity of clay minerals (if we except acid-activated and thermally-treated clay minerals) limits the diffusion process that may strongly increase the adsorption kinetic, as described on activated carbon (Baccar, Sarrà, Bouzid, Feki, & Blánquez, 2012; Delgado, Charles, Glucina, & Morlay, 2012; Qurie et al., 2014). The adsorption of PPs onto activated carbons in dynamic experiments has been extensively studied (Delgado et al., 2012; Katsigiannis, Noutsopoulos, Mantziaras, & Gioldasi, 2015; Mailler et al., 2016), whereas a limited number of studies have focused on clay adsorbents. Yet, the adsorption kinetic of PPs onto clay minerals is considered as spontaneous for the cation exchange mechanism, and other interactions are also significant for a very short interaction time (Z. Li et al., 2016; Thiebault, Boussafir, Le Forestier, et al., 2016). These materials appear therefore to be suitable for this type of application.

Among the few studies that have tested the dynamic adsorption of PPs onto clays, their adsorbent potential was systematically demonstrated. For example, the adsorption of tetracycline (zwitterionic at the investigated pH) onto stevensite under dynamic experiments reached three times the CEC of the raw clay mineral, highlighting

the combined effect of cation exchange and other interaction mechanisms in such conditions (Fernández et al., 2018). Another study, performed with lower starting concentrations (i.e. ~25 µg.L^{-1}) exhibited very significant removal rates of cationic PPs onto Ca-montmorillonite in both pure water and wastewater effluent matrixes (96 and 90% respectively), while the removal of neutral and anionic PPs was lower, but significant, with mean values of 61 and 68 % in pure water and wastewater effluent, respectively (Thiebault, Boussafir, Guégan, et al., 2016). It is interesting to note here that these results are in accordance with the previous discussion on the negative impact of the enrichment of the solution (i.e. inorganic cation, organic matter) on the removal of cationic PPs and the positive impact on the removal of anionic and neutral PPs. The complete removal capacity in real effluents is therefore better balanced between positively charged PPs and other charge states, improving the whole efficiency of the proposed solution.

However, the transition from batch experiments to dynamic experiments is seldom performed in the current literature, limiting our understanding of the potential of such a solution.

Another adsorbent has been extensively studied for its adsorption properties of PPs, LECA. As previously described, LECA is a thermally modified clay mineral with a limited adsorption capacity (Drizo et al., 1999). However, thermal treatment causes the collapse of the interlayer space, limiting the swelling behavior which is the main limitation for the use of this adsorbent in fixed-bed columns (Le Forestier et al., 2010; Lozano-Morales et al., 2018), and increases the porosity of the media, increasing the adsorption kinetic in comparison to raw clay minerals (Dordio, Estêvão Candeias, et al., 2009). Several mesocosm studies have demonstrated the significant removal (i.e. ~90%) of recalcitrant PPs such as carbamazepine and ibuprofen onto LECA (Dordio et al.,

2010). . The removal capacity of this type of adsorbent (i.e. expanded clay) was also successfully tested in dynamic conditions for the adsorption of recalcitrant PPs (Dordio, Pinto, et al., 2009; Machado et al., 2017), and highlighting the limited energy requirement of such solutions (Matamoros, Arias, Brix, & Bayona, 2009; Rossi, Queloz, Brovelli, Margot, & Barry, 2013). According to these results, expanded clay minerals appear to be suitable for the removal of PPs from water, and can be considered as effective as activated carbons. Moreover, these adsorbents are biocompatible, which is both an advantage and a disadvantage depending whether one considers regeneration of the filter by biodegradation, or biofouling that limits the interaction between PP and media surface (Rajabi et al., 2014; Spettmann, Eppmann, Flemming, & Wingender, 2007).

It is therefore very promising that a thermally modified clay mineral without any impact of interlayer space and limited cation exchange capacity may be suitable for the removal of PPs from wastewater effluents (Dordio & Carvalho, 2013). Such studies would pave the way for the testing of more reactive clay minerals (i.e. vermiculite, smectite) in an appropriate mixing with permeable material for an efficient removal of PPs in field experiments.

Regeneration of the adsorbent

To determine the potential of an adsorbent for the removal of chemicals, several parameters need to be taken into account. Less attention is generally paid to the management costs associated to the use of the adsorbent than to the initial cost, despite their importance (Ali et al., 2012; Gupta, Carrott, Carrott, & Suhas, 2009). For example, the use of agricultural wastes could be promising because their initial cost is very low, but the lack of knowledge about their management costs and durability raises serious

issues about their real potential to treat complex solutions.

Hence, the whole life cycle of the adsorbent should be taken into account when speaking about a good solution. However, no study in the literature focuses on the regeneration of clay or modified clay-based adsorbents. As already described for activated carbons, the growth of biofilms on the surface of the adsorbent is one way to regenerate the adsorbent in situ (Rattier, Reungoat, Keller, & Gernjak, 2014). However, uncontrolled growth of such biofilms could lead to severe biofouling that limits the adsorption capacity of the filtering media (Matamoros et al., 2009), even if some controls are practicable (G. L. Li, Zhou, Fiore, & Yu, 2019). As a result, other ways should be promoted for regeneration such as thermal treatment (for dehydroxylated clay minerals only) in order to degrade the adsorbed organic moieties onto clay surfaces (de Andrade et al., 2018; Rakić et al., 2013). For raw clay minerals, the immersion in oversaturated saline solutions could be a sustainable way for the regeneration of these adsorbents (W. T. Tsai, Chen, Hsieh, Sun, & Lai, 2003). This type of solution had not been yet tested after PPs adsorption, however.

In conclusion, although potential regeneration is essential for the proper evaluation of the feasibility of clay-based adsorbents for the removal of PPs from wastewater, no study has tested it, which is a gap in the current literature.

Discussion and perspectives on the removal of PPs by clay-based adsorbents

Based on the literature reviewed, most authors concur in the potential of clay minerals for the adsorption of PPs from aqueous solutions. However, very few studies have tested the potential of such materials in dynamic experiments, and even less on environmental solutions. Several limitations were pointed out to explain this discrepancy. The swelling capacity of most of the promising clay minerals is the first

obstacle for their use in dynamic experiments, and their limited adsorption of neutral and anionic PPs has been considered as a limitation. However, we have demonstrated that the enrichment of the solution can be favorable for the adsorption of such contaminants, confirming the potential of such materials.

In the literature, dynamic experiments were mostly performed with thermally treated clay minerals such as expanded clays. These materials exhibit appropriate hydrodynamic properties, such as high porosity, due to the thermal treatment. However, the thermal treatment strongly affects their structure and derived properties such as CEC and SSA. While these adsorbents can be considered as suitable for the removal of PPs from wastewater, despite very low CEC and SSA as exhibited by batch experiments, it can be considered that there is a paucity in the literature of experiments on raw clay-based sorbents for the filtration of wastewater. Obviously, swelling clay minerals cannot be used as sole materials due to their waterproof nature. Mixing them with permeable materials such as sand or expanded clay minerals, however, could be a promising way to remove PPs from wastewater as a result of their very high affinity for cationic and zwitterionic PPs and significant affinity for neutral and anionic PPs.

As a conclusion, future research on the potential of clay-based adsorbents for the removal of PPs should emphasize the use of raw clay minerals rather than thermally modified ones due to the higher adsorption potential of the former. Due to their non-porous nature, thermally modified adsorbents appear inappropriate to be used pure in the filter medium (i.e. unlike activated carbons for example) rather than mixed with more permeable mineral phases (e.g. sand). Hence, their use in the mineral filter of vertical flow constructed wetlands would be a promising way to optimize the removal of PPs from wastewater and limited their further propagation through the environment. Also, future prospects on the development of a innovative solution for the removal of

PPs from wastewater could benefit from the advantages of clay minerals as smectite (i.e. removal of positively charged contaminants) in association with other adsorbents such as activated carbons, displaying higher affinity for neutral and anionic PPs.

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Tables and Figures

Table 1. Classification of the clay minerals reviewed in this study

Clay type	Net layer charge	Group	Octahedral character	Species	CEC $cmol.kg^{-1}$	N_2 SSA $m^2.g^{-1}$
1:1	~0	Serpentine-Kaolin	Di	Kaolinite (Kaol.)	2[a];3.3[a];3.8[b];7.3[c]	10.1[d];13.1[a];21.7[a]; 23.5[d];24[b];33[c]
				Halloysite (Hall.)	4.9[e];11.5[f]	16.5[e];59.6[g];65[f,h]
2:1	~0.2-0.6	Smectite	Di	Montmorillonite (Mt.)	72.4[i];76.4[a];84.4[a]; 106.5[i];120[a]	22.7[b];31.8[a];65.2[b]; 83.8[a];97.4[a]
			Tri	Stevensite (Stev.)	36[j];65[k];76.5[l]	133.7[l];221[k]
				Hectorite (Hect.)	43.9[m];52.6[n];70[o]; 84[p]	35.6[d];63[n];63.2[m]; 114[p]
				Laponite (Lap.)	47[q];56.8[n];65[r]; 70[s];72[t];91[q]	245[t];354[u];360[n]; 370[s]
	~0.6-0.9	Vermiculite	Di,Tri	Vermiculite (Verm.)	85[v];133[w];142[w]; 146[w]	3.5[x];4.1[v]
	~0.6-1.0	Mica	Di	Illite (Ill.)	7.5[y];13.9[c];14[z]; 20.5[y];27[b]	41[aa];51[z];68[c];105[b]; 184[ab];195[ab]
2:1 (fibrous)				Palygorskite (Pal.)	14[ac];16.5[ad];17.5[q]; 19.5[a]	126[ad];136.4[a]; 173[ae];222[ac]
				Sepiolite (Sep.)	1.5[ad];8.2[af];11[ac]; 17[a];54.4 [ag]	250[ad];317[a];384[ac]; 426[ag]

With [a](Van Olphen & Fripiat, 1979); [b](Kahr & Madsen, 1995); [c](Hang & Brindley, 1970); [d](M. Dogan et al., 2007); [e](Tarì et al., 1999); [f](W.-T. Jiang et al., 2016) ; [g](Jinhua et al., 2010); [h](Lvov, Shchukin, Möhwald, & Price, 2008) ; [i](He, Ma, Zhu, Yuan, & Qing, 2010); [j](Faust & Murata, 1953); [k](Antón-Herrero et al., 2018); [l](Benhammou, Yaacoubi, Nibou, & Tanouti, 2005); [m](Baskaralingam, Pulikesi, Ramamurthi, & Sivanesan, 2006); [n](Cenens & Schoonheydt, 1988); [o](Traynor, Mortland, & Pinnavaia, 1978); [p](Schlegel, Manceau, Chateigner, & Charlet, 1999); [q](Borden & Giese, 2001); [r](Thompson & Butterworth, 1992); [s](Negrete Herrera, Letoffe, Reymond, & Bourgeat-Lami, 2005); [t](Esumi et al., 1998); [u](Valencia et al., 2018); [v](L. Tran, Wu, Zhu, Liu, & Zhu, 2015); [x](Ravichandran & Sivasankar, 1997); [y](Baeyens & Bradbury, 2004); [z](Kahle & Stamm, 2007); [aa](Macht, Eusterhues, Pronk, & Totsche, 2011); [ab](Aylmore, Sills, & Quirk, 1970); [ac](Shariatmadari, Mermut, & Benke, 1999); [ad](Z. Li, Willms, & Kniola, 2003); [ae](A. U. Dogan et al., 2006); [af](Lemić, Tomašević-Čanović, Djuričić, & Stanić, 2005) and [ag](Özcan & Özcan, 2005)

Table 2. Adsorption capacities of cationic and zwitterionic PPs by various clay minerals, with Adsorbent the commercial name of clay minerals, Cl. Min. the principle clay type and compensating cations, CEC the cation exchange capacity in $cmol.kg^{-1}$, SSA the N_2 BET specific surface area in $m^2.g^{-1}$, C_{max}/CEC the ratio between the starting amount of PP and the CEC of clay minerals, Charge the charge state of PP at the tested pH (with C for cationic, Z for zwitterionic, A for anionic and N for neutral charge state), Temp, the interaction temperature (RT is room temperature), Q_{max} the maximum adsorption capacity in $cmol.kg^{-1}$ and NA for non-available data.

PP	M $g.mol^{-1}$	Adsorbent	Cl. Min.	CEC $cmol.kg^{-1}$	SSA $m^2.g$	C_{max} /CEC	Charge†	pH	Temp °C	Q_{max} $cmol.kg^{-1}$	Reference
Amitriptyline	313.9	KGa-2	Na-Kaol.	4	18	0.54	C	6-7	RT	1.5	(Lv et al., 2013)
		SAz-2	Ca-Mt.	120	97	1.06	C	~7	NA	105.1	(Chang et al., 2014)
		PFl-1	Ca-Paly.	17	173	2.25	C	6-7	RT	16.8	(Y.-L. Tsai et al., 2016)
		SepSp-1	Ca-Sep.	17	317	2.25	C	6-7	RT	8.0	
Amoxicillin	365.4	Cloisite®	Na-Mt	93	23[a]	1.47	CZ	4	RT	70.0	(Rebitski, Souza, Santana, Pergher, & Alcântara, 2019)
		SWy-2	Na-Mt	76	32	2.68	ZA	6.5	NA	24.0	(de Oliveira et al., 2018)
Atenolol	266.3	Bentonil A	Mt.	80	NA	0.15	C	7-8.5	20	9.1	(Lozano-Morales et al., 2018)
		Kaol.	Na-Kaol.	6	NA	0.81	C	6-6.5	30	2.5	(Rakić et al., 2013)
		KGa-2	Na-Kaol.	4	22	1.08	C	NA	NA	2.5	(Hu et al., 2015)
Buspirone	385.5	Bentonite	Mt.	91	45	2.84	C	4.5	30	57.6	(Joshi, Kevadiya, & Bajaj, 2010)
Chlorpheniramine	391.0	Halloysite	Ca-Hall.	11.5	65	1.74	C	5.4	NA	5.5	(W.-T. Jiang et al., 2016)
		SAz-1	Ca-Mt.	123	65	0.83	C	NA	NA	72.0	(Z. Li, Chang, Jean, Jiang, & Hong, 2011)
		SWy-2	Na-Mt.	85	32	1.20	C	NA	NA	64.0	(Lv, Liu, Li, Liao, & Liu, 2012)
		KGa-1b	Na-Kaol.	3	10	3.41	C	NA	NA	2.5	(Lv, Wu, Li, Liao, & Liu, 2014)
		Albagel	Na-Mt.	80	NA	3.5	C	~7	40	76.0	(Camazano, Sanchez, Vicente, & Dominguez-Gil, 1980)
Chlortetracycline	478.9	Minclear N100	Ca-Stev.	65	221	0.64	ZC	3.8	25	29.2	(Antón-Herrero et al., 2018)
Ciprofloxacine	331.3	Bentonite	Na-Mt	123	67	1.08	C	3	20	100.4	(Roca Jalil, Baschini, & Sapag, 2015)
		Halloysite	Ca-Hall	11.5	65	1.74	CZ	5.6	NA	8.4	(W.-T. Jiang et al., 2016)
		SAz-1	Ca-Mt.	123	65	0.98	CZ	4-5.5	NA	119.2	(C.-J. Wang, Li, & Jiang, 2011)
		Rectorite	Ca-Rec	41	10	1.47	CZ	4-5.5	NA	40.7	
		IMt-2	Ca-Ill.	11.5	22	2.62	CZ	4-5.5	NA	10.0	
		Kaolin	Kaol.	8	NA	1.41	Z	7.4	NA	12.0	(Hamilton et al., 2014)
		Laponite RD	Na-Hect.	53	370	5.69	Z	7.4	NA	215.6	
		Vermiculite	Mg-Verm.	85.5	NA	0.35	C	4	30	11.1	(S. Liu et al., 2017)
Diphenhydramine	291.8	Halloysite	Ca-Hall.	11.5	65	1.74	C	6.4	NA	6.5	(W.-T. Jiang et al., 2016)
		SAz-1	Ca-Mt.	123	65	1.11	C	6.9-7.3	22	88.0	(Z. Li, Chang, Jiang, et al., 2011)
Donepezil	379.5	Kunipia-F	Na-Mt.	100	NA	2.00	C	NA	NA	89.1	(J. K. Park et al., 2008)
		Laponite XLG	Na-Hect.	71	354[b]	2.00	C	NA	NA	59.7	
		Sumecton SA	Na-Sap.	63	NA	2.00	C	NA	NA	45.4	
Doxepin	279.4	SWy-2	Na-Mt.	84	32	5.33	C	6.5	25	100.0	(Thiebault et al., 2015)
Enrofloxacin	359.4	Zettlitz la	Kaol.	3	10	27.82	C	2	20	5.8	(Rivagli et al., 2014)
		SWy-1	Na-Mt.	84	35	0.99	C	2	20	53.9	
		STx-1	Ca-Mt.	82	45	1.02	C	2	20	64.7	
		IMt-2	Ca-Ill.	11.5	22	3.88	Z	7	RT	22.7	(Wan, Li, Hong, & Wu, 2013)
		SWy-2	Na-Mt.	76	32	1.10	Z	7	RT	66.7	
		Kga-1b	Na-Kaol.	2	10	1.25	Z	7	RT	2.0	
		Zettlitz la	Kaol.	3	10	27.82	Z	7.5	20	7.0	(Rivagli et al., 2014)
		SWy-1	Na-Mt.	84	35	0.99	Z	7.5	20	44.7	
		STx-1	Ca-Mt.	82	45	1.02	Z	7.5	20	70.8	
Mafenide	186.2	Laponite XLG	Na-Hect.	50	354[b]	3.22	C	3	RT	214.0	(Ghadiri et al., 2014)
Marbofloxacin	362.4	Zettlitz la	Kaol.	3	10	29.44	C	2	20	5.9	(Rivagli et al., 2014)
		SWy-1	Na-Mt.	84	35	1.05	C	2	20	65.4	
		STx-1	Ca-Mt.	82	45	1.08	C	2	20	64.1	
		Zettlitz la	Kaol.	3	10	29.44	Z	7.5	20	5.4	
		SWy-1	Na-Mt.	84	35	1.05	Z	7.5	20	45.6	
		STx-1	Ca-Mt.	82	45	1.08	Z	7.5	20	56.5	
Metformin	165.6	Cloisite®	Na-Mt	93	23[a]	21.64	C	NA	25	101.8	(Rebitski, Aranda, et al., 2018)
Metoprolol	267.3	KGa-2	Na-Kaol.	4	18	1.08	C	4	NA	2.5	(Z. Li, Fitzgerald, Albert, Schnabl, & Jiang, 2015)
		SAz-2	Ca-Mt	120	97	5.61	C	6.6	NA	154.4	(Z. Li et al., 2019)
Neomycin	614.4	Cloisite®	Na-Mt	93	23[a]	6	C	6	25	16.3	(Rebitski, Alcântara, et al., 2018)
		PangelS9	Mg-Sep.	15	342	NA	C	6	25	6.7	
Ofloxacin	361.4	Halloysite	Hall.	12	29	2.41	CZ	5.4	35	12.4	(Q. Wang et al., 2014)
Oxytetracycline	460.4	Vermiculite	Mg-Verm.	85.5	NA	0.25	ZC	4	30	8.0	(S. Liu et al., 2017)
		Minclear N100	Ca-Stev.	65	221	0.67	ZC	3.8	25	27.4	(Antón-Herrero et al., 2018)
		Kaolin	Na-Kaol.	4	25	1.09	Z	5.5	NA	3.0	(Figueroa et al., 2004)
		SWy-2	Na-Mt.	76	32	5.43	C	1.5	NA	173.7	(Kulshrestha et al., 2004)
		SWy-2	Na-Mt	76	32	5.43	Z	5	NA	174.1	
Promethazine	320.9	Bentonite	Ca-Mt.	85	23	0.73	C	NA	25	47.4	(Salihi & Mahramanlıoğlu, 2014)
		Bentonite	Ca-Mt	8[c]	109[c]	NA	C	NA	25	29.6	(Seki & Yurdakoç, 2009)
Propranolol	259.3	Albagel	Na-Mt	80	NA	4	C	~7	40	78.0	(M. J. S. Martin, Camazano, Hernández, & Gil, 1981)
Ranitidine	350.9	PFl-1	Ca-Pal.	17.5	173	1.14	C	7.3-7.8	NA	17.5	(Z. Li et al., 2016)

Tetracycline	444.4	Halloysite	Ca-Hall.	11.5	65	1.74	ZC	3.7	NA	7.7	(W.-T. Jiang et al., 2016)
		SWy-2	Na-Mt.	85	32	1.59	Z	4-5	NA	79.9	(Chang, Li, Jiang, & Jean, 2009)
		SAz-1	Ca-Mt.	123	65	1.10	Z	4-5	NA	103.5	
		IMt-2	Ca-Ill.	14	51	0.80	Z	5-6	NA	7.2	(Chang et al., 2012)
		Laponite XLG	Na-Mt.	60	354[b]	1.13	Z	6	NA	58.7	(Ghadiri, Hau, Chrzanowski, Agus, & Rohanizadeh, 2013)
		KGa-1b	Na-Kaol.	2	10	5.00	ZC	4.5-5.5	NA	0.9	(Z. Li, Schulz, Ackley, & Fenske, 2010)
		SWy-2	Na-Mt.	91	32	1.24	Z	5.5	NA	56.3	(Zhao et al., 2012)
		PFl-1	Na-Pal.	17.5	173	2.06	Z	5-6	NA	12.4	(Chang, Li, Yu, et al., 2009)
		Bentonite	Na-Mt.	104	30[d]	1.08	ZA	7	NA	38.0	(Parolo, Savini, Vallés, Baschini, & Avena, 2008)
		Bentonite	Na-Mt.	104	30[d]	1.08	Z	4	NA	88.0	
		Bentonite	Na-Mt.	138.8	84	7.88	Z	5.5	25	76.9	(N. Liu et al., 2012)
		Minclear N100	Ca-Stev.	65	221	1.38	Z	6-7.5	21	106.9	(Fernández et al., 2018)
		Minclear N100	Ca-Stev.	65	221	0.69	ZC	3.8	25	28.6	(Antón-Herrero et al., 2018)
Timolol	316.4	Bentonite	Na-Mt.	91	40	1.04	C	5.7	30	68.6	(Joshi, Kevadiya, Patel, Bajaj, & Jasra, 2009)
Tramadol	263.4	Bentonite	Na-Mt.	127	45	2.99	C	NA	30	133.2	(Y. Chen et al., 2010)
		SWy-2	Na-Mt.	84	32	5.65	C	6.5	20	80.0	(Thiebault et al., 2015)
Triflupromazine	388.9	Bentonite	Ca-Mt.	85	23	0.61	C	NA	25	37.4	(Salihi & Mahramanlıoğlu, 2014)
Trimethoprim	290.3	Bentonite	Ca-Mt.	85	23	0.81	CN	NA	25	34.4	(Salihi & Mahramanlıoğlu, 2014)
		SWy-2	Na-Mt	76	32	0.56	CN	6.5	NA	32.0	(de Oliveira et al., 2018)
Venlafaxine	277.4	Bentonite	Na-Mt	91	-	0.99	C	NA	50	64.8	(Patel et al., 2011)

†in the event of the coexistence of several charge states, the most important one is presented first, for example CN corresponds to mostly cationic and to a lesser extent neutral

with [a](Ribeiro, Estevão, & Nascimento, 2008), [b](Valencia et al., 2018), [c](Seki & Yurdakoç, 2007) and [d](Viseras et al., 2006)

Table 3. Adsorption capacities of neutral (N) and anionic (A) PPs by various clay minerals, Adsorbent the principal clay type and compensating cations, CEC the cation exchange capacity in cmol.kg^{-1}, SSA the BET specific surface area in m².g^{-1}, Charge the charge state of PP at the tested pH (with C for cationic, Z for zwitterionic, A for anionic and N for neutral charge state), Temp, the interaction temperature (RT is room temperature), Q_{max} the maximum adsorption capacity in cmol.kg^{-1}, Log K_d the solid water partition of PP, and NA for non-available data.

PP	M g.mol^{-1}	Adsorbent	CEC cmol.kg^{-1}	SSA m².g^{-1}	Charge†	pH	Temp. °C	Q_{max} cmol.kg^{-1}	Log K_d L.kg^{-1}	Reference
Acetylsalicylic Acid	180.2	Mt.	92	NA	A	6-6.6	30	1.20	0.95	(Rakić et al., 2013)
		Kaol.	6	NA	A	6-6.6	30	1.20	0.82	
Amoxicillin	365.4	Bent.	NA	91.6	NC	7.0	30	12.96	1.98	(Putra et al., 2009)
Carbamazepine	236.3	Ca-Mt.	85	23	N	NA	25	38.97	2.89	(Salihi & Mahramanlıoğlu, 2014)i
		Na-Mt.	82	21.3	N	7	23	0.06	1.70	(W. Zhang et al., 2010)
		Pal./Mt.	15	130.3	N	6.2	NA	0.15	2.26	(Berhane et al., 2015)
		Bent.	46	69.5	N	NA	25	13.22	3.59	(Khazri et al., 2017)
		Mt.	NA	40	N	8.4	20	0.05	1.15	(Styszko et al., 2015)
		Kaol.	NA	20	N	6.0	20	0.02	0.84	
		Verm.	NA	6	N	6.5	20	0.08	1.54	
Diazepam	284.7	Na-Mt.	76	32	N	7.5	RT	3.6	2.33	(Thiebault & Boussafir, 2019)
Diclofenac	296.2	Mt.	80	NA	A	7-8.5	20	0.96	2.51	(Lozano-Morales et al., 2018)
		Na-Mt.	76	32	A	6.5	NA	4.50	0.83	(de Oliveira & Guégan, 2016)
		Mt.	NA	40	A	8.4	20	0.04	1.19	(Styszko et al., 2015)
		Kaol.	NA	20	A	6.0	20	0.03	0.82	
		Verm.	NA	6	A	6.5	20	0.07	1.51	
Ketoprofen	254.3	Mt.	NA	40	A	8.4	20	0.05	1.17	(Styszko et al., 2015)
		Kaol.	NA	20	A	6.0	20	0.03	0.81	
		Verm.	NA	6	A	6.5	20	0.07	1.43	
Ibuprofen	206.3	Ca-Mt.	85	23	A	NA	25	7.96	2.10	(Salihi & Mahramanlıoğlu, 2014)
		Bent.	80	34.3	A	7	25	2.62	1.99	(Behera et al., 2012)
		Kaol.	2	2.3	A	7	25	0.85	1.48	
		Bent.	46	69.5	A	NA	25	17.70	3.56	(Khazri et al., 2017)
		Mt.	NA	40	A	8.4	20	0.03	0.80	(Styszko et al., 2015)
		Kaol.	NA	20	A	6.0	20	0.06	1.25	
		Verm.	NA	6	A	6.5	20	0.10	1.51	
Metronidazole	171.2	Kaol.	8	2.3	N	6.8	37	14.61	2.39	(Aleanizy et al., 2015)
Nalidixic Acid	232.2	Na-Kaol.	2	13	A	8.5	NA	0.35	1.54	(Q. Wu et al., 2013)
		Ca-Mt.	120	80	A	8.5	NA	0.99	1.94	
		Na-Kaol.	2	13	N	4	NA	0.44	1.65	
		Ca-Mt.	120	80	N	4	NA	10.29	3.59	
Naproxen	230.3	Bent.	46	69.5	A	NA	25	15.58	3.48	(Khazri et al., 2017)
Oxazepam	286.7	Na-Mt.	76	32	N	7.5	RT	9.5	2.77	(Thiebault & Boussafir, 2019)
Oxytetracycline	460.4	Na-Mt.	76	32	A	11.0	NA	86.9	2.39	(Kulshrestha et al., 2004)
Salicylic Ac	138.1	Mt.	92	NA	A	6-6.6	30	2.40	2.00	(Rakić et al., 2013)
		Kaol.	6	NA	A	6-6.6	30	1.05	1.02	
Sulfamethoxazole	253.3	Na-Mt.	76	32	AN	6.6	RT	12.0	1.90	(de Oliveira et al., 2018)
Triclosan	289.5	Kaol.	2	2.3	N	7	25	2.08	1.83	(Behera, Oh, & Park, 2010)
		Mt.	80	34.3	N	7	25	0.62	2.56	

†in the event of the coexistence of several charge states, the most important one is presented first, for example CN corresponds to mostly cationic and to a lesser extent neutral

Table 4. Examples of acid-activation of clay minerals according to the acid type and amount and resulting properties (SSA and CEC)

Clay Mineral	Activation	CEC $cmol.kg^{-1}$	N_2 SSA $m^2.g^{-1}$	Reference
Bentonite	untreated	60	6	(Tomić et al., 2011)
	1.5M (H_2SO_4)	62	84	
	3M	52	120	
	4.5M	25	341	
	6M	14	387	
Bentonite	untreated	104.4	59	(Christidis et al., 1997)
	1M (HCl)	88.0	79	
	2M	87.1	127	
	3M	80.1	148	
	5M	73.4	166	
Montmorillonite	untreated	80.2	38.03	(P. Kumar et al., 1995)
	1 g $eq.L^{-1}$ (H_2SO_4)	76.8	138.36	
	2 g $eq.L^{-1}$	77.0	189.84	
	3 g $eq.L^{-1}$	65.8	326.27	
	4 g $eq.L^{-1}$	67.2	347.74	
	5 g $eq.L^{-1}$	42.2	370.41	
	6 g $eq.L^{-1}$	34.2	370.36	
	7 g $eq.L^{-1}$	25.6	297.49	
	8 g $eq.L^{-1}$	23.1	377.10	
Palygorskite	untreated	30.0	48.7	(W. Wang, Chen, & Wang, 2007)
	2M (HCl)	14.4	192.9	
	4M	13.7	221.2	
	6M	13.6	224.3	
	8M	11.7	234.5	
	12M	9.9	267.5	
Palygorskite	untreated	30.0	48.7	(H. Chen, Zhao, & Wang, 2007)
	2M (HCl)	14.4	192.9	
	4M	13.7	221.2	
	6M	13.6	224.3	
	8M	11.7	234.5	
	12M	9.9	267.5	

Table 5. Examples of thermal modification of clay minerals (Species) with the resulting properties of the modified clay minerals (SSA and CEC) as a function of the thermal treatment temperature.

Species	Temperature	CEC $cmol.kg^{-1}$	N_2 SSA $m^2.g^{-1}$	Reference
Bentonite	100	52.0	43.8	(Sarikaya et al., 2000)
	200	50.8	59.1	
	300	47.9	52.9	
	400	44.8	62.0	
	500	43.0	89.4	
	600	31.9	48.2	
	700	31.0	60.0	
	800	10.8	33.2	
	900	1.9	19.4	
	1000	1.6	14.2	
	1100	0.9	4.1	
	1200		2.2	
	1300		0.3	
Bentonite	50		44	(Bayram et al., 2010; Önal & Sarıkaya, 2007)
	100	53.7	87	
	200	50.8	98	
	300	48.3	105	
	400	45.0	93	
	500	42.6	92	
	600	32.0	95	
	700	31.8	96	
	800	11.0	51	
	900	2.0	37	
	1000	1.5		
	1100	0.9		
	1200	0.1		
	1300	0.1		
Kaolinite	Untreated	13.49	16.87	(Suraj et al., 1998)
	350	12.79	14.32	
	600	6.01	14.77	
Kaolinite	200	5.61	29.3	(Drzal et al., 1983)
	400	5.04	28.2	
	600	3.38	28.9	
	800		27.8	
	1000	1.79	19.0	
Palygorskite	30	23.1	163.2	(H. Chen et al., 2011)
	100	24.5	166.8	
	200	24.9	170.4	
	300	25.9	179.4	
	400	32.1	129.6	
	500	35.0	119.2	
	600	37.1	107.3	
	700	37.9	82.8	
	800	21.2	48.5	
Palygorskite	untreated	4.31	51.3	(Gan et al., 2009)
	300	4.60	53.5	
	350	4.48	50.0	
	400	4.77	47.9	
	600	1.04	44.4	
	700	0.60	47.0	
	800	0.60	33.5	
	1000	0.60	3.7	

Table 6. Adsorption properties of PPs by activated clay minerals, with Adsorbent the commercial name of the adsorbent, CEC the cation exchange capacity in $cmol.kg^{-1}$, SSA the BET specific surface area in $m^2.g^{-1}$, Charge the charge state of PP at the tested pH (with C for cationic, Z for zwitterionic, A for anionic and N for neutral charge state), Temp, the interaction temperature (RT is room temperature), Q_{max} the maximum adsorption capacity in $cmol.g^{-1}$, Log K_d the solid water partition of PP, and NA for non-available data.

PP	M ($g.mol^{-1}$)	Adsorbent	CEC $cmol.kg^{-1}$	SSA $m^2.g^{-1}$	Charge†	pH	Q_{max} $cmol.kg^{-1}$	Log K_d $L.kg^{-1}$	Reference
Amoxicillin	365.4	Bent. (500°C)	NA	NA	Z	NA	0.221	1.51	(Maia, Andrade, Oliveira, Vieira, & Silva, 2017)
		Bent. (750°C)	NA	NA	Z	NA	0.324	1.75	
Atenolol	266.3	Mt.-KSF	65.2[a]	36[a]	C	8	32.4	2.36	(Seema & Datta, 2013)
Carbamazepine	236.3	Mt.-K10	NA	269	N	8.3	0.055	1.26	(Styszko et al., 2015)
		Mt.-K30	NA	330	N	6.8	0.112	1.74	
		Pal./Mt.	15.0[b]	130.3[b]	N	NA	0.57	3.35	(Harker, 2018)
		Pal./Mt. (300°C)	NA	NA	N	NA	0.50	3.26	
		Pal./Mt. (500°C)	NA	NA	N	NA	0.61	3.39	
		LECA	9.5[c]	11.5[d]	N	NA	0.013	0.17	(Dordio, Estêvão Candeias, et al., 2009)
Chloramphenicol	323.1	Mt.-K10	89[e]	183.2[e]	A	NA	0.71	NA	(Lawal & Moodley, 2015)
Chlortetracycline	478.9	Mt.-K10	42.9	NA	Z	5.5	16.7	3.01	(Figueroa et al., 2004)
Cinnamic Acid	148.2	Mt.-K10	NA	220	A	6	14.1	1.21	(Calabrese et al., 2017)
Ciprofloxacine	331.3	Mt.-K10	119	NA	Z	7.4	37.3	2.51	(Hamilton et al., 2014)
Diclofenac	296.2	Mt.-K10	NA	269	A	8.3	0.026	0.96	(Styszko et al., 2015)
		Mt.-K30	NA	330	A	6.8	0.128	2.24	
		Bent. (500°C)	NA	NA	A	NA	0.102	1.11	(Maia et al., 2017)
		Bent. (750°C)	NA	NA	A	NA	0.026	0.47	
Diphenydramine	291.8	Pal./Mt.	15.0[b]	130.3[b]	C	NA	1.42	4.28	(Harker, 2018)
		Pal./Mt. (300°C)	NA	NA	C	NA	1.35	4.17	
		Pal./Mt. (500°C)	NA	NA	C	NA	1.60	4.75	
Furosemide	330.7	LECA	9.5[c]	11.5[d]	A	NA	0.004	1.01	(Machado et al., 2017)
Gemfibrozil	250.3	Exp-Verm.	NA	NA	A	7	0.42	0.67	(Dordio et al., 2017)
		LECA	9.5c	11.5[d]	A	7	0.008	0.08	
Ibuprofen	206.3	Mt.-K10	NA	269	A	8.3	0.080	1.38	(Styszko et al., 2015)
		Mt.-K30	NA	330	A	6.8	0.160	2.01	
		LECA	9.5[c]	11.5[d]	A	NA	0.014	-0.06	(Dordio, Estêvão Candeias, et al., 2009)
Ketoprofen	254.3	Mt.-K10	NA	269	A	8.3	0.020	0.76	(Styszko et al., 2015)
		Mt.-K30	NA	330	A	6.8	0.116	1.85	
Mefenamic Acid	241.3	Exp-Verm.	NA	NA	A	7	0.84	0.68	(Dordio et al., 2017)
		LECA	9.5[c]	11.5[d]	A	7	0.010	0.06	
Metronidazole	171.2	Mt.-K10	NA	NA	C	2	25	3.81	(Calabrese et al., 2013)
		Mt.-K10	NA	NA	N	5	8	3.35	
		LECA	9.5[c]	11.7[d]	N	7	32.9	2.99	(Kalhori et al., 2017)
Nalidixic Acid	232.2	Mt.-K10	89[e]	183.2[e]	A	NA	3.87	NA	(Lawal & Moodley, 2018)
Naproxen	230.3	Exp-Verm.	NA	NA	A	7	0.03	0.41	(Dordio et al., 2017)
		LECA	9.5[c]	11.5[d]	A	7	0.007	0.12	
Ofloxacin	361.4	Hall. (2M HCl)	NA	40.3	CZ	4.5	11.6	1.53	(Q. Wang et al., 2014)
		Hall. (6M HCl)	NA	39.9	CZ	4.3	11.1	1.52	
		Hall. (12M HCl)	NA	37.9	CZ	4.2	10.5	1.48	
		Hall. (300°C)	NA	NA	CZ	5.1	8.4	1.34	
		Hall. (400°C)	NA	NA	CZ	5.1	7.6	1.28	
		Hall. (500°C)	NA	NA	CZ	4.7	4.3	0.97	
Oxytetracycline	460.4	Mt.-K10	42.9	NA	Z	5.5	7.2	2.55	(Figueroa et al., 2004)
Promethazine	284.4	Mt.-KSF	65.2[a]	36[a]	C	3.5	30	3.82	(Seki & Yurdakoç, 2006)
		Mt.-K10	NA	NA	C		25.2	3.91	(Gereli, Seki, Murat Kuşoğlu, & Yurdakoç, 2006)
Propranolol	259.3	Bent. (500°C)	NA	NA	C	NA	0.946	4.67	(Maia et al., 2017)
		Bent. (750°C)	NA	NA	C	NA	0.411	1.92	
Sulfamethoxazole	253.3	Mt.-K10	89[e]	183.2[e]	A	NA	34.5	NA	(Lawal & Moodley, 2018)
Tetracycline	444.4	Mt.-K10	89[e]	183.2[e]	ZA	NA	34.2	NA	(Lawal & Moodley, 2018)
		Mt.-K10	42.9	NA	Z	5.5	11.2	2.78	(Figueroa et al., 2004)
		Mt.-KSF	65.2[a]	4.8	Z	7	63.4	3.61	(Y. Liu, Lu, Wu, & Deng, 2011)
Trimethoprim	290.3	Mt.-KSF	65.2[a]	36[a]	C	3	25.2	3.10	(Bekçi, Seki, & Yurdakoç, 2006)
Venlafaxin	277.4	Exp-Verm.	38	9	C	NA	1.40	2.87	(Silva et al., 2018)

†in the event of the coexistence of several charge states, the most important one is presented first, for example CN corresponds to mostly cationic and to a lesser extent neutral

With [a](Ait-Akbour, Boustingorry, Leroux, Leising, & Taviot-Guého, 2015),[b](Berhane et al., 2015) [c](Drizo et al., 1999), [d](Kalhori, Yetilmezsoy, Uygur, Zarrabi, & Shmeis, 2013) and [e](Lawal & Moodley, 2015),

Table 7. Solid/water partition (Log K_d)of PPs onto clay minerals, with Sorption mechanism the main adsorption mechanisms of PP onto clay minerals, Adsorbent the main clay species and compensating cation, Temp, the interaction temperature (RT is room temperature), Log K_d the solid water partition of PP, and NA for non-available data.

Sorption Mechanism	PP	Adsorbent	Temp (°C)	Log(K_d)	Reference
Cation Exchange	Amitryptiline	Na-Kaol	23	1.61	(Lv et al., 2013)
			33	1.67	
			43	1.73	
			53	1.78	
		Ca-Mt.	30	3.84	(Chang et al., 2014)
			45	4.02	
			60	4.15	
		Ca-Pal.	30	1.88	(Y.-L. Tsai et al., 2016)
			40	1.93	
			50	1.98	
	Atenolol	Na-Kaol.	22	1.22	(Hu et al., 2015)
			32	1.13	
			42	1.06	
	Ciprofloxacin	Ca-Hall.	25	1.75	(W.-T. Jiang et al., 2016)
			45	1.66	
			65	1.57	
		Pal-Mt	25	2.03	(Berhane, Levy, Krekeler, & Danielson, 2016)
			40	2.12	
			65	2.26	
	Chlorpheniramine	Ca-Hall.	25	1.67	(W.-T. Jiang et al., 2016)
			45	1.36	
			65	1.05	
	Diphenydramine	Ca-Hall.	25	1.84	(W.-T. Jiang et al., 2016)
			45	1.21	
			65	0.58	
	Doxepin	Na-Mt.	20	1.67	(Thiebault et al., 2015)
			40	1.47	
	Metoprolol	Ca-Mt.	25	2.46	(Z. Li et al., 2019)
			45	2.33	
			60	2.32	
	Promethazine	Ca-Mt.	18	3.85	(Salihi & Mahramanlıoğlu, 2014)
			25	3.96	
			37	4.12	
		Mt K10	18	3.91	(Gereli et al., 2006)
			25	3.87	
			30	3.89	
		Mt KSF	17	4.02	(Seki & Yurdakoç, 2006)
			25	3.81	
			37	3.97	
	Ranitidine	Ca-Pal.	22	2.54	(Z. Li et al., 2016)
			32	2.39	
			42	2.35	
	Tramadol	Na-Mt.	20	1.78	(Thiebault et al., 2015)
			40	1.76	
		Ca-Mt.	30	1.73	(Y. Chen et al., 2010)

			40	1.76	
			50	1.79	
			60	1.77	
	Tetracycline	Ca-Hall.	25	1.52	(W.-T. Jiang et al., 2016)
			45	2.22	
			65	2.92	
		Ca-Pal.	25	2.80	(Chang, Li, Yu, et al., 2009)
			40	3.66	
			55	3.99	
	Triflupromazine	Ca-Mt.	18	3.70	(Salihi & Mahramanlıoğlu, 2014)
			25	3.79	
			37	4.11	
	Trimethoprim	Ca-Mt.	18	3.42	(Salihi & Mahramanlıoğlu, 2014)
			25	3.31	
			37	3.31	
		Mt KSF	30	3.10	(Bekçi et al., 2006)
			38	2.58	
			45	2.46	
Physisorption	Carbamazepine	Pal.-Mt.	25	2.13	(Berhane et al., 2015)
			40	1.91	
			60	1.43	
		Ca-Mt.	15	4.00	(Khazri et al., 2017)
			30	3.65	
			50	3.49	
		Ca-Mt.	18	3.03	(Salihi & Mahramanlıoğlu, 2014)
			25	2.89	
			37	2.83	
	Ibuprofen	Ca-Mt.	15	3.51	(Khazri et al., 2017)
			30	3.34	
			50	3.07	
		Ca-Mt.	18	2.83	(Salihi & Mahramanlıoğlu, 2014)
			25	2.12	
			37	1.79	
	Naproxen	Ca-Mt.	15	3.59	(Khazri et al., 2017)
			30	3.19	
			50	3.06	

Table 8. Solid/water partition (Log K_d) of PPs onto clays and activated clay minerals as a function of the competing inorganic cation, with Charge the charge state of PP at the tested pH (with C for cationic, Z for zwitterionic, A for anionic and N for neutral charge state), Cl. Min. the principal clay type and compensating cations with C_{Salt} the concentration of inorganic cation, Salt/PP the ratio between inorganic cation concentration and PP concentration

Sorption mechanism	Cations	PP	Charge†	Cl. Min.	C_{Salt} mM	Salt/PP	log(K_d)	Reference
Cation exchange	Na^+	Amitryptiline	C	Na-Kaol.	10	12.5	1.56	(Lv et al., 2013)
					100	125	1.38	
					1,000	1,250	1.13	
		Amitryptiline	C	Ca-Mt.	1	0.78	3.59	(Chang et al., 2014)
					10	7.8	3.66	
					100	78	3.47	
					1,000	780	3.15	
		Amitryptiline	C	Ca-Pal.	1	0.63	2.43	(Y.-L. Tsai et al., 2016)
					10	6.3	2.44	
					100	63	2.47	
					1,000	630	2.52	
		Atenolol	C	Na-Kaol.	0.1	0.05	1.60	(Hu et al., 2015)
					1	0.5	1.35	
					10	5	0.73	
					100	50	0.37	
					1,000	500	-0.59	
		Metoprolol	C	Ca-Mt.	10	8.55	5.67	(Z. Li et al., 2019)
					50	42.7	4.94	
					100	85.5	4.75	
					500	427	4.51	
					1,000	855	4.54	
		Metoprolol	C	Na-Kaol.	0.1	0.1	1.02	(Z. Li et al., 2015)
					1	1	0.73	
					10	10	0.50	
					100	100	-0.12	
					1,000	1,000	-0.38	
		Ranitidine	C	Ca-Pal.	0.1	0.08	2.58	(Z. Li et al., 2016)
					1	0.8	2.61	
					10	8	2.54	
					100	80	2.32	
					1,000	800	2.10	
		Oxytetracycline	Z	Mt.-K10	10	43	2.55	(Figueroa et al., 2004)
					110	478	2.53	
					510	2,217	2.45	
		Oxytetracycline	Z	Na-Kaol.	10	43	2.54	
					110	478	1.88	
					510	2,217	2.17	
		Tetracycline	Z	Ca-Ill.	10	11	2.05	(Chang et al., 2012)
					100	111	2.00	
					1,000	1,111	1.52	
		Tetracycline	Z	Na-Kaol.	1	1	1.77	(Z. Li et al., 2010)
					10	10	1.69	
					100	100	1.45	
		Tetracycline	Z	Ca-Pal.	1	2.2	2.96	(Chang, Li, Yu, et al., 2009)
					10	22	2.75	
					100	220	2.41	
		Tetracycline	ZP	Na-Mt.	0.1	0.13	3.17	(Parolo et al., 2008)
					1	1.3	3.15	
					10	13	3.11	
					100	130	2.96	
					1,000	1,300	2.73	
		Tetracycline	ZA	Na-Mt.	0.1	0.13	2.74	
					1	1.3	2.72	
					10	13	2.70	
					100	130	2.58	
					1,000	1,300	2.39	
	Ca^{2+}	Enrofloxacin	C	Ca-Mt.	0	-	2.84	(Rivagli et al., 2014)
					10	2.4	2.27	
		Enrofloxacin	Z	Ca-Mt.	0	-	3.05	

					10	2.4	2.23	
		Enrofloxacin	C	Na-Mt.	0	-	2.56	
					10	2.4	2.11	
		Enrofloxacin	Z	Na-Mt.	0	-	2.36	
					10	2.4	2.38	
		Enrofloxacin	P	Na-Kaol.	0	-	1.18	
					10	2.4	0.82	
		Enrofloxacin	Z	Na-Kaol.	0	-	1.26	
					10	2.4	0.80	
		Lincomycin	C	Ca-Mt	0	-	3.50	(C. Wang et al., 2009)
					10	4,000	2.42	
					50	20,000	2.28	
		Marbofloxacin	C	Ca-Mt.	0	-	2.72	(Rivagli et al., 2014)
					10	2.3	2.38	
		Marbofloxacin	Z	Ca-Mt.	0	-	2.55	
					10	2.3	2.12	
		Marbofloxacin	C	Na-Mt.	0	-	2.76	
					10	2.3	2.71	
		Marbofloxacin	Z	Na-Mt.	0	-	2.33	
					10	2.3	2.10	
		Marbofloxacin	C	Na-Kaol.	0	-	1.15	
					10	2.3	0.78	
		Marbofloxacin	Z	Na-Kaol.	0	-	1.11	
					10	2.3	0.77	
	Cu^2	Ciprofloxacin	C	Na-Mt.	0	-	4.82	(Pei et al., 2010)
					0.1	1	4.82	
		Ciprofloxacin	Z	Na-Mt.	0	-	3.86	
					0.1	1	4.82	
		Ciprofloxacin	C	Na-Kaol.	0	-	2.39	
					0.1	1	2.03	
		Ciprofloxacin	Z	Na-Kaol.	0	-	2.08	
					0.1	1	2.14	
		Norfloxacin	C	Na-Mt.	0	-	∞	(Pei et al., 2011)
					0.15	0.7	∞	
		Norfloxacin	Z	Na-Mt.	0	-	4.52	
					0.15	0.7	4.86	
		Tetracycline	Z	Ca-Mt.	0	-	2.77	(Y.-J. Wang, Jia, Sun, Zhu, & Zhou, 2008)
					0.25	0.025	2.88	
	K^+	Enrofloxacin	C	K-Mt.	10	200	4.99	(Yan, Hu, & Jing, 2012)
					50	1,000	4.65	
					100	2,000	4.15	
		Oxytetracycline	ZC	Na-Mt.	0	-	3.37	(Aristilde et al., 2016)
	Ca^{2+}				0.32	1	3.65	
	Mg^{2+}				0.32	1	3.43	
		Oxytetracycline	Z	Na-Mt.	0	-	2.65	
	Ca^{2+}				0.32	1	3.11	
	Mg^{2+}				0.32	1	3.09	
		Oxytetracycline	AZ	Na-Mt.	0	-	2.28	
	Ca^{2+}				0.32	1	2.80	
	Mg^{2+}				0.32	1	2.78	
Physisorption	Na^+	Ibuprofen	NA	Kaol.	1	3.4	1.75	(Behera et al., 2012)
					5	17	1.79	
					10	34	1.81	
					50	170	1.83	
					100	340	1.84	
					500	1,700	1.87	
		Ibuprofen	A	Kaol	1	3.4	1.41	
					5	17	1.41	
					10	34	1.46	
					50	170	1.46	
					100	340	1.48	
					500	1,700	1.49	
		Ibuprofen	NA	Mt.	1	3.4	2.11	
					5	17	2.12	
					10	34	2.13	
					50	170	2.19	
					100	340	2.26	
					500	1,700	2.42	
		Ibuprofen	A	Mt.	1	3.4	1.88	
					5	17	1.89	
					10	34	1.92	
					50	170	1.93	
					100	340	2.03	
					500	1,700	2.05	

	Triclosan	N	Kaol.	1	4.8	2.03	(Behera et al., 2010)
				5	24	1.96	
				10	48	2.02	
				50	240	1.98	
				100	480	2.60	
				500	2,400	2.84	
	Triclosan	A	Kaol	1	4.8	1.54	
				5	24	1.53	
				10	48	1.54	
				50	240	1.56	
				100	480	1.64	
				500	2,400	1.81	
	Triclosan	N	Mt.	1	4.8	2.21	
				5	24	2.21	
				10	48	2.25	
				50	240	2.30	
				100	480	2.35	
				500	2,400	3.01	
	Triclosan	A	Mt.	1	4.8	1.13	
				5	24	1.13	
				10	48	1.44	
				50	240	1.54	
				100	480	1.56	
				500	2,400	1.58	
Ca^{2+}	Carbamazepine	N	Pal.-Mt	0	-	1.92	(Berhane et al., 2015)
				0.1	2.4	2.07	
				10	240	2.08	
				100	2,400	2.26	
Cu^{2+}	Ciprofloxacin	A	Na-Kaol.	0	-	1.55	(Pei et al., 2010)
				0.1	1	2.39	
	Ciprofloxacin	A	Na-Mt.	0	-	3.13	
				0.1	1	3.95	
	Norfloxacin	AZ	Na-Mt.	0	-	3.33	(Pei et al., 2011)
				0.15	0.7	4.32	
	Tetracycline	A	Kaol.	0	-	3.39	(Zhao et al., 2011)
				0.1	0.9	3.80	
CO_3^{2-}	Metronidazole	N	Exp.-Verm.	1.7	7	3.02	(Kalhori et al., 2017)
				2.5	11	2.98	
				5	21	2.97	
NO_3^-	Metronidazole	N	Exp.-Verm.	0.4	1.7	2.91	
				0.8	3.4	2.93	
				1.2	5.1	2.98	

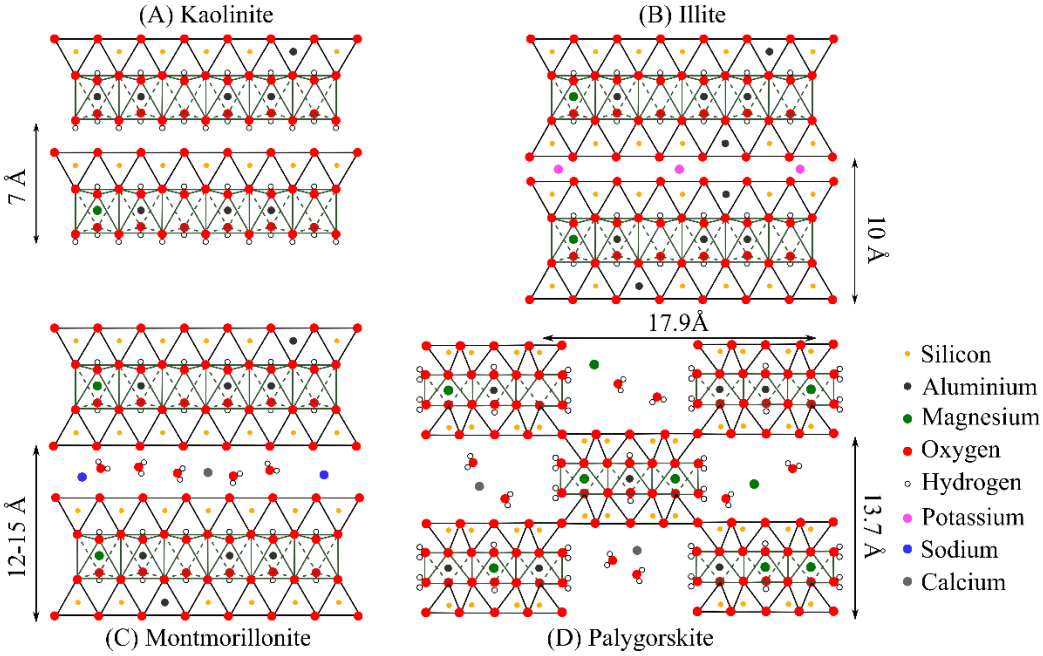


Figure 1. Examples of different layer structures of clay minerals with (A), kaolinite (1:1), (B), illite (non-expanded 2:1), (C), smectite (expanded 2:1) and (D), palygorskite (fibrous 2:1).

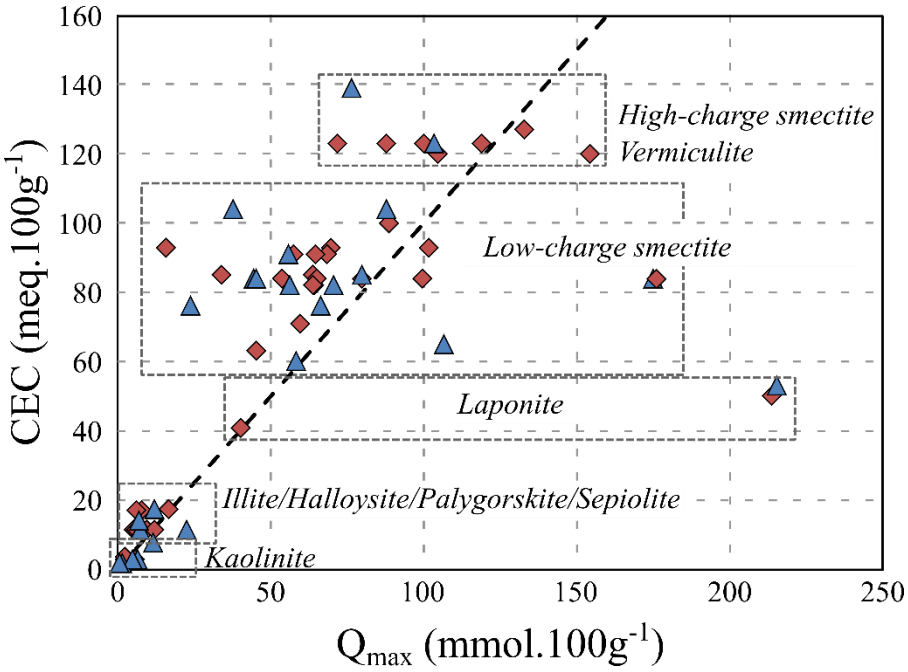


Figure 2. Maximum adsorbed amount of zwitterionic (blue triangles) and cationic (red diamonds) PPs as a function of the CEC of adsorbent, only values with C_{max}/CEC > 0.8 from Table 2 are displayed.

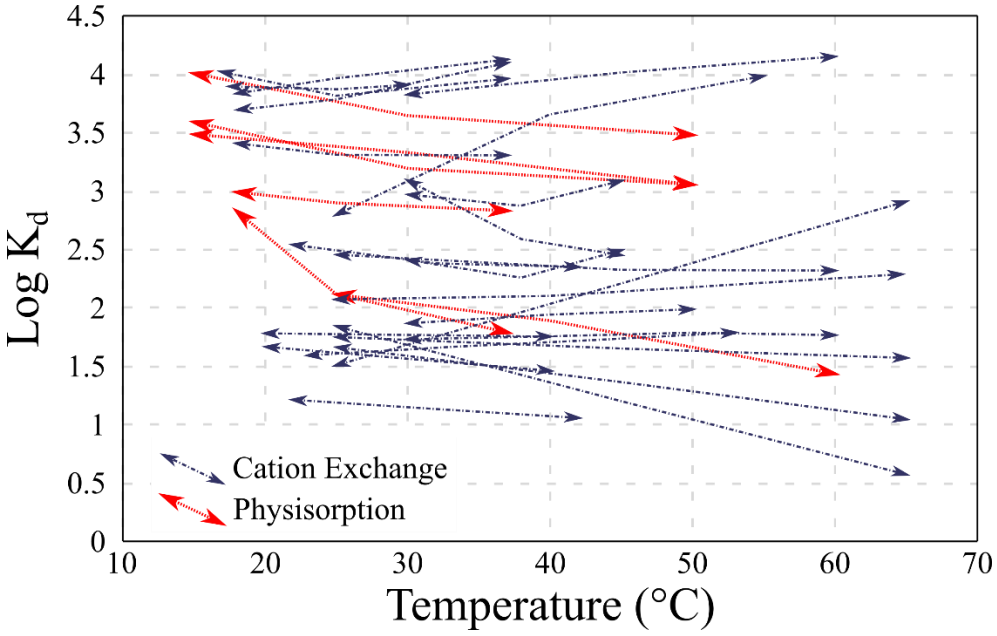


Figure 3. Impact of the temperature on the variation of the solid/water partition (Log K_d) of PP onto adsorbent as a function of the sorption mechanisms, with cation exchange (blue dashed lines) and physisorption (red dashed lines), raw data and references are available in Table 7.

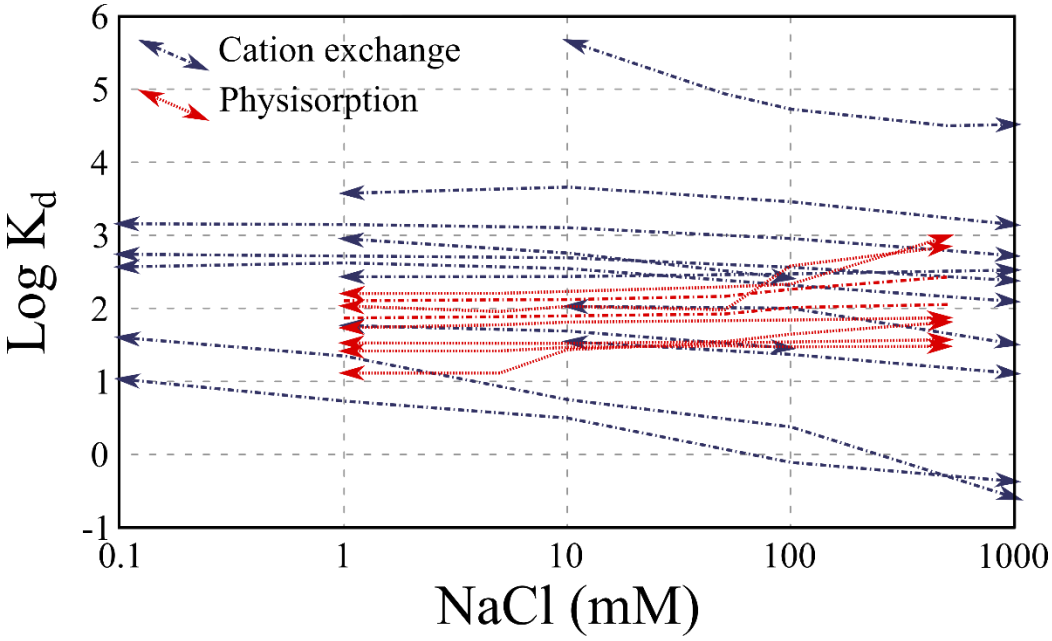


Figure 4. Impact of NaCl concentration (in mM) on the solid/water partition of PP (Log K_d) onto adsorbent as a function of the adsorption mechanism with cation exchange (blue dashed lines) and physisorption (red dashed lines), raw data and linked references are available in Table 8.

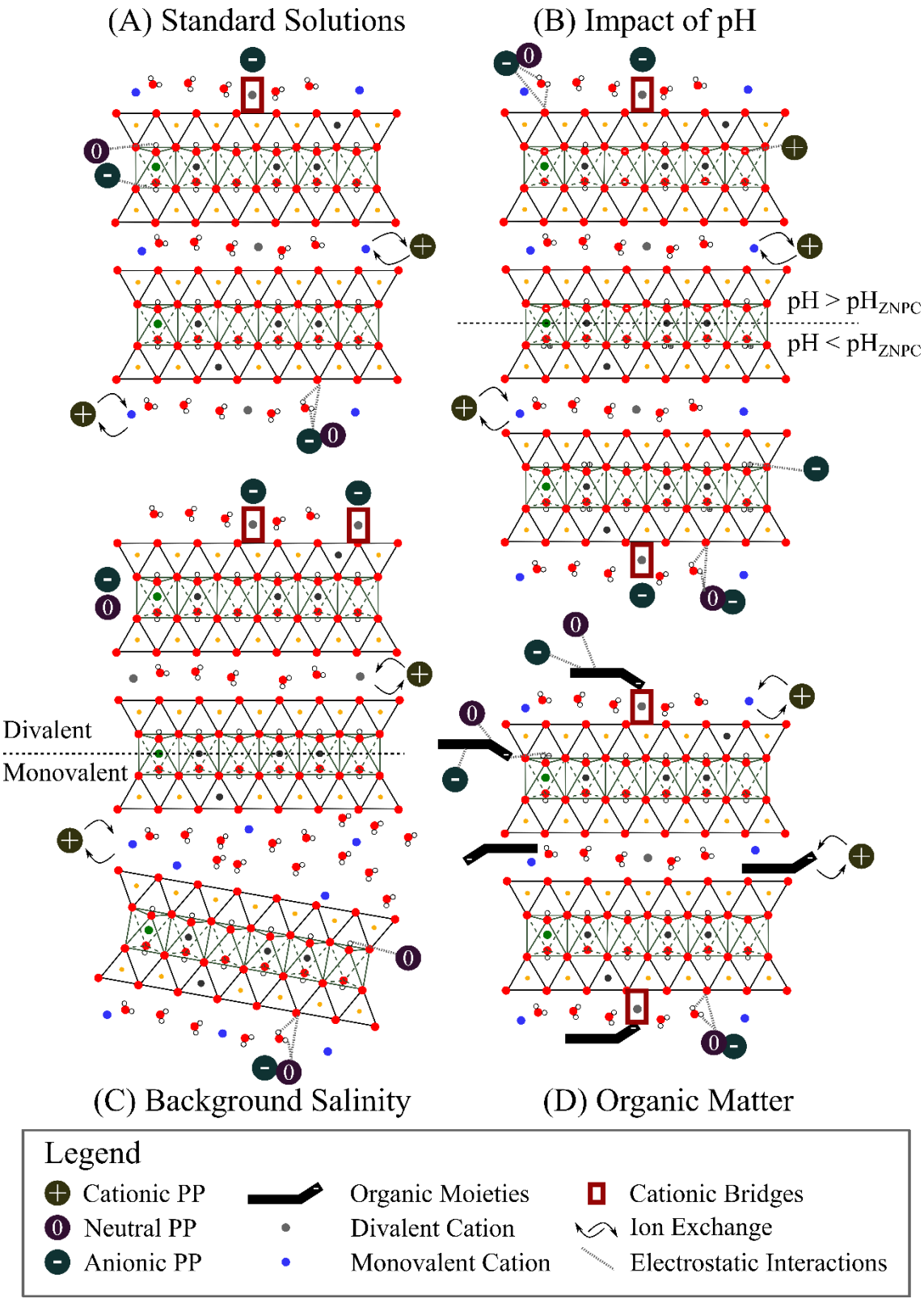


Figure 5. Schematic representation of the impact of the enrichment of the solution from standard solution (A), to impacts of pH (B), background salinity (C) and organic matter (D) on the adsorption mechanisms of PPs for different charge states

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