Optimizing a low added value bentonite as adsorbent material to remove pesticides from water

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1 ABSTRACT

2 A local low value bentonite from Southern Spain (Raw Bentonite), previously decarbonated
3 (Bent), was modified to improve its pesticide adsorption capacity with Fe^{3+} ,
4 hexadecyltrimethylammonium (HDTMA) and the biopolymer chitosan (CH). Adsorption of
5 pesticides on powdered samples showed that Fe^{3+} and HDTMA were appropriate modifiers for
6 this purpose. The modification was optimized by saturation with Fe^{3+} (Bent-Fe) and
7 hexadecyltrimethylammonium (Bent-HDTMA) and the obtained adsorbents were
8 characterized by several physicochemical techniques (X-ray diffraction, thermogravimetric
9 analysis, X-ray fluorescence, physisorption of N_2). Their adsorption capacity to remove three
10 widely used pesticides in Andalusian crops (terbuthylazine, tebuconazole and MCPA) from
11 water was assessed and compared with the commercial organoclay Cloisite® 10A (Clo10). The
12 modified bentonites adsorbed the selected pesticides in a percentage ranging from 30-100%,
13 whereas sorption on Clo10 ranged from 30-90%. For their possible use as filtering beds, Bent-
14 HDTMA, Bent-Fe and Clo10 were granulated by using three different binders (colophony resin
15 and carnauba and bee waxes) at three different mixing ratios and the water resistance and
16 pesticide adsorption of the granules were measured. Results showed that the granulation process
17 did not alter the pesticide adsorption capacity of the powdered modified bentonites, and both
18 waxes granules (carnauba and bee wax) showed better behavior than resin granules. In this
19 work, we succeeded in the preparation of granulated adsorbents derived from a low cost
20 material with similar behavior against a high purity smectite (precursor of Cloisite® 10A). This
21 rises an alternative for this waste material to be used in filter systems for removing pesticides
22 from contaminated water.

23 *Keywords: Adsorption, Bentonites, Clay modification, Pesticides, Water contamination.*

25 **1. Introduction**

26 Water pollution is one of the most important environmental problems affecting the
27 ecosystems and, accordingly, legislation has become very strict in order to reach appropriate
28 levels of water quality (Schoumans et al., 2014; Iho et al., 2015). Agriculture is among the most
29 important sources of diffuse contamination derived from anthropogenic activities (Holt, 2000).
30 With the intensification of the modern agriculture, owing to the increasing demand for food,
31 together with specific edaphoclimatic conditions and the development of more precise
32 analytical techniques, the number of pesticides detected in surface and groundwater has
33 increased (Espigares et al., 1997; Garrido et al., 2000, Carabías-Martínez et al., 2003,
34 Belmonte-Vega et al., 2005, Hermosín et al. 2013, Fernández et al., 2014, Lorenzo et al., 2018,
35 Tsaboula, et al., 2018). Effective and economical technologies, such as filtering, are necessary
36 for elimination of pesticides from water (Campos et al., 2002, Majewska-Nowak et al., 2002).

37 Recently, there has been a renewed interest in the use of clay minerals as adsorbent material
38 for water decontamination since they are readily available and much cheaper than activated
39 carbon (Bhattacharyya and Gupta, 2008). Particularly, the 2:1-type phyllosilicates, such as
40 smectites, are good adsorbents for cationic and highly polar organic compounds because of
41 their small particle-size and hydrophilic and negatively charged surfaces, while anionic and
42 highly hydrophobic compounds are scarcely adsorbed on these materials (Hermosín and Pérez-
43 Rodriguez, 1981; Cox et al., 1997, Cornejo et al., 2008). The modification of bentonites has
44 been proposed as an efficient strategy to remove pesticides from water (Hermosín and Cornejo,
45 1992; Lagaly et al., 2001; Celis et al., 2007). The modification mechanism consists of replacing
46 the clay's natural inorganic exchange cations with organic cations through ion exchange
47 reactions (Boyd et al., 1991; Gámiz et al., 2012). Quaternary ammonium ions are one of the
48 most commonly used (Carrizosa et al., 2001, Redding et al., 2002, Gámiz et al., 2015), although
49 ultimately natural cations or biopolymers are being preferred. These organoclays increase the

50 affinity of bentonites for hydrophobic organic compounds, including neutral pesticides (Aguer
51 et al., 2000) and even acidic pesticides (Carrizosa et al., 2001). By contrast, modified bentonites
52 with iron cations increase the adsorption of basic pesticides (Laird et al., 1996; Celis, et al.,
53 1997).

54 A few studies have used modified clays in filtering systems, obtaining successful results in
55 pesticide removal from water (Beall, 2003, Gardi et al., 2015; Lelario et al., 2017). However,
56 the fine particles of raw bentonites can be an engineering drawback requiring a secondary
57 treatment called flocculation. For this reason, it is necessary to increase the size of bentonites
58 particles to facilitate their use as filtering material for water treatment (Holt, 2004; Müller et
59 al., 2015, Du et al., 2017). The clay granulation method by using a binder for the agglomeration
60 of fine particles is a common technique used for this purpose (Shanmugam, 2015). This process
61 consist in a wet mix of clay powder with a dense paste binder (Bardin et al., 2004; Cheknane et
62 al., 2010; Du et al., 2017). Cellulose (Zamorani et al., 1992; Kleinebudde et al., 1993,
63 Mangwandi et al., 2014; Zhao et al., 2014), food gums (Auta et al. 2012), waxes (Mysore et al.
64 2005), silicones (Zhao et al., 2012), polylactic acid (Chen et al., 2011), vinyl, latex or acrylic
65 derivatives (Cheknane et al., 2010; Neppalli et al., 2014) have been used as binders. However,
66 in some cases, the incorporation of the binder has been shown to modify the sorption capacity
67 of organic compounds on bentonite (Müller et al., 2015).

68 In this work, we hypothesized that the proper treatment and modification of a low value
69 bentonite can display high affinity for pesticides, and it could be used as sorbent material in
70 filter systems. Hence, the aim of this study was to optimize the modification of a bentonite from
71 the Guadalquivir valley (Bailén; Southern Spain) with inorganic and organic cations and to
72 prepare granulates which could facilitate its use as sorbents for water decontamination. The
73 modified bentonite was granulated by natural and innocuous binders: carnauba wax, bee wax
74 and colophony resin. Adsorption of terbuthylazine, tebuconazole and MCPA on modified

75 bentonite and how this process is affected by granulation was assessed. These pesticides were
76 chosen because of their different chemical properties and reported presence in water of
77 Guadalquivir Valley (Espigares et al., 1997; Belmonte-Vega et al., 2005; Hermosín et al.,
78 2013). This work was frame worked in a technological project which global objective was to
79 assess feasible technologies that could help to improve the socioeconomic conditions in rural
80 areas of Andalusia by possible new applications of their raw materials and products.

81

82 **2. Materials and methods**

83 *2.1. Materials and chemicals*

84 A bentonite clay, known as Bailén White Clay, from sediments of the Neocene Basin of
85 Guadalquivir River (González et al., 1998) was provided by Commercial Ceramics of Bailén
86 quarry from Jaén (Spain). Mineralogical composition is given in Table 1. Semi-quantitative
87 identification of the mineral phases present in the raw bentonite was determined by XRD, using
88 a Siemens D-diffractometer 500, with Cu-K α radiation and Ni filter. The quantification of the
89 samples was completed by the relative reflective powers method as described in Schultz (1964).
90 A commercial organoclay, Cloisite® 10A (Clo10), which is a smectite with the interlayer cation
91 dimethyl, benzyl, hydrogenated alkyl tallow quaternary ammonium, was used as reference
92 material. Ferric chloride (QualityChemicals, Spain), hexadecyltrimethylammium chloride
93 (HDTMA, Tokyo Chemical Industry Co. Ltd, Japan) and low molecular weight chitosan (CH)
94 (LMW, Sigma –Aldrich) were used for bentonite modification.

95 Several binders were tested for the granulation of the modified bentonites: natural bee
96 wax (B), provided by Ceras Bellido, S.A, Spain, carnauba wax (C) and colophony resin (R),
97 supplied by Gran Velada S.L, Spain. The binders have been selected prioritizing natural and
98 innocuous materials.

99 The pesticides used in this work were terbuthylazine, tebuconazole and MCPA, (purity >
100 98.8 %). MCPA and tebuconazole were supplied by Sigma –Aldrich (Seeze, Germany), while
101 terbuthylazine was provided by Dr. Ehrenstorfer GmbH (Ausburgo, Germany). The chemical
102 structures of the pesticides as well as their main characteristics are shown in Fig. 1 and Table
103 2, respectively.

104

105 2.2. Bentonite modification and characterization

106 The bentonite was modified with different cations in order to increase the affinity of the
107 raw material for the pesticides. The best conditions for their modification (optimum number of
108 saturations and concentration of the modifier) were assessed and the selected adsorbents were
109 characterized.

110 Before the modification of the bentonite, the carbonate was removed from the raw
111 material. For this aim, a slurry (15 wt.%) of the raw bentonite was decarbonated by the addition
112 (drop by drop) of HCl (37 %) while monitoring the pH of the suspension (pH meter XS PC
113 510), until a pH of 5 was reached. After this, the bentonite without carbonate (Bent) was
114 modified with the cations Fe^{3+} , HDTMA and chitosan. The modification with Fe^{3+} (Bent-Fe)
115 was carried out by saturation of 100 g of decarbonated bentonite with a 1 L of FeCl_3 solution
116 (1 M), this process was repeated up to 3 times. Similarly, the modification with HDTMA (Bent-
117 HDTMA) was done by saturation of 100 g of Bent with a 0.1 M solution of HDTMA chloride
118 but using 1 L of an ethanol:water medium (50/50), the modification was also carried out for 3
119 times. Then, the modified bentonites were washed several times with water to remove chlorides,
120 lyophilized and stored at room temperature. Bentonites modified with chitosan (Bent-CH4 and
121 Bent-CH6) were prepared by the method described by Celis et al., (2012). The main difference
122 between both samples was that Bent-CH4 was prepared using acetic acid to reach appropriate

acidic pH whereas HCl was used for the preparation of Bent-CH6. Under these conditions, a preliminary adsorption experiment was performed and is detailed in section 2.4.

The optimized modified bentonites (Bent, Bent-Fe and Bent-HDTMA) and the commercial one were characterized by specific surface area (S_{BET}), X-ray diffraction (XRD) and thermogravimetric analysis (TGA). The chemical composition of the raw bentonite and modified bentonites was determined by X-ray fluorescence (Philips PW 1404/10). Physisorption of N_2 at 77K, using a Carlo Erba Sorptomatic 1900 (Fisons Instruments, Milan) gas adsorption analyzer, was used to obtain the specific surface area (S_{BET}) by applying the BET method. The basal space (d_{001} -value) of the modified bentonites was measured in air-dried oriented aggregates. Thermogravimetric analysis (TGA) was carried out with a Linseis, STA PT 1600 Series at a heating rate of 10 °C/min up to 1000°C, in static air atmosphere.

The particle size distribution of powder bentonites was obtained based on the standard UNE 103 101:1995. This procedure was established for a suspension of 50 g of bentonites in 125 mL of an aqueous solution with sodium hexametaphosphate as clay dispersant. Particle size distribution was determined from the retention of particles in the suspension in different sieve sizes (2, 1.25, 0.4, 0.160, 0.08 and 0.063 mm). The thinnest particle fraction ($< 63 \mu\text{m}$) was analyzed by the system Sedigraph (Micromeritics, EE.UU). Additionally, the absolute particle density was determined by Helium Pycnometer (Accupyc, Micromeritics, USA).

141

2.3. Performance of bentonite granules: preparation, characterization and efficacy

The granulation of modified bentonites was performed using different binders: B, C and R. For this purpose, 80 g of optimized Bent-Fe, Bent-HDTMA or Clo10, was introduced into the mixer with different amounts of binder 15%, 20% and 25% (w/w) of B or C, and 30 % (w/w) for R. Then, these mixtures were heated until binder melting point (80°C-95°C) and

147 slowly mixed by hand. In order to get a homogeneous mixture, water was slowly added.
148 Resulting mixture was heated at 50°C and meshed to obtain 1-3 mm diameter granules.

149 A water resistance (WR) test of granules was also carried out. In plastic recipients, 50 g
150 of granules (mi) were mixed with 100 mL of distilled water and shaken at 75 r.p.m. for 24 h in
151 a jar mill (Ceramic Instrument Srl., GR-2). After tests, all the samples were dried (50°C) sieved
152 (3 mm) and were weighted (mf). The percentage of WR was determined from the difference
153 between the initial mass (mi) and mass after the water resistance test (mf). WR was calculated
154 as: $WR (\%) = ((mi-mf)/mi)*100$. Duplicated measurements were conducted for each sample
155 and the average values were used for water resistance test.

156 In addition, the microstructural characteristics of the obtained granules were observed by
157 scanning electron microscopy (SEM) (JEOL, JSM-6010 LA, Japan) before and after the water
158 resistance test.

159

160 *2.4. Adsorption studies at laboratory scale*

161 Three pesticides with different physicochemical properties (Table 2) were used to assess
162 the adsorption capacity of the modified bentonites either as a powder or as granulates. For the
163 adsorption in powder, in duplicate, 20 mg of Bent-Fe, Bent-HDTMA, Bent-CH4, Bent-CH6
164 and Clo10 were placed in glass Pyrex® centrifuge tubes with 8 mL of the pesticide aqueous
165 solution at initial concentration of 1 mg/L (Ci). The samples were equilibrated for 24 h at 20 ±
166 2 °C, suspensions were centrifuged and the supernatant solution was removed, filtered and the
167 concentration of each pesticide (Ce) measured by high performance liquid chromatography
168 (HPLC) using a Waters 600E chromatograph coupled to a Waters 996 diode-array detector.
169 The analytical conditions used for each pesticide are shown in the Table A1 of the
170 Supplementary data. The percentage of adsorbed pesticides (% ADS) was calculated by using
171 the following formula: $\%ADS = [(Ci-Ce)/Ci] \times 100$.

172 Pesticide adsorption tests in granules were also carried out to compare the performance
173 of powder and granulated bentonites. The granules were made by bentonites that were selected
174 in the above study on powdered forms (Bent-Fe, Bent-HDTMA and Clo 10). The test followed
175 the same method than in study on powder bentonite. The amount of granules used was
176 equivalent to 20 mg of modified bentonites used as powder.

177

178 **3. Results and discussion**

179 *3.1. Characterization of the selected bentonites*

180 The chemical analysis of the raw and optimized bentonites is shown in Table 3. The most
181 remarkable feature was that Bent-Fe showed a reduction in Ca^{2+} and Mg^{2+} content as the amount
182 of Fe^{3+} increased after the modification (Table 3). The same was observed for Bent-HDTMA
183 indicating cation exchange by the modifiers. Additionally, for this adsorbent, an increase in the
184 calcination losses was also registered and it was attributed to the loss of the organic cation
185 (HDTMA) attached to bentonite layers. The elemental analysis of Bent-HDTMA was carried
186 out, showing the following distribution of elements associated with the organic fraction: 11.7%
187 of C, 2.4% of H and 0.7% of N, which is in agreement with the formula of the HDTMA cation
188 ($\text{C}_{19}\text{H}_{42}\text{N}^+$), compared to a zero content of these same elements for Bent and Bent-Fe. Higher
189 percentages than Bent-HDTMA were found in the case of Clo10 (26.8% of C, 4.4% of H and
190 3.6% of N), indicating greater amounts and, probably also, the greater size of the organic cation
191 of this clay.

192 Table A2 summarizes the density and particle size characterization. All samples presented
193 a low granulometry ($< 80\text{-}100\text{ }\mu\text{m}$). The bentonite and Bent-Fe showed the highest fine fraction
194 ($< 2\text{ }\mu\text{m}$) (Table A2), whereas, Bent-HDTMA showed a narrow particle size distribution
195 ranging between ($63\text{-}2\text{ }\mu\text{m}$) ($\approx 80\text{-}90\%$). The latter can be consequence of flocculation
196 processes or regrouping of particles in the aqueous medium because of the presence of the

197 organic cations. In fact, the lower density of Bent-HDTMA is in line with the expected trend
198 for a substitution with the organic cation. Similar tendency was observed for the commercial
199 Cloisite® 10A (Clo10) (Table A2).

200 Specific surface area (S_{BET}) values for the different clays are presented in Table A3. Bent-
201 HDTMA and Clo10 presented the lowest S_{BET} values of 19.7 and 20 m²/g, respectively. Most
202 likely, the modification treatment changes the aggregation state of clay platelets, or embeds
203 them in an organic matrix covering the clay surface (Gámiz et al., 2015). The highest value of
204 S_{BET} was observed in Bent-Fe (105 m²/g). Precipitates of amorphous oxohydroxides, which are
205 undetectable by XRD, on the surface of bentonites can be responsible of the increase in the S_{BET}
206 values according to previous reported data (Borgnino et al., 2009).

207 The XRD diagrams of Bent, Bent-HDTMA, Bent-Fe and Clo10 are shown in Fig. 2. The
208 d_{001} -value of Bent was 1.37 nm and after the modification with Fe³⁺ (Bent-Fe), the d_{001} -value
209 increased from 1.37 nm to 1.42 nm, showing a poorly defined peak when compared to Bent,
210 Bent-HDTMA and Clo10 (Fig. 2). This fact suggests the partial intercalation of the hydrous
211 iron oxide in the interlayer space and on the external surface of the bentonite particles, since an
212 increase of the S_{BET} value is indicative of this type of arrangement. For the organo-clays, we
213 found the highest d_{001} -values, 1.97 nm and 2.00 nm for Bent-HDTMA and Clo10, respectively,
214 which is typical of bilayer arrangement of the cations in the interlayer as other authors have
215 reported (Jaynes and Boyd, 1991, Roberts et al., 2006).

216 The differential thermal analysis (DTA-TG) of the Bent, optimized bentonites (Bent-Fe
217 and Bent-HDTMA) and Clo10 are presented in Fig. 3. The DTA curves of the bentonite without
218 carbonates (Bent) were characterized by two mass losses. The first of them around 200°C is
219 assigned to water losses (Yariv, 2004). The second mass loss was registered near 700°C, as
220 consequence of the dehydroxylation of the clay mineral (Xi et al. 2004). After the modification
221 with Fe (Bent-Fe), the water mass loss was shifted towards lower temperature (100 C°) and can

222 be attributed to the weaker attraction between water molecules and Fe cations, as compared
223 with Ca which is the dominant exchangeable cation in Bent. The presence of Fe in Bent resulted
224 in undefined DTA curves and several small peaks were observed, mainly at 500 °C and others
225 between 800-900 °C (Fig. 5). This is accordance with data from literature which indicated that
226 ferric iron hydrates in bentonites showing undefined peaks at 400 °C difficult to discern from
227 the clay mineral (Grim and Rowland, 1942). However, the two small losses observed between
228 800-900 °C, can be attributed to the hydroxylation of the clay layer since hydrated ion have
229 shown enhance the stability of the bentonite (Zhou et al. 2001).

230 For the organoclays, Bent-HDTMA, losses occurred in three steps: a very small first
231 attributed to the loss of residual hydration water (50- 100°C), a second mass-loss step and more
232 important (200-500°C), which can be related to the oxidation and loss of organic cations, and a
233 third mass loss at temperatures higher than 500°C, which is attributed to the dehydroxylation of
234 the bentonites sheets (Lapides et al., 2011). In the case of the commercial clay (Cloisite®) losses
235 occurred in two steps: the first at 250-300°C, as consequence of the loss of organic cations, and
236 the second mass loss at 650°C, that is assigned to the dehydroxylation of the clay as
237 aforementioned. The latter occurred at lower temperatures in comparison to Bent-HDTMA
238 since the interactions between the organic cations with sheets of the Cloisite® were different
239 as compared to HDTMA with Bent (Fig. 3).

240

241 3.2. Optimization process in the preparation of modified bentonites

242 In order to optimize the amount of chemicals used in the modification of the bentonite for
243 latter granulation, the adsorption capacity of modified bentonites was determined after the
244 saturation of the material with ferric or ammonium cations, which varied between one and two
245 saturations. According to the results in Fig. 4A, one saturation with HDTMA renders similar
246 adsorptive properties for Bent-HDTMA than two saturations for the three pesticides. In the case

247 of Bent-Fe, two saturations greatly improve the sorption capacity for the anionic herbicide
248 MCPA (Fig. 4B).

249 Once the number of saturations was optimized, different concentrations of chloride iron
250 (1M, 0.5M, and 0.33M) and HDTMA (0.1M, 0.05M, 0.033M) were also tested (Fig. 5) for 100
251 g of Bent in 1 L of solution. According to the adsorption percentages of pesticides in Fig. 4 and
252 Fig. 5, it can be concluded that the most ideal conditions were two saturations with
253 concentrations 1M of FeCl_3 and one saturation with 0.1 M of HDTMA.

254

255 *3.3. Effectiveness of granules*

256 The results obtained from the water resistance test of granules are shown in Table 4.
257 Granules made with bee wax showed percentages of water resistance between 45-90%, better
258 results than carnauba wax granules with 35-80% of water resistance. The lowest percentages of
259 water resistance were obtained for the resin. Thus, waxes are expected to develop better
260 mechanic behavior as binders of granules in filtering beds.

261 In SEM photographs of Bent-HDTMA granules made with 20% (w/w) carnauba wax as
262 binder, before (a) and after (b) water resistance test (Fig. A.1), it is possible to appreciate that
263 the texture of the particles is much smoother due to the friction between granules during water
264 resistance test, but size of granules persist similar to those of the ones before the test.

265

266 *3.4. Adsorption study of pesticide in powdered modified and commercial bentonites*

267 Adsorption percentages of pesticides in modified powder and commercial bentonites are
268 shown in Fig. 6. For all pesticides, the modification of the bentonite improved its sorption
269 capacity when compared to unmodified bentonite (Bent), although the removal efficiency
270 depended on the modifier cation (Fig. 6). It is necessary to highlight that after removing the
271 carbonate present in the raw material, the amount of clay minerals in Bent reached 60% instead

272 of the initial 38%. Likewise, the sorption capacity of quartz, the other major component (24 %
273 in bentonite samples), has been reported to play a smaller role than clay minerals in their ability
274 to adsorb pesticides with similar characteristics than those used in this work (Clausen et al.
275 2000). For that reason, the adsorption behavior can be basically attributed to the clay mineral
276 fraction of the material.

277 The bentonite modified with Fe^{3+} (Bent-Fe) and with HDTMA (Bent-HDTMA) showed
278 the best adsorption behavior (40-100%) compared to chitosan modified bentonites.
279 Specifically, Bent-HDTMA was a good adsorbent for tebuconazole and MCPA, with
280 adsorption percentages ranging from 80% to 95%, respectively. Previous works have reported
281 the ability of the HDTMA-modified montmorillonites to remove pesticides from water. The
282 hydrophobic environment provided by the cation HDTMA can explain this fact (Jaynes and
283 Vance, 1996), considering the very low S_{BET} values registered (Table A.3). According to the
284 basal spacing recorded of 1.97 nm, as explained in section 3.1, the intercalated cations generated
285 a partitioning medium, which favored the adsorption of both pesticides by hydrophobic
286 interactions (Hermosín and Cornejo, 1992; Cornejo et al., 2008; Gámiz et al., 2015). On the
287 contrary, lower adsorption was observed for terbuthylazine (40%) in spite of this hydrophobic
288 environment (Fig. 6). In general, large-cation organo-clays have less accessible internal surface,
289 which could difficult the access of this pesticide to the interlayer space (Jaynes and Vance,
290 1996; Celis et al., 2007). Bent-Fe increased the adsorption of the three pesticides compared to
291 the unmodified bentonite, particularly, the sorption percentage was very high (nearly 90 %) for
292 tebuconazole (Fig. 2). This result was in line with the greater S_{BET} value measured for this
293 sample compared to the decarbonated and organically modified Bent (Table A.3.). Moreover,
294 the adsorption capacity of bentonite modified with Fe for weak bases, such as terbuthylazine
295 and tebuconazole, has been attributed to the polarization of the hydration sphere of Fe^{3+} . This
296 favors the formation of hydronium ions that promotes the protonation of these type of

pesticides, taking place the subsequent adsorption as protonated species on the negative charged bentonite surfaces (Celis et al., 1997; Cornejo et al. 2008). The latter was expected since the pH of the suspension of the adsorption experiment, ranging between 3-4 units, was close to the pKa of the both pesticides (Table 2). Hence, differences observed in adsorption percentages between tebuconazole and terbuthylazine can be attributed to different pKa values (Table 2), and more protonated molecules of tebuconazole were present in solution favoring its higher adsorption as cation on the negative charged bentonite surfaces. Additionally, since Fe increases the surface of the bentonite and induces changes in the charge of the bentonite by reducing the pH (pH=3-4), sorption of the acidic herbicide MCPA in its neutral form was also favored by reducing repulsion with bentonite surface (Cox et al., 2000, Cabrera et al. 2016). Regarding modified bentonite with chitosan, Bent-CH4 and Bent-CH6 displayed the lowest adsorption for the pesticides compared to the other modified bentonites, specially, in the case of terbuthylazine where no sorption was measured. Presumably, as it has been observed for other polymers modifying clay minerals, chitosan can be arranged on bentonite surface blocking the adsorption sites and the access to interlayer surface (Lagaly, 1981; He, et al., 2006; Gámiz et al., 2015). Particularly, Bent modified with CH only improves the adsorption percentage (40%) for the anionic pesticide due to positive charges of the biopolymer exposed on the bentonite surface that act as new adsorption sites, as reported for the herbicide clopyralid on its adsorption on montmorillonite-chitosan nanocomposites (Celis et al., 2012). The commercial clay Cloisite® 10A (Clo10) showed a very high affinity for all pesticides (terbuthylazine, tebuconazole and MCPA), with adsorption percentages ranging from 50% to 90% (Fig. 6). This is probably due to the large excess of alkylammonium over the CEC which should facilitate hydrophobic interactions increasing pesticide adsorption.

320 Based on the adsorption results, Bent-Fe and Bent-HDTMA, with similar sorption
321 behavior to the commercial clay, were selected for subsequent experiments designed to
322 optimize the granulation process.

323

324 3.5. Pesticide adsorption tests in granules

325 The percentages of adsorption of the three pesticides on the different granules are
326 presented in Fig. 7, together with adsorption percentages in powder-modified bentonites. For
327 the Bent-HDTMA (Fig. 7a), no significant differences were observed between the adsorption
328 on powder and on granulated bentonites (100%-40%). The adsorption decreases slightly when
329 the amount of binder increased, which can be attributed to the surface pores and interlayer
330 access of Bent-HDTMA being blocked by resin (Mysore et al., 2005). The highest percentage
331 of adsorption in granules with bee and carnauba wax was obtained for the acidic pesticide (90%-
332 100%) as compared to tebuconazole or terbuthylazine, as it was observed for their adsorption
333 using the material as powder. On the contrary, for Bent-Fe, the highest adsorption percentages
334 were found for tebuconazole and terbuthylazine, 70%-50%, respectively (Fig. 7b). As it has
335 been aforementioned in section 3.4., the presence of Fe^{3+} in this bentonite could still ionize the
336 water molecules of its hydration sphere, in spite of the presence of the binder, reducing the pH
337 of the bentonite surface. This allowed the protonation of both weak bases, which were adsorbed
338 as cationic species as they reached bentonite surface (Celis et al., 1997). The effect was more
339 pronounced for tebuconazole for the same reason justified in the previous section. The granules
340 of the commercial clay Clo10 (Fig. 7.c) showed a similar behavior in the percentages of
341 adsorption of pesticides to those obtained in Bent-HDTMA. In this case, neither the type of
342 binder nor its percentage affected the pesticide sorption capacity of both organic clays. In all
343 cases, the granules prepared with resin (Fig. 7.) presented the lowest percentages of adsorption.
344 Hence, the adsorption results obtained for the granules demonstrated that our material Bent-

345 HDTMA was as efficient as the commercial product, which makes bentonite suitable for its
346 commercialization as a cheaper alternative.

347

348 **4. Conclusion**

349 Modified bentonite with Fe^{3+} (Bent-Fe) and HDTMA (Bent-HDTMA) were effectively
350 used as sorbent of MCPA, terbuthylazine and tebuconazole. Organoclay (Bent-HDTMA) and
351 commercial bentonite Cloisite® 10A (Clo10) showed better adsorption capacity for the selected
352 pesticides in comparison to Bent-Fe. In addition, this work reveals that the process of
353 granulation does not significantly affects bentonites sorption capacity and that granules show
354 an excellent water resistance at the end of the sorption experiment. These results also suggest
355 that carnauba wax could be used as a binder of bentonite and these granules could be used as
356 sorbent in filters for water contaminated with pesticides. Considering that Bent-HDTMA had
357 similar adsorption behavior than the commercial Cloisite® 10A, we can conclude that we
358 succeeded in the preparation of an adsorbent based on a ceramic bentonite of very low value
359 against a high purity smectite (precursor of Cloisite® 10A). This rises an alternative use for this
360 waste material regarding its use in the construction industry, being its preparation cheaper than
361 the commercial one, which at the same time could suggest the possible development of a local
362 industry devoted to its preparation and commercialization.

363

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370 **Appendix A. Supplementary data**

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372

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FIGURE CAPTIONS

Fig. 1. Chemical structure of a) terbuthylazine, b) tebuconazole and c) MCPA.

Fig. 2. XRD diagrams of oriented specimens of air dried Bent and modified (Bent-Fe and Bent-HDTMA) and commercial (Clo10) bentonites.

Fig. 3. First derivate of the TGA mass loss of Bent and modified bentonites (Bent-HDTMA, Bent-Fe, Clo10).

Fig. 4. Adsorption percentages of pesticides adsorbed by A) Bent-HDTMA or B) Bent-Fe after one or two modifier cation saturations.

Fig. 5. Adsorption percentages of the pesticides adsorbed on A) Bent-HDTMA and B) Bent-Fe after saturation with the corresponding modifier at different concentrations.

Fig. 6. Adsorption percentage of pesticides adsorbed on powder unmodified, modified and commercial bentonites.

Fig. 7. Percentages of pesticides adsorbed on powder and granulates of modified bentonites (Bent-HDTMA, Bent-Fe, Clo10) treated with the binders at different rates (15, 20, 25 and 30% w/w).

Table 1

Mineralogical composition of Raw Bentonite.

Quartz	Feldspar	Calcite	Dolomite	Gypsum	Phyllosilicates		
(%)	(%)	(%)	(%)	(%)	(%)		
16	5	36	5	-	38		
					smectite	illite	kaolinite
					(%) ^a		
					72	20	8

^a Percentage of each phyllosilicate in the 38% of the total phyllosilicate content

Table 2

Main characteristics of pesticides tested for each pesticide analysis.

	MCPA	Terbuthylazine	Tebuconazole
Water solubility (mg/L)	293.9	8.5	36
pKa	3.7 (Weak Acid)	1.9 (Weak Base)	5.0 (Weak Base)
Molecular weight (g/mol)	200.62	229.7	307.8
Kow Log (P)	-0.81(pH=7)	3.21	3.7

Table 3

Chemical composition of raw bentonite, bentonite without carbonates (Bent), and modified with an organic cation (Bent-HDTMA) and with ferric cation (Bent-Fe)

	SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	MnO (%)	MgO (%)	CaO (%)	Na ₂ O (%)	K ₂ O (%)	TiO ₂ (%)	P ₂ O ₅ (%)	SO ₃ (%)	Mass Loss ^a (%)
Raw Bentonite	43.9	8.5	3.3	0.1	2.1	20.0	0.2	1.6	0.4	0.1	0.1	19.9
Bent	52.5	11.6	4.3	0.0	2.1	9.4	0.4	2.2	0.6	0.1	n.d. ^b	14.5
Bent-HDTMA	52.3	10.0	4.0	0.0	1.8	5.2	0.3	1.7	0.5	0.1	n.d.	22.6
Bent-Fe	60.9	11.3	13.8	n.d.	1.5	0.2	0.4	2.0	1.0	0.0	0.2	6.9

^a Calculated by calcination;

^b n.d.: Not detected

Table 4

Percentage of water resistance of modified bentonite granulates depending on the type and amount of binder used.

	Bee Wax (%)			Carnauba Wax (%)			Resin (%)
	15	20	25	15	20	25	30
Bent-Fe	75 ± 2	61 ± 3	71 ± 13	34 ± 5	80 ± 0	56 ± 2	49 ± 9
Bent-HDTMA	44 ± 1	44 ± 3	50 ± 6	35 ± 4	45 ± 3	54 ± 8	41 ± 6
Clo10	87 ± 1	nt ^a	nt	nt	73 ± 4	71 ± 7	68 ± 2

^a nt= Not tested

a)

b)

c)

Fig. 1. Chemical structure of a) terbuthylazine, b) tebuconazole and c) MCPA.

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Fig. 7. Percentages of pesticides adsorbed on powder and granulates of modified bentonites (Bent-HDTMA, Bent-Fe, Clo10) treated with the binders at different rates (15, 20, 25 and 30% w/w).

Highlights

HDTMA and Fe increased the adsorption of pesticides by a low-value bentonite.

Granules of modified bentonites with different binders showed good water resistance.

The binders in the granules did not affect the adsorption of the modified bentonites.

Granules could be used as filtering bed for decontamination of water with pesticides.

GRAPHICAL ABSTRACT