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Clay minerals for the removal of pharmaceuticals: Initial investigations of their adsorption properties in real wastewater effluents

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Abstract

The adsorption of pharmaceutical products (PPs) onto kaolinite and raw and sodium-exchanged montmorillonite was investigated in real wastewater effluents (WWE). The important role of the charge state of the PPs in controlling the adsorption extent was highlighted. Whereas cationic PPs were mostly adsorbed through cation exchange, the adsorption of neutral and anionic PPs appeared to be controlled by the nature of compensating inorganic cations and/or the simultaneous adsorption of organic moieties onto clay minerals. In raw WWE, the concentration of PPs is indeed far lower than the concentration of other organic molecules. Among the adsorbents tested, kaolinite displayed the lowest adsorption capacity of both PPs and other organic molecules, compared to raw montmorillonite which presented the highest adsorption capacity. The sodium-exchanged montmorillonite displayed intermediate adsorption properties, highlighting the key role of divalent inorganic cations in the adsorption of non-cationic PPs and other organic molecules. Hence, raw

25 montmorillonite appears to be the most promising adsorbent for further investigations aiming to
26 test the practicability of a clay-based adsorbent for the removal of organic contaminants, such as
27 PPs, in WWE.

28 **Keywords**

29 Pharmaceutical Products, Clay minerals, Adsorption, Wastewater Treatment, Organic Matter

30 **1. Introduction**

31 The occurrence of pharmaceutical products (PPs) in numerous environmental compartments (da
32 Silva et al., 2011; Patel et al., 2019) raises serious concerns about their potential hazard for living
33 organisms (Richmond et al., 2018; Saaristo et al., 2018). Contamination by PPs is mostly generated
34 by excretion through urine and feces following both human and veterinary uses (Baker et al., 2014;
35 Choi et al., 2018). Then, PP-contaminated wastewaters are transferred toward wastewater treatment
36 plants, in which current treatment chains remain inappropriate for their complete removal
37 (Grandclément et al., 2017; Petrie et al., 2015). This contamination therefore challenges the
38 scientific community and water treatment operators in order to find efficient and economically
39 practicable removal solutions. Among the innovative treatments for the removal of organic
40 contaminants, adsorption is considered as a promising way if the selected adsorbent displays a high
41 adsorption capacity and moderate cost (de Andrade et al., 2018). Most of the literature focuses on
42 activated carbons, which are currently used for the treatment of drinking water (Cuthbertson et al.,
43 2019; Wong et al., 2018), even though the potential of clay minerals for the removal of organic
44 contaminants has already been demonstrated (Thiebault, 2019; Zhu et al., 2016). Moreover, clay
45 minerals can be considered as cheap and widely available materials. Yet, several studies pointed
46 out their limitations for the adsorption of non-cationic PPs (Gao and Pedersen, 2005; Zhang et al.,
47 2010). These limitations, however, were mostly found during batch experiments, in which the

48 starting concentration of PPs was much higher than their environmental occurrences, and in
 49 idealized solutions (i.e. pure water, no competing compounds). Several studies have recently
 50 demonstrated that the affinity of anionic and neutral PPs with clay minerals can be improved in the
 51 presence of other organic moieties (de Oliveira et al., 2017; Wu et al., 2019). Therefore, it appears
 52 necessary to assess as precisely as possible the potential of a clay-based solution for the removal
 53 of PPs in real WWE in order to determine the affinity of such contaminants with adsorbents and to
 54 evaluate which type of clay minerals would be the most versatile for the design of a removal
 55 solution. The purpose of this work was therefore to investigate the PP removal potential of three
 56 clay minerals in raw WWE.

57 2. Material and methods

58 2.1. Chemical reagents and adsorbents

59 Standards for atenolol (ATE), bezafibrate (BZB), carbamazepine (CBZ), codeine (COD),
 60 diazepam (DIA), diclofenac (DCF), doxepin (DOX), gemfibrozil (GEM), ketoprofen (KET),
 61 naproxen (NAP), metoprolol (MET), norfloxacin (NOR), oxazepam (OXA), sulfamethoxazole
 62 (SUL), tramadol (TRA) and trimethoprim (TMP) were purchased from Sigma-Aldrich with a
 63 purity > 98%. Separation solvents, methanol (MeOH) and acetonitrile (AcN) were purchased from
 64 Fisher-Scientific, assuming an analytical grade (purity higher than 99.95 %).

65 Table 1: Physico-chemical properties of the targeted PPs, with Abb. the abbreviation, M_w the molecular
 66 weight in $\text{g}\cdot\text{mol}^{-1}$, pK_a the acid dissociation constant, $\log K_{ow}$ the octanol/water partition coefficient, S_w the
 67 solubility in water at 25°C in $\text{mg}\cdot\text{L}^{-1}$, and Charge the dominant form at the effluent pH (i.e. = 6.4)

PP	Abb.	Formula	CAS-Number	M_w	pK_a^a	$\log K_{ow}^b$	S_w^a	Charge
Atenolol	ATE	$\text{C}_{14}\text{H}_{22}\text{N}_2\text{O}_3$	29122-68-7	266.3	9.6	0.16	430	+
Bezafibrate	BZB	$\text{C}_{19}\text{H}_{20}\text{ClNO}_4$	41859-67-0	361.8	3.9	4.25	1.5	-
Carbamazepine	CBZ	$\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}$	298-46-4	236.3	13.9	2.45	152	0
Codeine	COD	$\text{C}_{18}\text{H}_{21}\text{NO}_3$	76-57-3	299.4	8.2	1.28	577	+
Diazepam	DIA	$\text{C}_{16}\text{H}_{13}\text{ClN}_2\text{O}$	439-14-5	284.7	3.4	2.70	50	0
Diclofenac	DCF	$\text{C}_{14}\text{H}_{11}\text{Cl}_2\text{NO}_2$	15307-79-6	296.1	4.2	4.02	4.5	-
Doxepin	DOX	$\text{C}_{19}\text{H}_{21}\text{NO}$	1229-29-4	279.4	9.0	3.86	32	+
Gemfibrozil	GEM	$\text{C}_{15}\text{H}_{22}\text{O}_3$	25812-30-0	250.3	4.8	4.33	28	-
Ketoprofen	KET	$\text{C}_{16}\text{H}_{14}\text{O}_3$	22071-45-4	254.3	4.4	3.00	21	-
Metoprolol	MET	$\text{C}_{15}\text{H}_{25}\text{NO}_3$	56392-17-7	267.4	9.6	1.69	502	+
Naproxen	NAP	$\text{C}_{14}\text{H}_{14}\text{O}_3$	22204-53-1	230.3	4.2	3.10	16	-

Norfloxacin	NOR	C ₁₆ H ₁₈ FN ₃ O ₃	70458-96-7	319.3	5.7-8.7	-0.31	1,010	+/-
Oxazepam	OXA	C ₁₅ H ₁₁ ClN ₂ O ₂	604-75-1	287.0	1.7-11.6	3.34	88	0
Sulfamethoxazole	SUL	C ₁₀ H ₁₁ N ₃ O ₃ S	723-46-6	253.3	6.2	0.48	459	-
Tramadol	TRA	C ₁₆ H ₂₅ NO ₂	27203-92-5	263.4	9.4	3.01	750	+
Trimethoprim	TMP	C ₁₄ H ₁₈ N ₄ O ₃	738-70-5	290.3	7.2	0.73	615	+/-0

68 With ^adrugbank.ca and ^bchemspider.com (predicted KOWWIN v.1.67)

69
70 The selected adsorbents were Georgia kaolinite KGa-2 and Wyoming smectite SWy-2 both
71 obtained from the Source Clay Minerals Repository, University of Missouri (Columbia, MO). The
72 two adsorbents were fractionated < 2µm by gravity sedimentation prior to use in order to limit the
73 impact of mineralogical impurities (Chipera and Bish, 2001). In order to investigate the impact of
74 compensating inorganic cations on the removal capacity of SWy-2, this adsorbent was used raw
75 (~20% of Ca²⁺ and 80% of Na⁺) and Na-exchanged through well-established procedures (Le
76 Forestier et al., 2010).

77 The resulting materials, labelled KGa2, SWy2 and Na-SWy2 display a cation exchange capacity
78 of 3.7, 85 and 85 meq.100g⁻¹ respectively, and a specific surface area of 18, 32 and 32 m².g⁻¹
79 respectively with the N₂ BET method (Le Forestier et al., 2010; Lv et al., 2013).

80 **2.2.Sample collection and batch experiments**

81 10 L of WWE were sampled at the outlet of a vertical-flow constructed wetland in one intake
82 (central part of France). The design of this sewage treatment plant consists of two stages of
83 unsaturated vertical-flow constructed wetlands in series, with the first one planted with *Phragmites*
84 *Australis* (Paing and Voisin, 2005). After collection, WWE were filtered with glass-fiber filters
85 (GF/F, Whatman) prior to storage at 4°C in amber glass bottles.

86 Batch experiments were systematically conducted in triplicate on the day following the sampling.
87 The WWE solutions (200 mL) were put in 250 mL bottles, mixed with 100 or 200 mg of adsorbents
88 (i.e. KGa2, Na-SWy2 and SWy2) and then wrapped in aluminum foil in order to prevent light-
89 induced degradation. The solutions were stirred for 2 hours at 500 rpm with a magnetic stirrer. This

90 time was considered as appropriate to reach equilibrium in such conditions (Thiebault et al.,
91 2016a). A volume of 100 mL of supernatant was recovered by centrifugation at 8,000 rpm during
92 10 minutes prior to the extraction and analysis of the PPs. In parallel, blank experiments (i.e. Blank)
93 were conducted in the same conditions without adsorbent, in order to estimate the initial PP
94 concentration and avoid any misinterpretation due to degradation.

95 **2.3.Quantification and validation**

96 The quantification procedure of PPs, and its validation, were already presented in detail (Thiebault
97 et al., 2019). Briefly, a solid phase extraction was performed on the supernatant using Chromabond
98 HR-X cartridges (6 mL x 500 mg, Macherey-Nagel) prior to analysis and quantification in high
99 pressure liquid chromatography coupled with tandem mass spectrometry. The equipment,
100 analytical procedures and quantification performances are detailed in the supplementary material
101 (Table S1-2).

102 **2.4.Processing of the results and analysis of the adsorbents**

103 The removal of PPs after interaction was calculated using the following equation:

$$104 \quad \text{Removal} = 100 - \left(\frac{100 \times C_{eq}}{C_{st}} \right)$$

105 with the Removal in %, C_{eq} the equilibrium concentration in $\mu\text{g.L}^{-1}$ and C_{st} the starting
106 concentration in $\mu\text{g.L}^{-1}$

107 In order to evaluate the amount of organic matter adsorbed onto the clay minerals after interaction,
108 carbon analyses were performed on powdered samples by using a Thermo Scientific Flash 2000
109 organic analyzer. These analyses were systematically triplicated. XRD and FTIR analysis
110 conditions are given in the supplementary material.

111 **3. Results and Discussion**

112 **3.1.Wastewater effluent basic parameters**

113 The concentrations of PPs and the physico-chemical characterization of the raw WWE were
 114 determined in triplicate experiments. The most concentrated PPs were TRA and DCF with
 115 concentrations of 12.48 and 8.23 $\mu\text{g.L}^{-1}$, respectively. The concentrations of the other PPs mostly
 116 ranged between 0.03 and 1.32 $\mu\text{g.L}^{-1}$ (Table 2).

117 The analysis of the WWE provided the following values: pH = 6.4, Total Organic Carbon content
 118 was 27.6 mg.L^{-1} , P- PO_4 content was 12.0 mg.L^{-1} , N- NO_2 content was 59.2 mg.L^{-1} , Suspended
 119 solids concentration was 5 mg.L^{-1} and the conductivity was 950 $\mu\text{S.cm}^{-1}$.

120 Table 2: Concentrations of the targeted PPs (in $\mu\text{g.L}^{-1}$) in the raw effluent (Blank) and after interaction with
 121 100 and 200 mg of the selected clay minerals, with LOD the limit of detection

PP	Blank	KGa2		Na-SWy2		SWy2	
		100mg	200mg	100mg	200mg	100mg	200mg
ATE	0.55 ± 0.10	0.52 ± 0.16	0.46 ± 0.10	0.40 ± 0.13	0.25 ± 0.00	0.42 ± 0.15	0.23 ± 0.10
BZF	0.19 ± 0.08	0.14 ± 0.03	0.13 ± 0.04	0.12 ± 0.06	0.14 ± 0.09	0.11 ± 0.05	0.05 ± 0.01
CBZ	0.34 ± 0.03	0.34 ± 0.04	0.33 ± 0.04	0.33 ± 0.03	0.34 ± 0.02	0.31 ± 0.06	0.31 ± 0.07
COD	0.03 ± 0.01	0.02 ± 0.01	0.01 ± 0.00	0.00 ± 0.01	< LOD	0.00 ± 0.00	0.00 ± 0.00
DIA	0.03 ± 0.00	0.03 ± 0.00	0.03 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.01 ± 0.01
DCF	8.23 ± 1.69	7.46 ± 0.86	6.87 ± 1.59	8.05 ± 0.59	7.84 ± 1.99	6.91 ± 0.50	5.19 ± 0.42
DOX	0.84 ± 0.09	0.80 ± 0.08	0.67 ± 0.36	0.74 ± 0.26	0.30 ± 0.07	0.50 ± 0.41	0.07 ± 0.02
GEM	0.06 ± 0.02	0.06 ± 0.01	0.06 ± 0.02	0.06 ± 0.02	0.05 ± 0.01	0.05 ± 0.03	0.03 ± 0.01
KET	0.62 ± 0.04	0.58 ± 0.09	0.53 ± 0.11	0.58 ± 0.04	0.53 ± 0.14	0.51 ± 0.06	0.20 ± 0.16
MET	0.07 ± 0.03	0.06 ± 0.01	0.05 ± 0.02	0.04 ± 0.01	0.03 ± 0.02	0.05 ± 0.01	0.03 ± 0.01
NAP	1.32 ± 0.10	1.43 ± 0.31	1.35 ± 0.31	1.38 ± 0.18	1.13 ± 0.87	1.16 ± 0.15	0.58 ± 0.26
NOR	0.92 ± 0.78	0.03 ± 0.03	< LOD	0.12 ± 0.21	< LOD	0.28 ± 0.49	< LOD
OXA	0.16 ± 0.01	0.15 ± 0.01	0.14 ± 0.03	0.15 ± 0.02	0.15 ± 0.03	0.14 ± 0.01	0.12 ± 0.03
SUL	0.00 ± 0.01	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
TRA	12.48 ± 1.04	11.55 ± 0.61	10.6 ± 2.11	2.83 ± 1.35	2.87 ± 0.46	8.37 ± 7.78	3.47 ± 4.30
TMP	0.05 ± 0.02	0.05 ± 0.03	0.05 ± 0.04	0.03 ± 0.02	0.03 ± 0.01	0.04 ± 0.04	0.02 ± 0.01

122

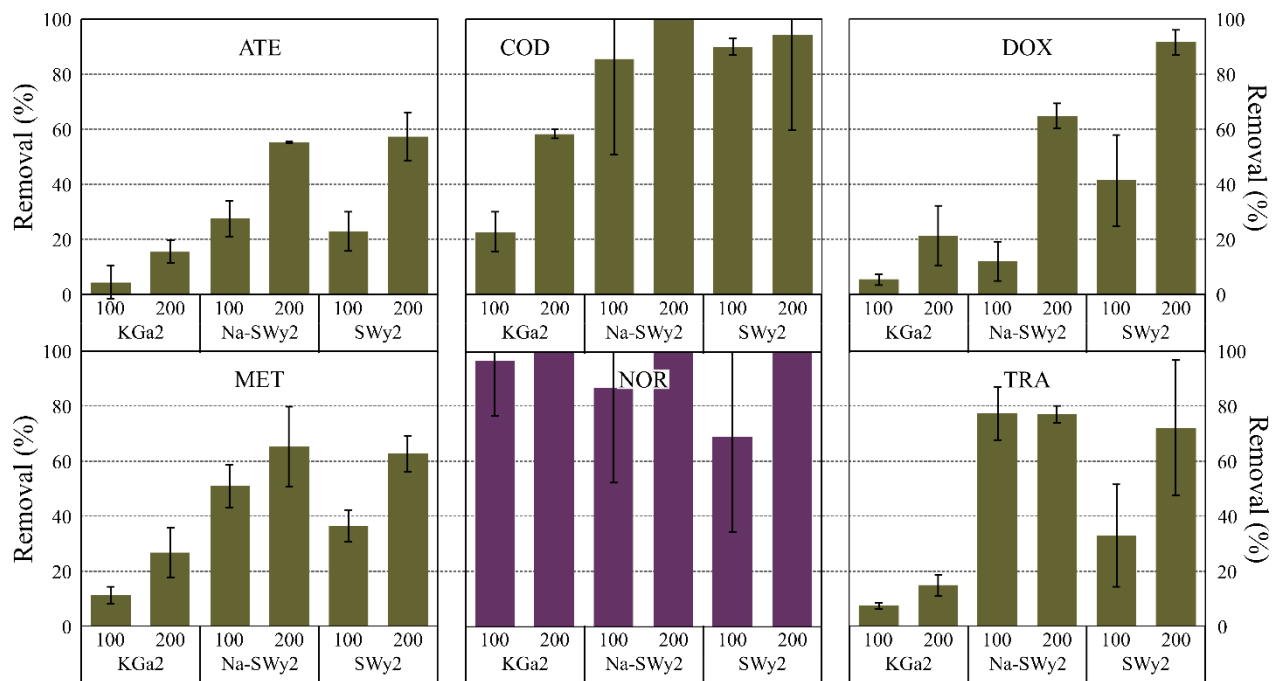
123 **3.2.Removal of PPs from wastewater effluents**

124 Due to the important role of the speciation on the affinity between PPs and clay minerals, the
 125 removal values after interaction with clay minerals are hereafter detailed according to the
 126 theoretical speciation of the PPs (Table 1).

127 **3.2.1. Positively charged PPs**

128 The removal values of cationic and zwitterionic PPs are presented in Figure 1. Except for NOR,
 129 which shows a high removal rate whatever the adsorbent, the removal rates of cationic PPs display

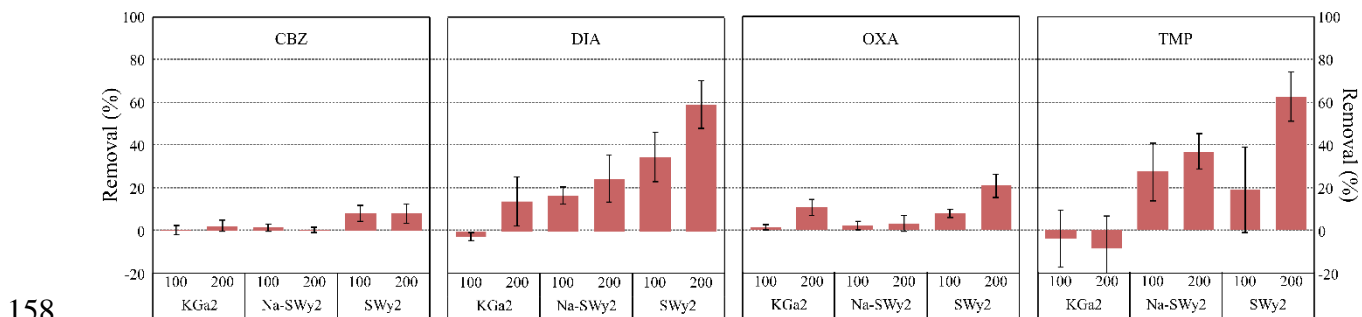
130 the same pattern. The removal is lower after interaction with KGa2, whereas very similar removal
 131 values are found for SWy2 and Na-SWy2. Moreover, increasing the mass of adsorbent increases
 132 the removal values of PPs (Figure 1). In general, with 200 mg of montmorillonite, the removal rate
 133 ranges from 58 to 100 %. Yet, for several cationic PPs such as DOX and TRA, it was expected that
 134 this removal would be total within this range of concentration due to the high affinity between these
 135 PPs and clay minerals, and the adsorption through cation exchange (Chen et al., 2010; Thiebault et
 136 al., 2015). However, the complexity of WWE (e.g. inorganic and organic compounds) associated
 137 with the low starting concentration of PPs in comparison to total organic carbon (i.e. < 0.1%),
 138 appear to strongly hinder the adsorption of cationic PPs, suggesting that the cation exchange
 139 mechanism between compensating inorganic cations and cationic PPs is limited due to the
 140 competition with other compounds for cation exchange (Thiebault et al., 2016b; Wang et al., 2009).



141
 142 Figure 1: Removal percentages of cationic (green bars) and zwitterionic (purple bars) PPs as a function of
 143 the mass of adsorbent (i.e. 100 and 200 mg), n=3
 144

145 3.2.2. Neutral PPs

146 The removal rates of neutral PPs are presented in Figure 2. Various patterns are exhibited as a
 147 function of the PP and/or the mass of adsorbent. TMP is a particular case as its speciation in this
 148 pH range is partially neutral and partially protonated (Table 1). As a result, its behavior appears to
 149 be intermediate between neutral and cationic molecules. CBZ and OXA are poorly adsorbed onto
 150 clay minerals whatever the clay type and the mass of adsorbent; the only significant removal rates
 151 displayed are onto SWy2 (Figure 2). DIA is conversely significantly adsorbed onto the three
 152 adsorbents with higher removal values on increasing the mass of adsorbent, and higher removal
 153 values on SWy2 (i.e. between 5 and 20%) in comparison with the other two adsorbents (i.e.
 154 between 0 and 11%). This variation between PPs with closely related properties highlights the
 155 important role of the starting concentrations of PPs in order to assess their affinity with clay
 156 minerals (Thiebault and Boussafir, 2019), and of the affinity of PPs with organic moieties for the
 157 adsorption onto clay minerals in effluent solutions (Torrents and Jayasundera, 1997).

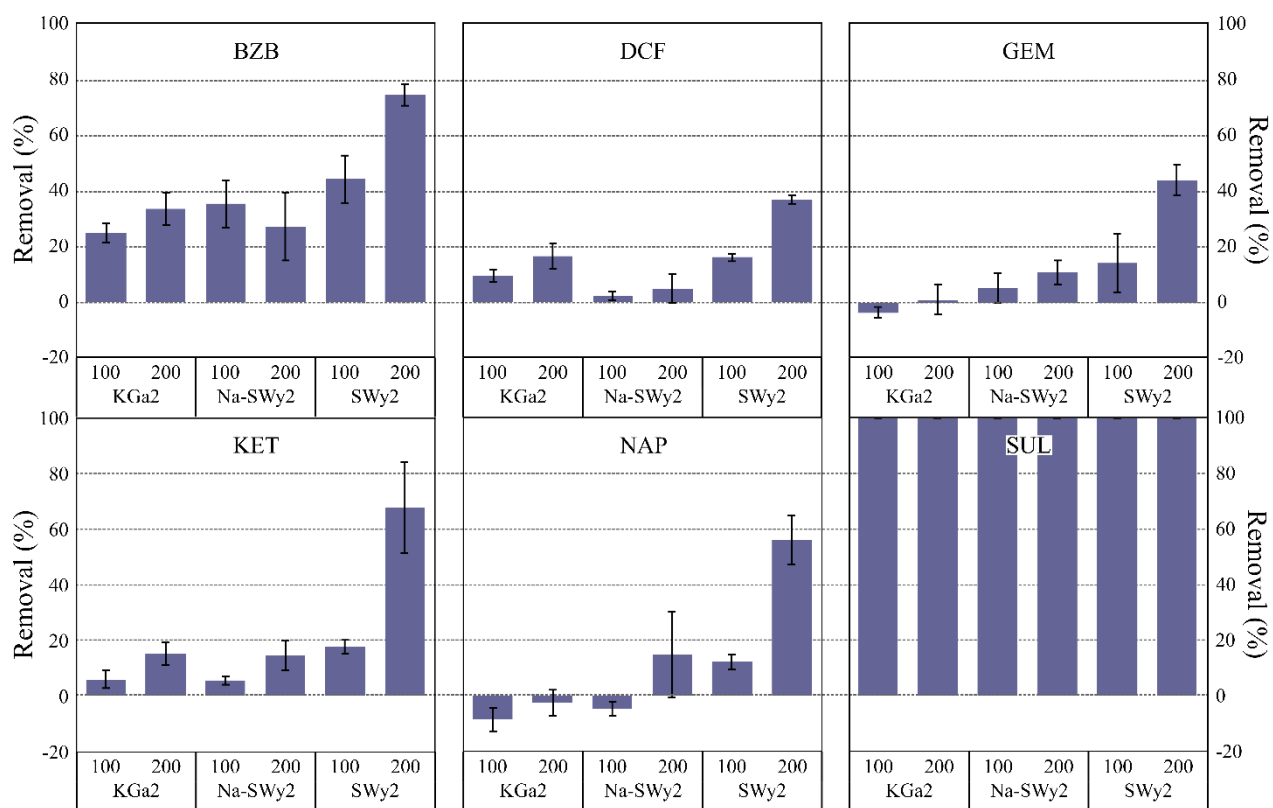


159 Figure 2: Removal percentages of neutral PPs as a function of the mass of adsorbent (i.e. 100 and 200 mg),
 160 n=3

161
 162 **3.2.3. Anionic PPs**

163 The removal rates of anionic PPs are displayed in Figure 3. Only SUL displays a total removal
 164 whatever the adsorbent, mostly due to its very low concentration in the selected effluent (Table 2).
 165 The other PPs present a similar pattern with lower removal rates onto KGa2 and higher rates after
 166 interaction with SWy2. Weak removal variations are displayed between KGa2 and Na-SWy2

167 highlighting the limited affinity of anionic PPs for these two clay minerals. The higher removal
 168 rates observed after interaction with 200 mg SWy2 (i.e. between 38 and 78% except for SUL)
 169 emphasize the impact of the compensating inorganic cations. The only variation between SWy2
 170 and Na-SWy2 is the homogenization of the compensating cations in the latter adsorbent. As a
 171 result, the significant amount of Ca^{2+} in SWy2 (i.e. ~20%) appears to significantly enhance the
 172 adsorption extent of anionic PPs, or the adsorption of organic moieties which may adsorb such PPs
 173 in a second phase.



174
 175 Figure 3: Removal percentages of anionic PPs as a function of the mass of adsorbent (i.e. 100 and 200 mg),
 176 n=3

177 3.3.Adsorbent characterization

178 Prior to characterization, the clay minerals were separated from the supernatant after the interaction
 179 experiment by centrifugation. XRD patterns and FTIR spectra exhibited no significant layer
 180 expansion or band stretching, respectively (data not shown).

181 Table 3: Carbon percentages of raw adsorbents (Raw) and after interaction (i.e. 100 and 200 mg) with the
 182 effluent, n=3

	KGa2	Na-SWy2	SWy2
Raw	0.256 ± 0.02	0.214 ± 0.03	0.312 ± 0.05
100 mg	0.336 ± 0.03	0.648 ± 0.04	1.027 ± 0.05
200 mg	0.341 ± 0.05	0.581 ± 0.07	0.959 ± 0.06

183

184 The organic carbon content adsorbed onto clay after interaction was estimated from the elemental
 185 analyses. This bonded organic carbon can be either PPs or organic complexes present in the WWE.
 186 All the clay minerals display an increase in the carbon content in comparison with the initial
 187 composition (Table 3). Moreover, due to the weak concentration of PPs in the raw effluents in
 188 comparison with the total organic carbon content (i.e. < 0.1%), it is highly possible that most of the
 189 adsorbed organic carbon was generated by other organic compounds, thus masking the PP
 190 contribution to the whole carbon content. The carbon content after interaction ranges from 0.34 %
 191 (or 0.08 % if we consider the carbon content of the raw adsorbent) for KGa2 to ~1 % (or 0.7% if
 192 we consider the carbon content of the raw adsorbent) for SWy2 (Table 3). On increasing the mass
 193 of adsorbent from 100 to 200 mg, the carbon content of the adsorbents did not significantly vary,
 194 highlighting that the adsorption of organic moieties onto these adsorbents may be controlled by the
 195 solid/water partition. Therefore, an increase in the mass of adsorbent proportionally increases the
 196 amount of organic carbon adsorbed. From a global point of view, the displayed pattern is equivalent
 197 for PP removal and carbon analyses. The adsorption is weak onto KGa2 whereas it is higher onto
 198 SWy2, emphasizing the important role of the properties of the adsorbent, and the impact of the
 199 inorganic compensating cations.

200 **3.4.Comparative efficiency of clay minerals**

201 The removal capacity of the three selected clay minerals appears to be enhanced when a higher
 202 mass of adsorbent is used. This is consistent with previous studies, which emphasized the

203 contribution of the solid liquid partition coefficient in the adsorption of non-cationic PPs (Stein et
204 al., 2008). Hence, the higher the solid/liquid ratio of adsorbent, the higher the removal rate.
205 However, significant variations are found in the efficiency of the tested adsorbents. KGa2 presents
206 the lowest adsorption capacities of all the targeted PPs, whatever their charge state. This is probably
207 due to its weak CEC and SSA, limiting the affinity with organic moieties in comparison with
208 montmorillonites. Between SWy2 and Na-SWy2, the adsorption performance of the latter is
209 slightly better for the removal of cationic PPs whereas the opposite pattern is displayed for neutral
210 and anionic PPs. This can be attributed to the fact that the compensating inorganic cations of SWy2
211 are not only Na⁺, but also Ca²⁺ in a significant proportion, allowing the formation of cationic
212 bridges with negatively charged organic moieties such as anionic PPs, or organic complexes
213 present in the effluents (Aristilde et al., 2016; Zhang et al., 2019). These results on PPs are
214 confirmed by the elemental analyses, in which SWy2 displays the highest adsorbed amount of
215 carbon. The latter adsorbent, therefore, presents the most suitable adsorption properties for the
216 removal of PPs and potentially other organic contaminants, from WWE.

217 **4. Conclusion**

218 In this study, the potential of three clay minerals for the removal of PPs from raw WWE was studied
219 for the first time in batch experiments, thereby deepening our understanding of the affinity between
220 such adsorbents and PPs. The results clearly show that among the three adsorbents tested, KGa2
221 presents the lowest adsorption capacity for both PPs and other organic moieties present in the
222 effluent. Secondly, the homogenization of the compensating cations of SWy2 (i.e. Na-SWy2) is
223 not favorable for the adsorption of neutral and anionic PPs, which may interact with Ca²⁺ cations
224 through cationic bridges. This can be considered as a positive outcome, given the need to use as
225 raw as possible material. Hence, SWy2 presents suitable adsorption properties in batch experiments

226 for the removal of PPs from wastewater effluents. Finally, this work demonstrates that, in contrast
227 to many studies on idealized solutions, the organic compounds present in raw WWE contribute to
228 improving the adsorption capacity of neutral and anionic PPs by clay minerals in comparison to
229 experiments conducted in pure water. These adsorbed organic moieties increase the hydrophobicity
230 of the adsorbent and the number of adsorption sites. However, further studies remain necessary in
231 order to transfer these results from batch experiments to dynamic ones, closer to the design of a
232 field solution.

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