ADSORPTION OF PROPRANOLOL ONTO MONTMORILLONITE: KINETIC, ISOTHERM AND pH STUDIES

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Abstract

The objective of this study was to explore the potential use of the smectite clay mineral montmorillonite (Mt) as adsorbent in the removal of water containing the emerging compound propranolol. The Mt was deeply characterized by X-ray diffraction (XRD), Zeta potential and thermogravimetric analysis (DSC-TG), before and after adsorption experiments, and their isotherms and kinetic models were fitted to assess the adsorption of propranolol.

The incorporation of propranolol in the interlayer was demonstrated by XRD and DSC-TG. The results obtained by Zeta potential indicated no adsorption of propranolol in the surface. Kinetic of propranolol adsorption onto Mt was evaluated using pseudo-first-order, pseudo-second-order, intra-particle diffusion and Elovich models. Pseudo-second order was the kinetic model that best described the adsorption of propranolol (R^2> 0.999). It was possible to obtain a removal efficiency of approximately 96% in less than 1 minute. The adsorption equilibrium isotherm was fitted with the Langmuir, Freundlich and Dubinin-Radushkevitch mathematical models to obtain the respective parameters. Freundlich and Dubinin-Radushkevitch were the models that best fitted the experimental data (R^2> 0.999). Due to the cationic form of propranolol, the adsorption by ionic exchange between charged propranolol and sodium cations onto the interlayer space was the most favorable pathway proposed. Results indicate that adsorption onto Mt proved to be an efficient method for removing propranolol, thus being a viable alternative for the treatment of water contaminated with this drug.

Keywords: *Propranolol; Montmorillonite; Adsorption; Water samples*

1. Introduction

Water pollution by pharmaceutically active compounds is increasing in an alarming way (Basheer et al., 2018; Mompelat et al., 2009). Among various therapeutic groups, β-blockers are being used worldwide due to the increasing number of patients suffering from cardiovascular diseases (Ali et al., 2017; Ding et al., 2015). Several of these medicines, propranolol included, are in the top 200 prescribed medications (Maszkowska et al., 2014; Huggett et al., 2003). Propranolol is used as a hydrochloride salt in the treatment of hypertension, pheochromocytoma, angina pectoris, myocardial infarction and cardiac arrhythmia. It is also used to control hypertrophic cardiomyopathy, to control symptoms of sympathetic hyperactivity when treating hyperthyroidism, anxiety disorders, and tremor (Soni, 2014).

This drug may originate from hospital effluent, wastewater treatment plants, pharmaceutical industry waste, and excretion after drug administration to people or household surplus drugs' disposal (Deblonde et al., 2011). Its widespread use, together with its often-incomplete metabolism (Maszkowska et al., 2014), means that propranolol is commonly detected in sewage effluents and surface waters at concentration levels that range from ng/L to μg/L (Liu et al., 2018; Petrie et al., 2015; Maszkowska et al., 2014; Lopez-Serna et al., 2013; Santos et al., 2013; Deblonde et al., 2011). The process used in conventional wastewater treatment plants (WWTP) cannot remove this compound efficiently (Gao et al., 2018; Gabet-Giraud et al., 2010; Santos et al., 2013). For example, a study conducted by Santos et al. (2013) in effluent wastewaters from four different hospitals located in Coimbra (Portugal) showed the presence of different drugs, among them propranolol, in all hospitals samples analyzed and also in the WWTP influent and effluent. The removal efficiency for β-blockers was less than 17%. In another study carried out by Grover et al. (2011), a full-scale

76 granular activated carbon plant treating a WWTP effluent was assessed in terms of
77 removal efficiency of pharmaceuticals (Grover et al., 2011). Higher removal efficiency
78 (84–99%) was observed for mebeverine, indomethacine, and diclofenac, while
79 carbamazepine and propranolol displayed much less removal efficiency (17–23%).
80 Additionally, due to its characteristic of persistence against natural attenuation, it may
81 be maintained in the environment for a long period of time (Gao et al., 2018). Some
82 studies have suggested that propranolol may cause adverse effects on various aquatic
83 organisms (Ding et al., 2015; Maszkowska et al., 2014; Crane et al., 2006; Falconer et
84 al., 2006; Fent et al., 2006; Ferrari et al., 2004; Huggett et al., 2002). Propranolol has
85 the highest acute and chronic toxicity within the class of β-blockers (Maszkowska et al.,
86 2014; Brausch et al., 2012; Fent et al., 2006; Stanley et al., 2006; Huggett et al., 2002).
87 In addition, propranolol is also known as an effective antagonist for 5-HT
88 (hydroxytryptamine) receptor, which is a potential target receptor in wildlife (Alexander
89 and Wood, 1987). The endocrine-disrupting potential of propranolol on aquatic
90 organisms was recently emphasized by Massarsky et al. (2011). This is an emerging
91 issue for the environment, and it can pose a new challenge to water treatment processes.
92 Several techniques are being studied to treat waters that are contaminated with
93 pharmaceutically active compounds such as photolysis, photo-Fenton, photocatalysis,
94 ozonation, nanofiltration and adsorption (Tarpani and Azapagic, 2018; Gao et al., 2018;
95 Rodríguez-Narváez et al., 2017). Adsorption becomes an interesting alternative for the
96 treatment of water that is contaminated with pharmaceuticals, since it is versatile, easy
97 to operate and efficient in removing many pharmaceutical compounds (Singh et al.,
98 2018). In view of this, the use of natural clays as adsorbents becomes attractive due to
99 their high capacity to remove a great variety of dissolved organic and inorganic
100 contaminants and to their large surface area, pore structure and thermal stability, which

improves their ability to remove various contaminants from aqueous media (Lozano-Morales et al., 2018). Montmorillonite (Mt), a smectite clay mineral, has attracted great interest in the biomedical field because of its high cation exchange capacity, easy degradation, large specific surface area, low price, easy availability, good adsorption capacity, and good biocompatibility (Gamba et al., 2015; Jiang et al., 2012). Mt is widely used in pharmaceutical applications (Farhadnejad et al., 2018; Ullah et al., 2016; Sánchez Martín et al., 1981). For example, Farhadnejad et al. (2018) designed and characterizated a nanocomposite hydrogel beads, based on carboxymethyl cellulose (CMC) and Mt-propranolol nanohybrid, for propranolol controlled release. Results indicated that the Mt-propranolol/CMC nanocomposite beads had high stability against stomach acid and a sustained- and controlled-release profile for propranolol under the simulated intestinal conditions. Besides clay minerals, graphene oxide, layered double hydroxides, mesoporous silica nanocontainers and oxide metallic and metallic nanoparticles have also evaluated to enhance the mechanical strength and stability of hydrogel compounds and decrease the drug release rate and burst initial drug release (Farhadnejad et al., 2018; Kuthati et al., 2015). Furthermore, Mt has also been used as an adsorbent for the removal of organic pollutants such as pesticides and emerging pollutants (Martín et al., 2019; Martín et al., 2018; Orta et al., 2018; Gamba et al., 2015; Marco-Brown et al., 2014; Rauf et al., 2012), heavy metals ions (Barbier et al., 2000) or organic compounds such as antibiotics (Parolo et al., 2013) from water samples. Mt adsorbs cationic organic pollutants through ion-exchange processes (Gamba et al., 2015), while anionic pollutants interact with the positively charged clay edges and therefore they are only so slightly absorbed; besides, the repulsion that is established with the negatively charged silicate surface also results in a certain level of desorption

(Sannino et al., 1997). To our knowledge, there is no published research regarding the use of Mt for the removal of β-blockers.

The aim of this study was to explore the potential use of Mt as an adsorbent for the decontamination of water containing the emerging compound propranolol. Mt was deeply characterized by X-ray diffraction (XRD), Zeta potential and differential scanning calorimetry and thermogravimetric analysis (DSC-TG), before and after the adsorption experiments. Their isotherms and kinetic models were fitted to assess the adsorption of propranolol.

2. Materials and methods

2.1. Materials and reagents

Mt provided by Castiglioni Pes y Cia, from North Patagonia, Argentina, was used as receiver. Previous studies had determined its mineralogy and chemical composition (Magnoli et al., 2008). XRD and chemical analysis indicated that the sample contained Na Mt (>99%) with quartz and feldspars as minor phases. The structural formula obtained from the chemical analysis was $[(Si_{3.83}Al_{0.11})(Al_{1.43}Fe^{3+}_{0.28}Mg_{0.30})O_{10}(OH)_2]$ $Na_{0.41}$. The cationic exchange capacity (CEC) determined by the Cu-triethylenetetramine method (Czímerová et al., 2006) was 0.8250 ± 0.0007 mmol/g of clay.

HPLC-grade, acetonitrile and water were supplied by Romil Ltd. (Barcelona, Spain). Hydrochloric acid, sodium hydroxide and formic acid were obtained from Panreac (Barcelona, Spain). Ammonium formate was purchased from Sigma-Aldrich (Steinheim, Germany). All of them were analytical grade.

High purity propranolol was purchased from Dr. Ehrenstorfer (Augsburg, Germany). Stock standard solution of propranolol (1000 mg/L) was prepared in methanol and

150 stored at 4°C. Fresh working solutions at different concentration levels were prepared in
151 deionized water before each experiment.
152
153 *2.2. Characterization methods*
154 *X-ray diffraction* patterns were carried out in a Bruker D8 Advance A25 diffractometer
155 (Bruker, Germany) in Bragg-Brentano configuration. The detector was a Lynxeye PSD
156 detector (Bruker, Germany) equipped with a copper K α radiation source (0.15405 nm
157 wavelength). Step-scan data was taken from 1° to 70° 2 θ , a step width of 0.03°, time
158 per step of 0.1 s, and tube conditions of 40 kV and 30 mA. The diffractometer was
159 calibrated mechanically according to the manufacturer's specifications and corundum
160 standard was used to check the resolution in a wide range of angles.
161 *Zeta potential* was obtained from the mobility of the particles using the Smoluchowski
162 equation (Smoluchowski, 1941). The Mt, before and after each adsorption experiment,
163 was suspended in water (1 g/L) and zeta potentials were measured on a Zetasizer
164 Nanosystem system (Malvern Instruments, Southborough, MA). The pH of the solution
165 was measured with a Crison GLP 21 pH meter.
166 *Thermal gravimetric analyses* were performed on a Q600 STD (TA instruments, USA).
167 The samples were heated from 20°C to 900°C at a scanning rate of 10°C/min in a
168 nitrogen atmosphere.
169 *Liquid Chromatography-tandem mass spectrometry* (LC-MS/MS) analyses were
170 performed on an Agilent 1200 series HPLC system (Agilent, USA) equipped with a
171 vacuum degasser, a binary pump, an autosampler and a thermostatic column
172 compartment. Separation of propranolol was carried out using a HALO C18 (50x4.6
173 mm i.d.; 2.7 µm) analytical column (Teknokroma, Spain) protected by a HALO C18
174 (5x4.6 mm 1.d.; 2.7 µm) guard column (Teknokroma, Spain). Elution was performed by

175 isocratic conditions with acetonitrile (0.1% formic acid) (50%) and a 10 mM aqueous
176 solution of ammonium formate (0.1% formic acid) (50%), at a flow rate of 0.6 mL min^{-1}
177 with a column temperature of 30°C.
178 A 6410 triple quadrupole (QqQ) mass spectrometer (MS) equipped with an electrospray
179 ionization source (Agilent, USA) was used for detection. Ionization of analytes was
180 carried out using the following settings: MS capillary voltage, 3000 V; flow rate of the
181 drying-gas, 9 L/min; drying-gas temperature, 350ºC; and nebulizer pressure was 40 psi.
182 MassHunter software (Agilent, USA) was used for instrument control and data
183 acquisition. Compounds were analyzed in multiple reaction monitoring (MRM) mode
184 and monitored in the positive ionization mode. Two MRM transitions were selected for
185 each analyte, one was applied for quantification (260 > 116) and another for
186 confirmation (260 > 56) using a fragmentor of 114 V and an energy collision of 16 eV.
187
188 *2.3. Adsorption batch experiments*
189 Batch adsorption experiments of propranolol onto Mt were assessed using a batch
190 equilibrium method at 25 ºC. Solutions with different initial propranolol concentrations
191 in deionized water (10 mL) containing 20 mg of Mt were added to 20 mL glass bottle
192 with teflon screw caps. The solutions were stirred at 800 rpm and samples were taken at
193 different time interval. A pH of approximately 6.5 remained constant during the
194 adsorption process in all samples. After the contact time, the suspensions were
195 centrifuged at 8000 rpm during 15 min and supernatants filtered through a 0.22 μm
196 nylon filter. The final concentrations of propranolol remaining in the aqueous phase
197 were determined using the LC-MS/MS system.
198 The parameters affecting propranolol adsorption, such as concentration (from 0.5 to 80
199 mg/L), time (from 0 s to 7 days) and sample pH (from 1 to 12) were evaluated. Each

200 experiment was run in triplicate. The linearity of the method was studied by analyzing
201 standard solutions in triplicate at concentrations ranging from 0.01 μ g/mL to 10000 μ
202 g/mL.
203 The difference in the amount before and after adsorption reveals the amount of adsorbed
204 propranolol (q):

205 $$q = \left(C_i \quad C_{eq}\right) \times \frac{V}{m} \qquad (1)$$

206 where V (L) is the volume of the solution, m is the weight of the clay (kg), C_i (mg/L)
207 and C_{eq} (mg/L) are the concentration of the propranolol in the initial and final solution,
208 respectively. Control experiments were performed without Mt and indicated the
209 negligible loss of propranolol by volatilization or by adsorption on the glass tubes.
210 The adsorption percentage was calculated as follows:

211 $$\%adsorption = \frac{C_i \quad C_{eq}}{C_i} \times 100 \qquad (2)$$

212 The adsorbent performance was determined by adjustment of the experimental
213 isotherms to Langmuir, Freundlich and Dubinin-Radushkevitch mathematical model
214 (Marco-Brown et al., 2014). The Langmuir model is described by the following
215 equation:

216 $$q = \frac{q_{\max} K_L C_e}{1 + \left(C_e K_L\right)} \qquad (3)$$

217 where, q_{max} is the maximum amount adsorbed within a monolayer (μ mol/g), and K_L (L/
218 μ mol) is the Langmuir dissociation constant, which is related to the adsorption energy.
219 The Freundlich model is described by Equation 4:

220 $$q = K_F C_e^{1/n} \qquad (4)$$

where K_F (L/μ mol) is the Freundlich constant, which is related to the affinity of the adsorbent to the adsorbate, and 1/n is a dimensionless parameter, which indicates how adsorption varies as a function of the concentration.

The Dubinin-Radushkevitch model is more general than the Langmuir model because the former does not assume a homogeneous surface or a constant adsorption potential. This model is described by the following equation:

$$q = q_{\max} e^{K_{DR}{}^2} \quad (5)$$

where K_{DR} (mol^2/J^2) is a Dubinin-Radushkevitch constant and ε (J/mol) is a Polanyi potential, which is related to C_e by the following equation:

$$= RT \ln\left(1 + \frac{1}{C_e}\right) \quad (6)$$

where R is the gas constant and T is the temperature in Kelvin. K_{DR} is related to the mean free energy of adsorption per mole of adsorbate (E, kJ/mol) according to Equation 7:

$$E = \left(2K_{DR}\right)^{1/2} \quad (7)$$

The following mathematical models were employed for the kinetic analysis: pseudo first order (PFO), pseudo second order (PSO), intra-particle diffusion (IDM), and Elovich models (Equations 8-11, respectively) (Marco-Brown et al., 2014).

$$\ln\left(q_e \quad q_t\right) = \ln q_e \quad k_1 t \quad (8)$$

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \quad (9)$$

$$q_t = C + k_{id}\sqrt{t} \quad (10)$$

$$\frac{dq_t}{dt} = \quad (\quad q_t) \quad (11)$$

where q_e and q_t are the amount of propranolol adsorbed at equilibrium and at time t, respectively; k_1, k_2 and k_{id} are the rate constants for PFO, PSO, and IDM models, respectively. C is a constant, and α and β are the Elovich coefficients.

To determine the goodness of fit of the model to the experimental data, in addition to the value of R^2, the percentage standard deviation [Δq (%)] was calculated from the following equation:

$$q(\%) = \sqrt{\frac{\sum\left(\frac{q_t - q_t^{calc}}{q_t}\right)^2}{n - 1}} 100 \quad (12)$$

where q_t^{cal} is the calculated amount of propranolol adsorbed and n is the number of measurements.

3. Results and discussion

3.1. Characterization of Mt and Mt-propranolol

X-Ray Diffraction: Precise information about position, intensity, width and shape of each individual peak in the diffraction pattern was obtained by Le Bail analysis (Le Bail, 2005), using the TOPAS 6 software (Bruker, 2017) (Orta et al., 2018; Martín et al., 2018). The values of the goodness of fit (GOF) of the adjustments were checked to obtain values close to the unit. At the same time, values of residual factors (R_{wp} and R_{Bragg}) were obtained. GOF value obtained from the Le Bail fitting for Mt was 2.89, and R_{wp} and R_{Bragg} were 12.14 and 0.916, respectively. These results were small, thus indicating coherent data (Young, 1993). The structure used was monoclinic in space group C2/m and the lattice parameters were: a = 5.12(14) Å, b = 9.2(2) Å, c = 12.8(3) Å, β = 97.4(6)°, and d = 12.70873 Å and 2Θ = 6.94985° for the (001) plane. After the adsorption process of propranolol, GOF, R_{wp} and R_{Bragg} were 1.31, 6.03 and 0.377,

265 respectively. The lattice parameters were: a = 5.28(3) Å, b = 8.71(6) Å, c = 13.59(11)
266 Å, β = 98.3(3) °, and d = 13.44653 Å and 2Θ = 6.56809°.
267 The Mt presents a monoclinic structure and XRD characterization tests showed a slight
268 increase from 12.71 Å (Mt) to 13.45 Å (Mt after the adsorption) in the interlayer space
269 (Figure 1).
270 *Zeta Potential*: The external surface charge of Mt before and after the adsorption assays
271 was studied at pH~6.5. The Zeta potential values were -31.1±1.1 mV and -32.8±0.9
272 mV, respectively. These values in the external surface charge of Mt and Mt-propranolol
273 indicate that there is no adsorption of propranolol in the surface.
274 *Thermal Gravimetric Analyses*: Figure 2 shows the results of DSC (b) and TG (a). The
275 DSC-TG curves of Mt before adsorption assays show two endothermic peaks around 90
276 and 680˚C associated with the dehydration and dehydroxylation of the clay and with
277 mass loss of around 12 and 4% respectively (Lapides et al., 2002). The mass loss of the
278 calcined sample was 16.59%.
279 After the adsorption of propranolol onto the clay, the endothermic decreases, and there
280 is a sudden loss of weight, approximately 9%, due to the dehydration of the water
281 contained in the interlayer space, which may be due to the propranolol displacing the
282 water present in the interlayer space. There is a slight loss of around 9% of weight up to
283 approximately 750˚C, which may be linked to the degradation of intercalated
284 propranolol and the loss of structural hydroxyl group. The mass loss of the calcined
285 sample was 18.12%.
286
287 *3.2. Adsorption of propranolol onto Mt*
288 Experimental data of propranolol adsorption onto Mt loaded samples is shown in Figure
289 3a as the function of the equilibrium adsorption capacity of propranolol (q) versus the

290 equilibrium concentration of propranolol (C_e) in the testing solutions. The adsorption
291 capacity is affected by the initial concentration of solute; lower values of initial
292 concentration provide greater efficiency in the adsorption process. As we can see from
293 Figure 3b, adsorption (91-99%) is relatively invariable in the range of 0.5 to 10 mg/L,
294 while a slight decrease to 81% is observed at 20 mg/L, down to 65% at 80 mg/L. The
295 adsorption efficiency is higher than the one previously reported for the adsorption of
296 propranolol onto graphene oxide materials (the greatest adsorption observed was 68%)
297 (Kyzas et al., 2015).
298 The shape of the isotherm showed L behavior according to Giles' classification (Giles et
299 al., 1960). The initial curvature here shows that, the more sites in the substrate are filled,
300 the more difficult it is for a bombarding solute molecule to find a vacant site available.
301 This also implies that the adsorbed solute molecule is not vertically oriented or that
302 there is no strong competition from the solvent.
303 In order to estimate whether the adsorption of propranolol in aqueous solution was
304 favorable or not, different isotherm models were taken into consideration (Langmuir,
305 Freundlich and Dubinin-Radushkevitch). The fit correlation coefficients (R^2) and the
306 adjustment parameters obtained from each model are shown in Table 1 and plotted in
307 Figure 4. The Freundlich and Dubinin-Radushkevitch models is more fitting, given the
308 correlation coefficient values (R^2). According to Giles et al. (1960), the analysis of the
309 term 1/n of Freundlich equation indicates that: when $n > 1$, the curve q_e versus C_e
310 presents a concave shape with respect to the abscissa axis, and thus the isotherm is
311 satisfactory to the adsorption; when $n = 1$, q_e presents a linear shape with variation of
312 C_e; when $n < 1$ the isotherm presents a convex shape with respect to the abscissa axis,
313 and it is characterized as unfavorable. Since the value of n obtained in this work is equal
314 to 1.63, the process is favorable, and as Fig. 3 shows, the isotherm has a concave shape

315 with respect to the abscissa axis. Kyzas et al. (2015) used Freundlich and Langmuir
316 isotherms to evaluate the propranolol and atenolol adsorption process using graphene
317 oxide as solid adsorbent. Adsorption isotherms were obtained by varying the initial
318 concentration of drug (10-150 mg/L) for 24 h and pH 2. Analyzing the Freundlich
319 isotherm, the authors found an n value of 2.61 and 3.49 for propranolol and atenolol,
320 respectively, at 25 ºC. Haro et al. (2017), in their study of atenolol adsorption in
321 granular activated carbon (adsorption experiments were performed under variable
322 atenolol concentrations (5-900 mg/L), adsorbent 10 g/L, pH 6.0), also found that the
323 model that fitted best the experimental data was the Freundlich model, and the value of
324 parameter n that they found was 2.4 (mg/g).
325 Regarding the Dubinin-Radushkevitch model, the free energy E of adsorption (kJ/mol)
326 with Eq. (7) provides information on the adsorption mechanism. If $E < 8$ kJ/mol, the
327 adsorption process follows a molecular interactional mechanism preferentially, while
328 for $E > 8$ kJ/mol ion-exchange is envisaged. E values showed in Table 1 could indicate
329 that an ionic exchange between charged propranolol and sodium cations in the free sites
330 of Mt could be the dominant adsorption mechanism.
331
332 *3.3. Adsorption kinetics*
333 The kinetic behavior of Mt was examined. The experiments were made using a
334 propranolol solution at C_i = 10 mg/L. Figure 5 shows the kinetic data obtained. The
335 most impressive piece of the kinetic data is that, in the first minute, propranolol
336 molecules were removed by ~96%, which is an extremely rapid kinetic behavior.
337 Afterwards, propranolol remained retained into the material for at least seven days after
338 the assay. When submitting these data to a statistical analysis, it can be observed that
339 between 5, 10, 30 and 60 min there was not a significant difference between the % of

adsorption (p= 0.05). Therefore, Mt required shorter equilibrium times compared to other adsorbents. For example, 24 h were needed to reach a removal of propranolol of 97% from water samples using synthetic mica Na-mica-4 or of 50% using C_{18}-mica-4 (Martín et al., 2018). Haro et al. (2017) and Kyzas et al. (2015) evaluated the removal of β-blockers in aqueous solutions through adsorption process using granular activated carbon as solid adsorbent and it was possible to reach a removal efficiency of approximately 88% after 90 min and 68% after 180 min for atenolol and propranolol, respectively. Recently, Ali et al. (2017) reported the sorption of propranolol on ionic liquid iron new generation adsorbent. The maximum removal of propranolol was 90% with varying times: 40 min, pH: 9.0, initial concentration 50 μ g/L; Dose: 1.0 g/L. The ionic liquid iron nanocomposite adsorbent was selective for propranolol.

In order to examine the rate-controlling mechanism of the adsorption process, the PFO, PSO, IDM and Elovich models were evaluated to fit the experimental data. The values of the kinetic parameters, calculated q_e, determination coefficient (R^2) and the experimental error (Δ q (%), chi-square error) are shown in Table 2. Data obtained from kinetic studies for both materials fit the PSO model better than the other models ($R^2 >$ 0.999). This result was expected since this model predicts that the adsorbate removal rate as a function of time is directly proportional to the difference between the adsorbed amount at equilibrium and the amount adsorbed at any time. Therefore, this model typically does not fit throughout the whole of the time range, only during the initial minutes of the adsorption process (Ho and Mckay, 1999). The kinetic curve is considered to be a classical example of kinetic adsorption plot, in which the pollutant's removal is very fast during the first minutes of contact. This kinetic behavior is common in adsorption of different pollutants onto polymeric adsorbents (Kyzas et al., 2015; Haro et al., 2017).

365

366 *3.4. Influence of the pH on the propranolol adsorption*

367 One of the most important factors which influence the adsorption behavior of any
368 adsorbent material is the pH of the solution. The adsorption of propranolol onto Mt as a
369 function of pH was investigated for pH values ranging from 1 to 12 with an initial
370 concentration of propranolol of 10 mg/L (Figure 6). The results show that the amount
371 adsorbed was independent of the pH of the solution between 2-9 (% adsorption > 94%).
372 Propranolol is a secondary amine with constant acidity (pKa) equal to 9.5 and thus the
373 species of the β-blocker present in solution at pHs ranging from 2 to 9 are mainly
374 positively charged. This phenomenon favors the adsorption process on Mt where the
375 main reaction that must take place is the exchange of the sodium ions of Mt with those
376 of the propranolol-ammonium ions of the solution. At very low pH (1) values, the
377 adsorption slightly decreased to 86%, which could indicate some substitution of sodium
378 by hydrogen ions. At pH > 9, the amine is released by hydrolysis and is precipitated
379 because of its low solubility, therefore impeding the study of adsorption at pH 12. This
380 same issue was observed by Sánchez Martín et al. (1981) when studying the interaction
381 of Mt with a constant release of propranolol.

382

383

384 **4. Conclusions**

385 The natural phyllosilicate Mt proved to be a suitable adsorbent for the elimination of the
386 β-blocker propranolol, being a viable alternative for the treatment of water
387 contaminated with this drug. According to the results, this adsorbent required shorter
388 equilibrium times compared with other adsorbents, reaching 96% adsorption in less than
389 one minute. It was observed that propranolol adsorption kinetics onto Mt followed the

PSO model. The adsorption capacity obtained depended on the initial concentration of solute; lower values of initial concentration provided greater efficiency in the adsorption process. Propranolol adsorption onto Mt was well described by the Freundlich and Dubinin-Radushkevitch models (R^2> 0.993), being the ionic exchange between charged propranolol and inorganic cations in the free sites the most favorable pathway. Additionally, the variable pH presented a low influence in the range of 1 to 9.

XRD, DSC-TG and potential Z were used in order to confirm the entrance of propranolol onto Mt. The XRD showed a slight increase in the interlayer space after the adsorption, suggesting that the retention of propranolol occurs in the interlayer space. The results of the DSC-TG also corroborated the adsorption. While the results obtained by Zeta potential indicated no adsorption of propranolol in the surface.

Studies like this one prove the potential of certain adsorbent materials for their use in the industrial treatment of waters affected by different types of pollutants. Obtaining universal materials, with a high elimination yield and that can be applied to a wide range of contaminants, is the main challenge in this field. Therefore, the following steps in this line of research would be: evaluating how these materials eliminate other families of water contaminants, their application on an industrial scale and, in parallel, improving the functionality of the material itself. On the other hand, its use in cleaning and preconcentration stages in analytical processes is also plausible according to some of the interesting properties of the materials tested.

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FIGURE CAPTION

Figure 1. Experimental diffractograms obtained for Mt (black) and Mt after the adsorption assay of propranolol (red).

Figure 2. Thermal gravimetric analysis ((a) TG (b) DSC) before and after adsorption of propranolol onto Mt.

Figure 3. (a) Propranolol adsorption vs. equilibrium concentration, and (b) percentage of propranolol adsorption vs. initial concentration.

Figure 4. Langmuir, Freundlich and DR models of propranolol adsorption on Mt.

Figure 5. Kinetic models of propranolol adsorption on Mt.

583 **Figure 6**. Effect of pH on propranolol adsorption on Mt.

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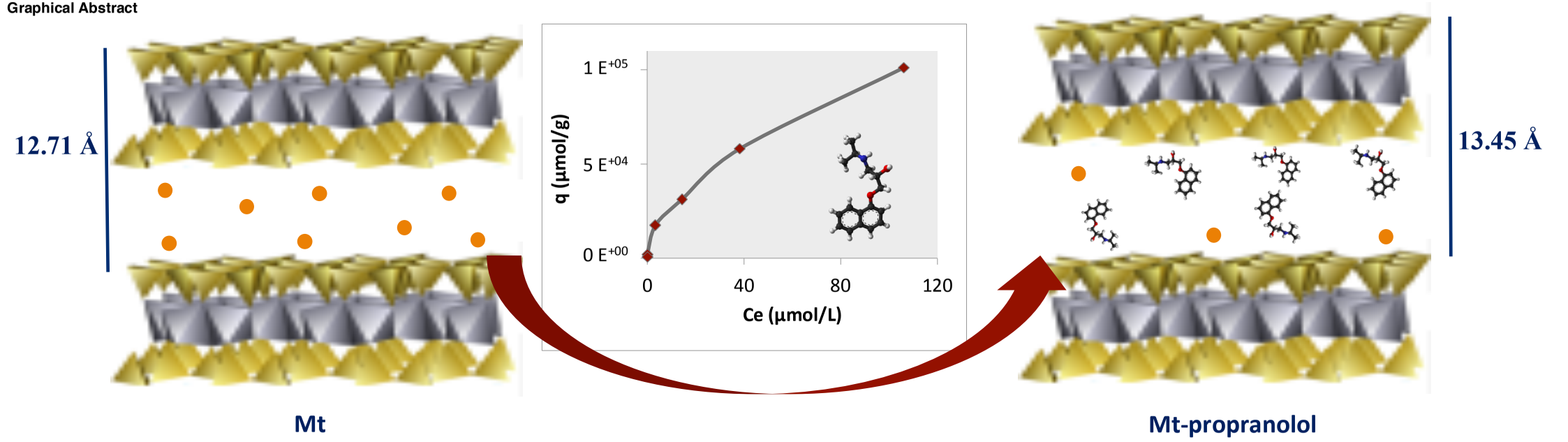
Graphical Abstract



Highlights

- Mt represents a suitable adsorbent of propranolol from aqueous samples
- XRD and DSC-TG indicate that propranolol adsorption occurs in the interlayer space
- Propranolol adsorption is described by Freundlich and Dubinin-Radushkevitch models
- Exchange between propranolol and sodium in Mt interlayer is the pathway proposed
- After 1 min propranolol is 96% removed which is an extremely rapid kinetic behavior

Table 1. Langmuir, Freundlich and Dubinin-Radushkevitch parameters for propranolol adsorption on Mt.

Model	Parameter	Mt
Langmuir	q_{max} (µmol/g)	$1.1E^{+05}$
	K_L (L/µmol)	0.05
	R^2	0.8947
	Δq (%)	47.7
Freundlich	K_F(L/g)	$6.5E^{+03}$
	1/n	0.61
	R^2	0.9932
	Δq (%)	15.0
Dubinin-Radushkevitch	q_{max} (µmol/g)	$6.2E^{+05}$
	KDR (mol^2/J)	$3.7E^{-09}$
	E (KJ/mol)	11.6
	R^2	0.9973
	Δq (%)	8.0

Table 2. Kinetic parameters of propranolol adsorption on Mt.

Model	Parameter	Mt
	q_e (µmol/g)	8.86 ± 0.01
PFO	q_e cal (µmol/g)	0.06 ± 0.01
	k_1 (1/min)	0.25 ± 0.05
	R^2	0.9053
	Δq (%)	61.9
PSO	q_e cal (µmol/g)	8.84 ± 0.01
	k_2 (g/µmol·min)	57.7 ± 16.9
	R^2	1.0000
	Δq (%)	0.5
IDM	k_i (µmol/g·$min^{1/2}$)	0.026 ± 0.005
	C (µmol/g)	8.78 ± 0.01
	R^2	0.8898
	Δq (%)	0.1
Elovich	α (µmol/g·min)	$3.7E^{272}$ ± $1.0E^{272}$
	β (g/µmol)	71.1 ± 5.28
	R^2	0.9837
	Δq (%)	0.0

Figure

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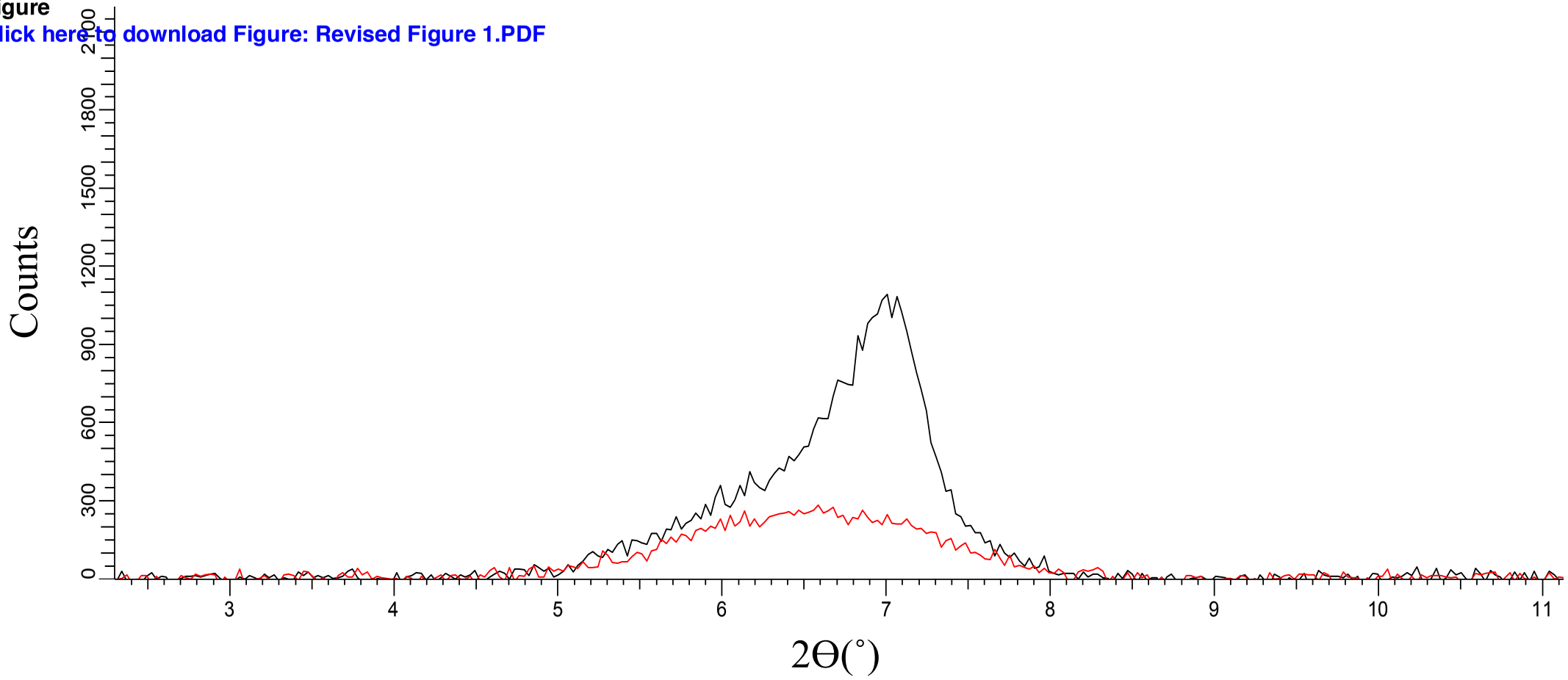

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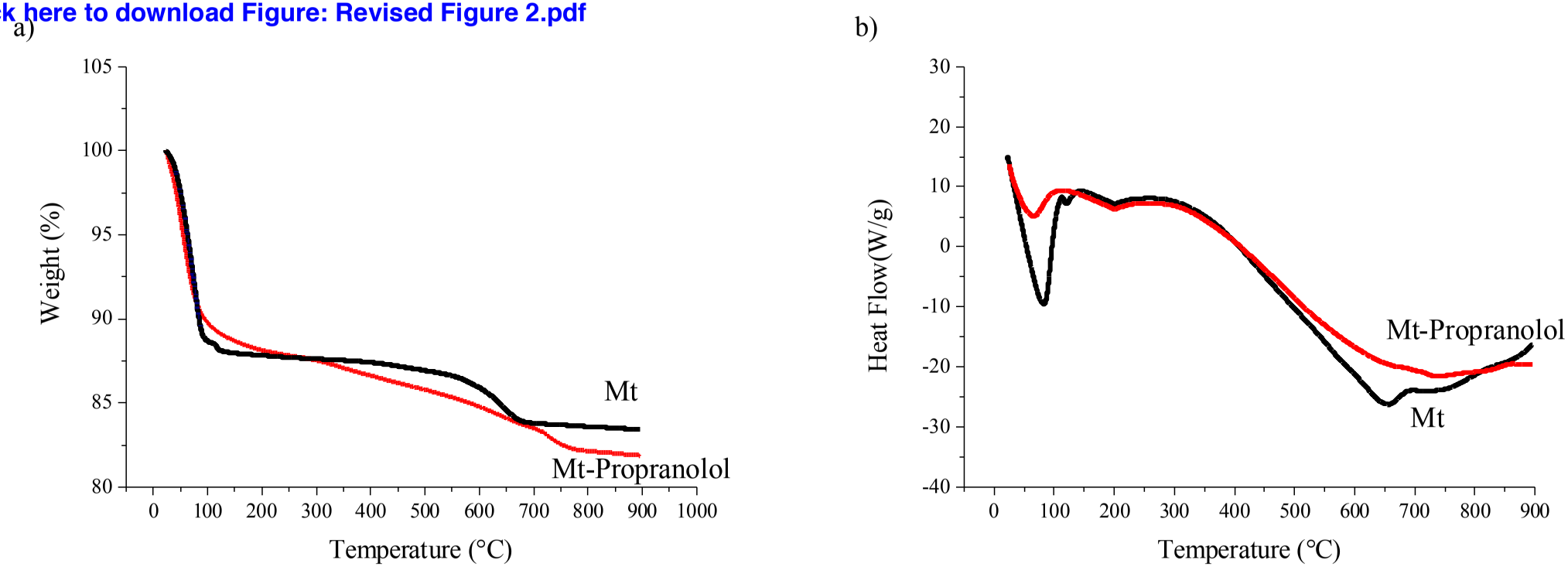

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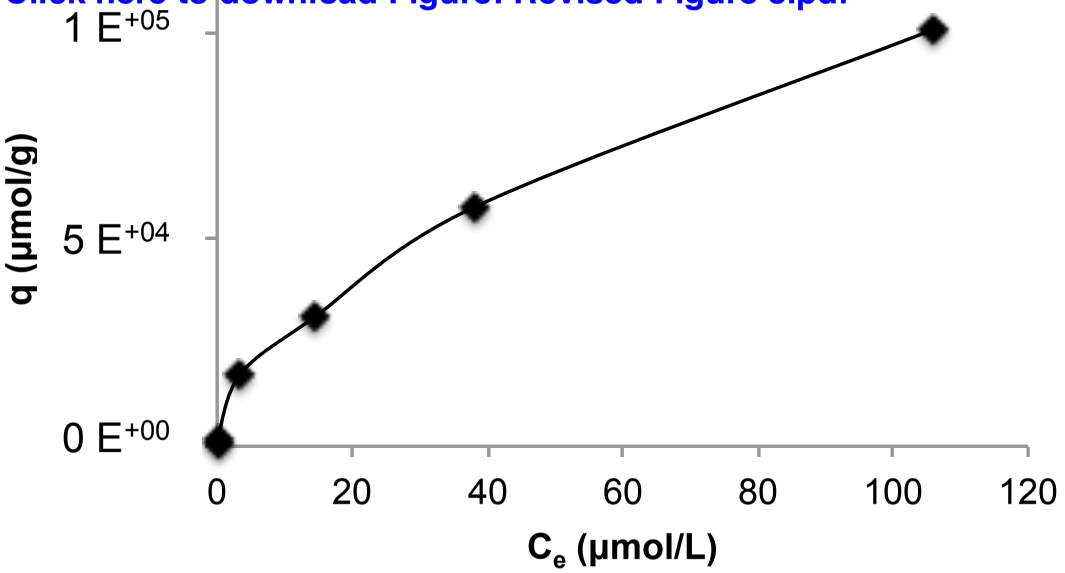

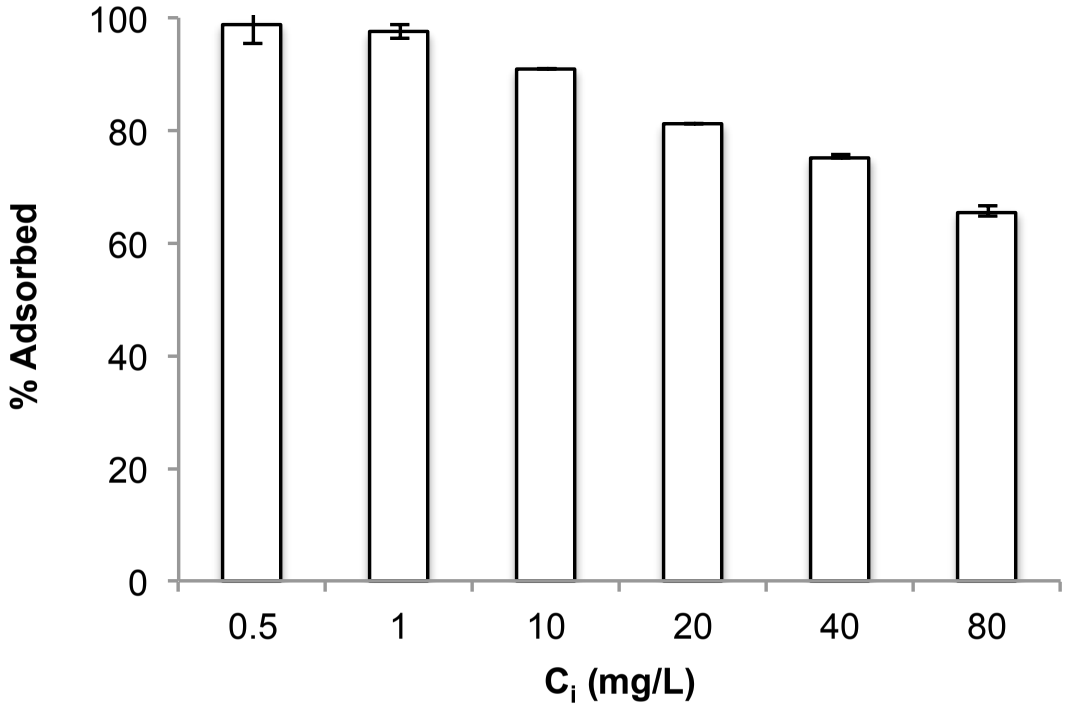

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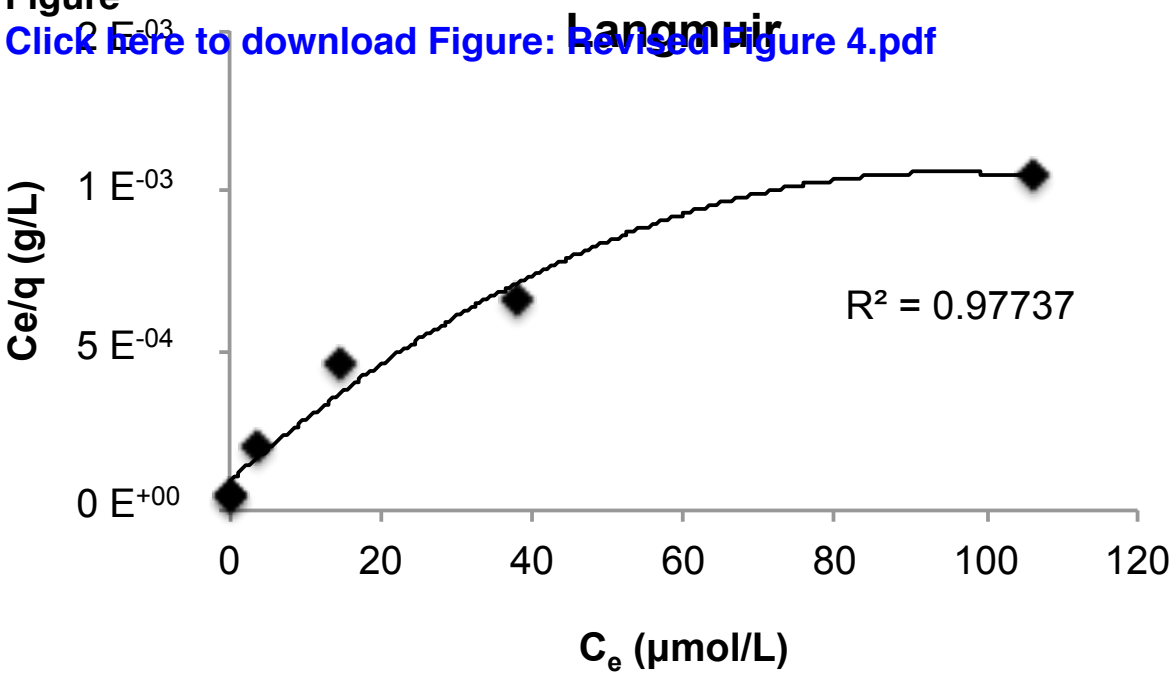

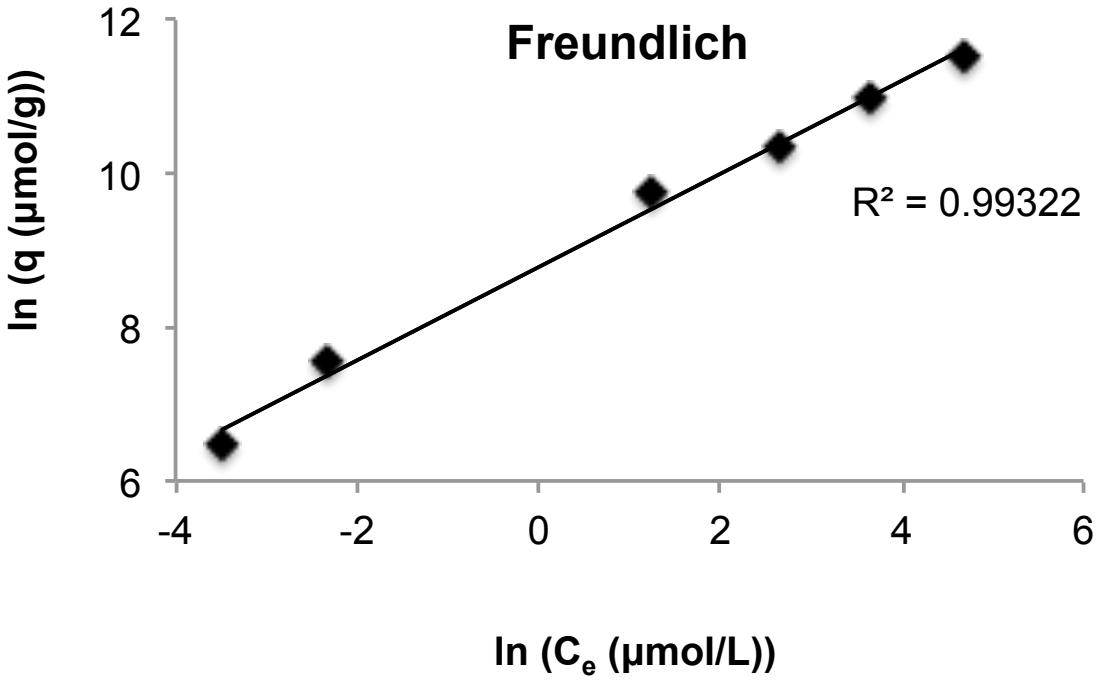

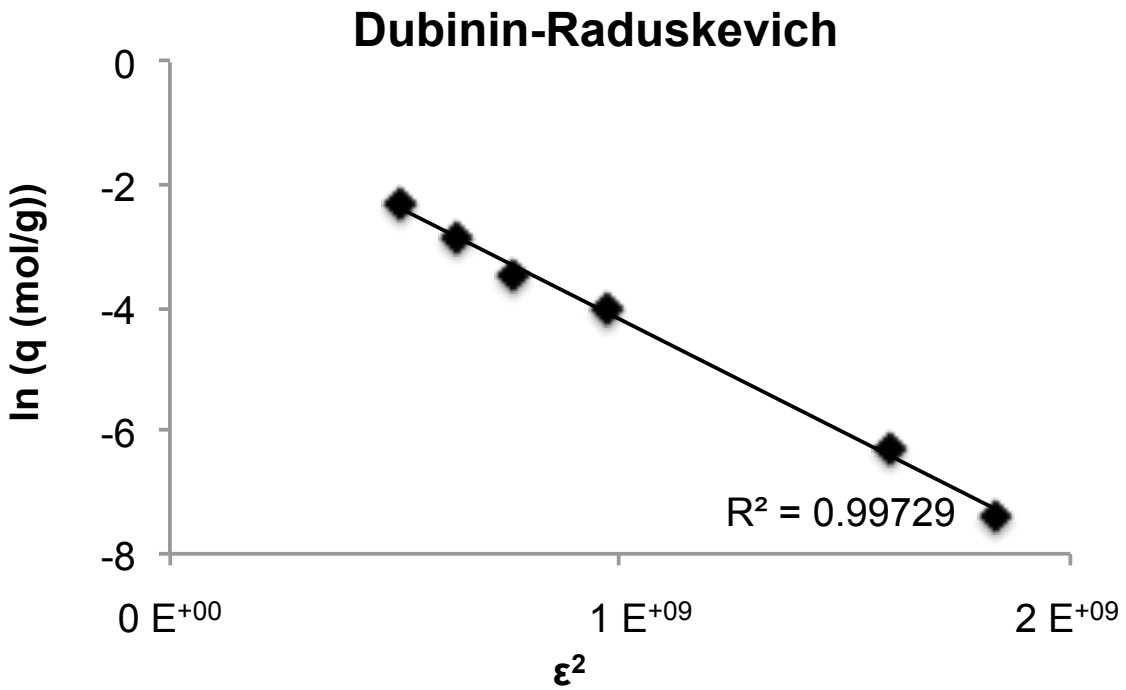

Figure

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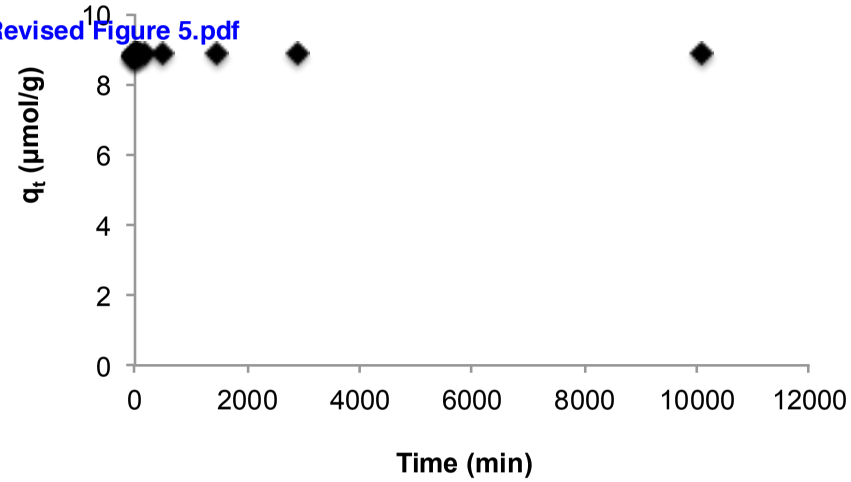

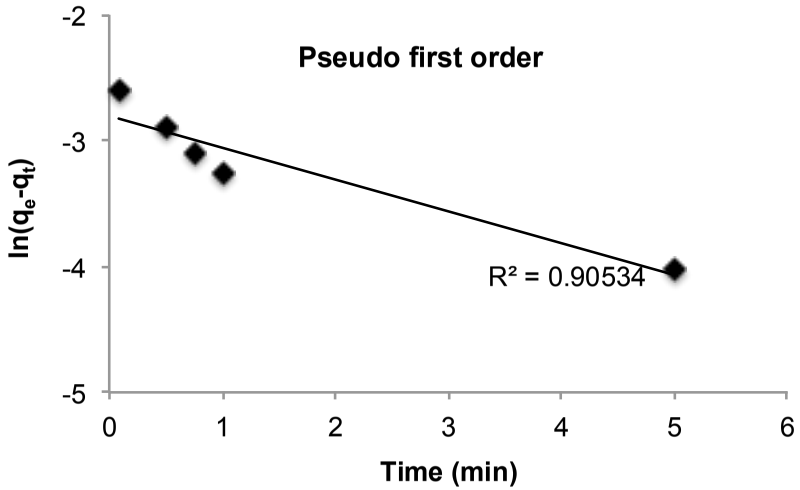

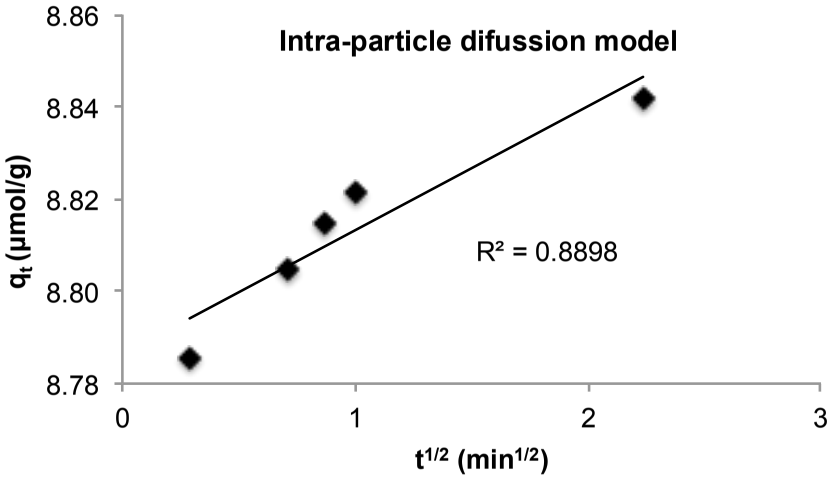

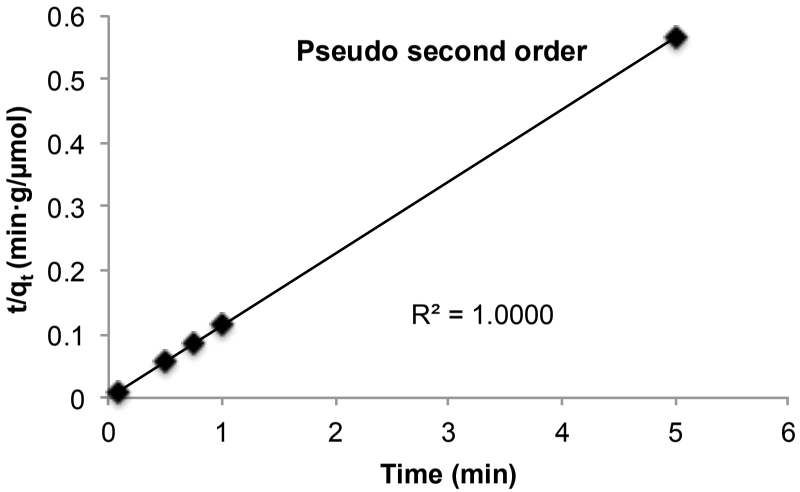

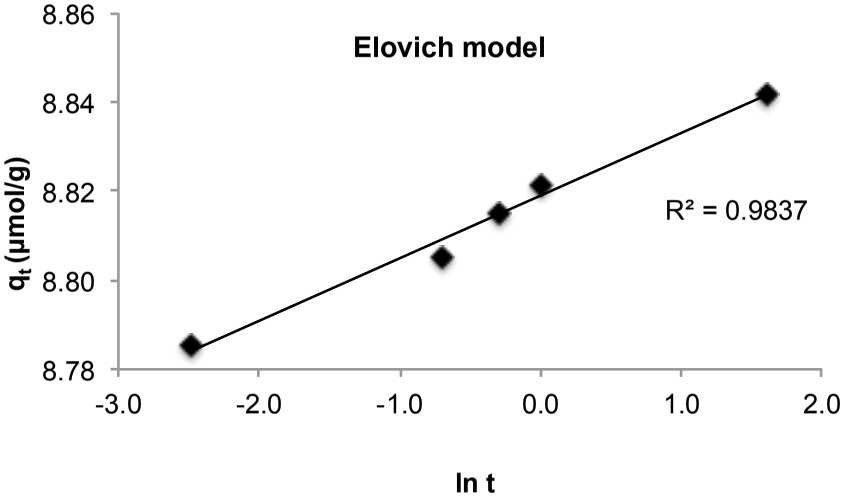

Figure

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