

1 *Removal of basic yellow cationic dye by an aqueous dispersion of*

2 *Moroccan stevensite*

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12

13 **Abstract**

14 The aim of this study was to investigate the adsorption of basic yellow, a
15 cationic dye, from aqueous solution by natural stevensite, with 104 m²/g of specific
16 surface area. The kinetics and the effects of several experimental parameters such as
17 the pH of the solution, adsorbent dose and initial dye concentration were researched
18 using a batch adsorption technique. The results showed that an alkaline pH favoured
19 basic yellow adsorption and the adsorption reached equilibrium in about 20 min. It
20 was concluded that the adsorption process was governed by the electrostatic
21 interaction. The isothermal data were fitted by means of Langmuir and Freundlich
22 equations, and a monolayer adsorption capacity of 454.54 mg/g was calculated.
23 Finally, a good agreement was found between the pseudo-second order model and the
24 experimental data. A high maximum adsorption capacity was obtained (526 mg/g)

25 and a maximum surface density of ~ 9 dye molecules/nm² was estimated, involving a
26 columnar arrangement of the adsorbed molecules.

27

28 **Keywords:** Adsorption kinetics; basic yellow; cationic dye; stevensite; wastewater;

29

30 **1. Introduction**

31 There are more than 100,000 commercially available dyes with over 7×10^5 t of
32 dyes produced annually (Zollinger, 1987). It is estimated that 2% of them are
33 discharged in effluent from manufacturing operations, while 10% are discharged from
34 textile and associated industries (Easton, 1995). Even in small amounts, they are
35 highly visible and have undesired effects to the environment. Furthermore, most
36 dyestuffs are stable to light and oxidation (Namasivayam et al., 2002; Mátivier-
37 Pignon et al., 2003; Orthman et al., 2003; Waranusantigul et al., 2003).

38 The removal of low levels of such compounds is difficult. Several treatment
39 methods have been developed for decontamination purposes including coagulation,
40 chemical oxidation, membrane separation, electrochemical processes, and adsorption
41 techniques. The last one has been recognised as a cost-effective process to remove
42 dyes from aqueous solution and it has been tested with many adsorbents; activated
43 carbon has been the most commonly used adsorbent because of its high adsorption
44 capacity. However, the operating cost of activated carbon adsorption is high (McKay,
45 1983; Leyva-Ramos, 1989; Tsai et al., 2001; Pendleton and Wu, 2003; Singh et al.,
46 2003), though some strategies to reduce costs were also proposed (Kannan and
47 Sundaram, 2001). Problems of regeneration and difficulty in separation from the
48 wastewater after use are the two major concerns of using this material. Other
49 commonly-used adsorbents are chitin (McKay et al., 1983), fly ash (Gupta et al.,

50 1988), silica gels (Ahmed and Ram, 1992), peat (Allen, 1996; Ho and McKay, 1998),
51 and more recently, heteropoly blue-intercalated layered double hydroxide (Bi et al.,
52 2011). A wide compilation of the different considered strategies can be found in a
53 review of Forgacs et al. (2004). However, the amount of adsorbed dye by these
54 methods is not very high. To improve the efficiency of the adsorption processes, it is
55 essential to develop more effective and cheaper adsorbents.

56 Clay minerals have a great potential to fix pollutants such as heavy metals, dye
57 wastewater and organic compounds, and they are widely applied in many fields of
58 science and technology, for example, for the removal of liquid impurities and the
59 purification of gases with surfactant-modified montmorillonite as adsorbent agent
60 (Juang et al., 2002), or the dyes and surfactants from tannery waste waters with
61 natural and acid-activated bentonite and sepiolite (Espantaleón et al., 2003). Kaolin
62 has also been considered for cationic dyes removal from aqueous solutions (Nandi et
63 al., 2009). The porous structure of clay minerals can adsorb large amounts of colorant
64 wastes and their use is justified by low cost, high specific surface area (SSA) and
65 structural properties. Recent studies have been devoted to the mineralogical
66 characterisation of stevensite from the Atlas Mountains of Morocco (called locally
67 “Ghassoul” or “Rhassoul”) and its possible applications in the water treatment field
68 (Elmchaouri and Mahboub, 2005; Benhammou et al., 2005; Bouna et al., 2010; Ellass
69 et al., 2011). SSA of 150 m²/g and 134 m²/g, and adsorption capacities from 240 mg/g
70 up to 600 mg/g were previously reported.

71 The objective of this work was to examine the effectiveness of this abundant
72 stevensite material in the removal of basic dyes. Basic yellow (BY) (Wu et al., 2011)
73 was selected as the modelled basic dye for this work. It is a dyestuff with

74 $C_{15}H_{19}N_3O_4S$ as its molecular formula (M.W.: 337.4 g/mol), and its chemical name is
75 1-methyl-4-((methylphenylhydrazono) methyl) pyridinium methylsulphate.

76

77 **2. Experimental**

78 *2.1. Sampling*

79 The clay mineral was extracted from the Ghassoul mountains (Milot, 1954)
80 and was considered as stevensite, or magnesian smectite (Caillère et al., 1982;
81 Benhammou et al., 2009). The raw clay sample was crushed, ground, sieved through a
82 200 μm sieve, and dried at 110°C in an oven for 2 h before use. Its chemical
83 composition was determined by X-ray fluorescence (Philips PW 1666) spectroscopy.
84 X-ray diffraction (XRD) experiments were performed using a Bruker diffractometer
85 (D8 Advance) with a graphite monochromator and Cu $K\alpha$ radiation. The intensities
86 were measured in a 2θ range (3° – 60°) with a step of 0.02° and a counting time of 5 s
87 per step. Physisorption experiments were performed in a Micromeritics device model
88 ASAP2010 at a constant temperature of 77.35 K. Samples were degasified at 150°C
89 under vacuum for 2 h prior to the experiment. The SSA and the pore size distribution
90 were determined by the Brunauer–Emmett–Teller (BET) method and the Barret-
91 Joyner-Hallenda (BJH) method, respectively.

92

93 *2.2. Adsorption tests*

94 Adsorption tests were carried out in a discontinuous reactor at room
95 temperature, using a volume $V = 50$ ml of distilled water, containing the adsorbent
96 material and the dye. The effect of the adsorbent dosage (m/V , where m is the
97 adsorbent mass), the initial pH and the initial concentration of the dye on adsorption

98 (C_0) were studied separately. The mixture was constantly stirred for a period of time
99 fixed by kinetic tests and then filtered (0.45 μm cellulose nitrate filters, Sartorius).

100 The equilibrium concentration (C_e) was determined using a UV-visible
101 spectrophotometer (JENWAY UV/VIS spectrophotometer model 6505) at the
102 maximum absorbance wavelength ($\lambda_{max} = 412 \text{ nm}$). The amount of metal adsorbed per
103 unit mass of adsorbent, or adsorption capacity, was calculated as:

$$104 \quad q_e = (C_0 - C_e) \times \frac{V}{m} \quad (1)$$

105 The pH of the solution was adjusted by adding 0.1M HNO_3 or 0.1M NaOH solution
106 as required. Blank tests (without dye) were done for each series of experiments as a
107 reference. All experiments were performed twice.

108

109 **3. Results and discussion**

110 The chemical composition of the analysed stevensite-rich sample is
111 summarized in Table 1. These results confirm the magnesium silicate nature of this
112 mineral, with a maximum Mg/Si molar ratio of 0.83. Very low concentrations of Fe or
113 Ca were also detected and Na was not detected in this analysis. The X-ray diffraction
114 pattern showed that Mg-rich trioctahedral smectite, stevensite-15A, was the dominant
115 phase, and minor proportions included reflections of quartz- α and dolomite (Fig. 1).
116 Moreover, the presence of reflections corresponding to other minerals from
117 the smectite group (montmorillonite, PDF files 00-011-0303 and 00-012-0219) was
118 detected.

119 The analysis of the microstructure by nitrogen physisorption reveals the
120 existence of channel-like pores (Kruk and Jaroniec, 2001). The calculated SSA $S_{BET} =$
121 $104 \text{ m}^2/\text{g}$, is roughly lower than those previously reported (Benhammou et al., 2005;
122 Bouna et al., 2010; Ellass et al., 2011), but almost an order of magnitude higher than

123 other considered adsorbents as kaolin, for example (Nandi, et al., 2009). The BJH
124 analysis yielded a well defined typical pore size of 3.9 nm.

125

126

127

Table 1.

128

Fig. 1.

129

130 *3.1. Effect of adsorbent dose (m/V)*

131 In Fig. 2a, the amount of BY removed for a constant dye concentration $C_0 = 1$
132 g/l and different adsorbent doses is shown. It can be seen that this amount increased
133 up to total adsorption. Obviously, the presence of more adsorption sites with higher
134 adsorbent dosage allows the increase of the amount of removed dye. But raising
135 adsorbent dose above 2 g/l, the increment of dye removal was very low until all the
136 dye was removed (e.g. 99.96% of removal for adsorbent dose = 3 g/l).

137

138

Fig. 2.

139

140 *3.2. Effect of initial pH*

141 The pH is the most important factor affecting the adsorption process. To study
142 the influence of pH on the adsorption capacity of stevensite, experiments were
143 performed with the initial pH varying from 2 to 11, for $C_0 = 1$ g/l and adsorbent dose
144 = 1.0 g/l. The results of the pH effect on the adsorption of BY onto stevensite are
145 shown in Fig. 2b. It can be seen that the BY dye removal increased from 2 to 7 and
146 then the removal remained almost the same at $\text{pH} > 7$. Two possible mechanisms of
147 BY adsorption by the stevensite may be considered: electrostatic interactions between

148 the surface groups of stevensite and the cationic dye, and a chemical reaction between
149 the adsorbate and the adsorbent. At $\text{pH} > 7$, a significantly high electrostatic attraction
150 existed between the negatively charged surface of the adsorbent and the cationic dye.
151 As long as the pH of the system decreased, the number of positively charged sites
152 increased, and the number of negatively charged sites decreased. Negatively charged
153 sites on the adsorbent surface favoured the adsorption of cationic dye due to this
154 interaction. On the other hand, the lower adsorption of BY at $\text{pH} < 7$ was due to the
155 presence of excess H^+ competing with the cationic dye for adsorption sites. This
156 suggests that the first mechanism, i.e. electrostatic interactions, might be operative.

157

158 *3.3. Kinetic study and effect of initial concentration of the dye*

159 The kinetics and the effect of initial dye concentration on the removal of dye
160 by stevensite are presented in Fig. 3. The adsorption capacity with initial adsorbent
161 concentration = 1 g/l increased with increasing time, attaining equilibrium after
162 approximately 20 min, independently of the initial dye concentration used in this
163 study ($C_0 = 0.25$ g/l, $C_0 = 0.50$ g/l and $C_0 = 1.0$ g/l).

164 The three kinetic curves follow a saturation-like behaviour, being the
165 characteristic time independent of the dye initial concentration C_0 . On the other hand,
166 an increase in the initial dye concentration led to an increase in the adsorption
167 capacity within the studied range. As the initial dye concentration increased from 0.25
168 g/l to 1.0 g/l, the maximum adsorption capacity of the dye onto the clay changed from
169 249 mg/g to 506 mg/g. This maximum value of 506 mg/g is significantly higher than
170 other reported adsorption capacity values for BY onto MCM41 or MCA (Wu et al.,
171 2011), or onto modified montmorillonite and other clay minerals (Turabik, 2008;
172 Monvisade and Siriphannon, 2009; Kaemkit et al., 2012).

173 At the same time, the obtained adsorption capacity value is also higher than
174 those reported for other anionic and cationic dyes onto stevensite, for example, orange
175 G (Bouna et al., 2010), methylene blue (Bouna et al., 2010, Ellass et al., 2010) or
176 malachite green (Karim et al., 2011), or even for other dyes onto kaolin (Nandi et al.,
177 2009), activated carbon (Kannan and Sundaram, 2001) or montmorillonite (Almeida
178 et al., 2009). However, a roughly higher adsorption capacity value is reported for
179 methyl violet onto stevensite (Elass et al., 2011).

180 Different factors may be responsible for the better performance found for BY
181 onto stevensite in comparison to other adsorbents, or for other dyes onto stevensite. In
182 the first case, the differences found in the nature and physicochemical properties as
183 SSA of the adsorbents can explain this phenomenon, revealing the natural untreated
184 stevensite as one of the best adsorbents. In the second case, the adsorption mechanism
185 discriminates anionic dyes as the orange G against the cationic dyes for adsorption on
186 the negatively charged surface of the stevensite (Bouna et al., 2010). Among cationic
187 dyes, features of the adsorbents as purity, homogeneity and SSA would influence the
188 surface charge density available for dye adsorption and consequently the adsorption
189 capacity.

190 **Fig. 3.**

191

192 3.4. Isotherm studies

193 BY adsorption isotherm data for different initial dye concentrations were
194 investigated to fit the Langmuir and Freundlich models. These data were obtained by
195 dye concentration measurements after adsorbent/adsorbate contact periods equal to
196 the equilibrium time.

$$197 \quad \frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \quad (2)$$

198 where q_e is the equilibrium dye concentration on the adsorbent (mg/g), C_e is the
199 equilibrium dye concentration in solution (mg/l), q_{\max} is the monolayer capacity of the
200 adsorbent (mg/g) and K_L is the Langmuir adsorption constant (l/mg) (Langmuir,
201 1918). A plot of C_e/q_e versus C_e (Fig. 4, top) gave a straight line for the slope $1/q_{\max}$
202 and intercepted the ordinate axis at $1/q_{\max}K_L$. The Langmuir equation is applicable to
203 systems where homogeneous adsorption occurs; this means that the adsorption of each
204 adsorbate molecule onto the surface has equal adsorption activation energy (Juang et
205 al., 1997).

206 On the other hand, the Freundlich equation is

$$207 \quad \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (3)$$

208 where q_e is the equilibrium dye concentration on the adsorbent (mg/g), C_e is the
209 equilibrium dye concentration in solution (mg/l), and K_F (l/g), the Freundlich constant
210 and n , the adsorption intensity, are characteristic parameters of the system, related
211 with the adsorption capacity and surface heterogeneity, respectively. The Freundlich
212 equation is employed to describe heterogeneous systems and reversible adsorption
213 and is not restricted to monolayer formation (Freundlich, 1906). A plot of $\ln(q_e)$ vs.
214 $\ln(C_e)$ for the adsorption of BY onto clay (Fig. 4, bottom) was employed to generate
215 the ordinate K_F and the slope $1/n$.

216 In addition, the other Freundlich constant ($1/n$) is also a measure of the
217 adsorption deviation from linearity. If n is equal to unity, the adsorption is linear. This
218 means that the adsorption sites are homogeneous (as in the Langmuir model) in
219 energy and no interaction takes place between the adsorbed species. In the case $1/n <$
220 1 , which indicates favourable adsorption, the adsorption capacity increases and new
221 adsorption sites appear. When $1/n > 1$, the adsorption bond becomes weak;

222 unfavourable adsorption takes place as a result of the diminution in adsorption
223 capacity (Jiang et al., 2002; Tsai et al., 2003).

224

225 **Fig. 4**

226

227 The values of q_{\max} , K_L , K_F , and $1/n$ and the correlation coefficients for
228 Langmuir (R^2_L) and for Freundlich (R^2_F) models are given in Table 2, and the linear
229 fittings are plotted in Fig. 4. The values of the correlation coefficients showed an
230 almost perfect agreement between the experimental data and both models. The
231 correlation coefficient close to 1 for the Langmuir model indicates that the adsorption
232 took place in the interlayer pores. Moreover, the values of $1/n$ for stevensite were < 1 ,
233 which indicates that adsorption processes are favourable and high adsorption took
234 place.

235 The adsorption of the dye was characterized by the calculated Langmuir
236 monolayer capacity value $q_{\max} = 454.54$ mg/g. In Fig. 3, the value of the monolayer
237 capacity q_{\max} is indicated by a dashed line for comparison purposes. Comparing this
238 value with the experimental saturation values for different dye concentrations, it can
239 be inferred that for low dye concentrations (< 0.50 g/l), a complete monolayer is not
240 formed (saturated value below the theoretical monolayer adsorption capacity),
241 whereas for 0.5 g/l, the adsorption could be described as the complete monolayer
242 formation. Moreover, the 1.0 g/l experiment corroborates the appearance of new
243 adsorption sites, above the monolayer theoretical capacity, in coherence with the $1/n <$
244 1 obtained from the Freundlich model. In summary, these values confirm that
245 stevensite has a high affinity for dye removal.

246

247 **Table 2.**

248

249 *3.5. Adsorption kinetic study*

250 In order to investigate the adsorption processes of BY on stevensite, several
251 simplified kinetic models, namely pseudo-first-order and pseudo-second-order, were
252 considered. The pseudo-first-order kinetic model (Lagergren, 1898) can be expressed
253 as:

254
$$\frac{dq_t}{dt} = k_F(q_e - q_t) \quad (4)$$

255 where q_t is the amount of adsorbate adsorbed in time t (mg/g), q_e is the adsorption
256 capacity at equilibrium (mg/g), k_F is the pseudo-first-order rate constant (min^{-1}), and t
257 is time (min). The integration of Eq (4) for the boundary conditions, $q_t=0$ to q_t and $t=0$
258 to t , results in:

259
$$\log(q_e - q_t) = \log q_e - \frac{k_F}{2.303} t \quad (5)$$

260 The values of the adsorption rate constant (k_F) for BY adsorption on stevensite
261 were determined from linear fitting of the experimental values of $\log(q_e - q_t)$ vs. t . The
262 best description of the adsorption kinetics was obtained by the pseudo-first-order
263 model for the first 30 min; thereafter, the data departed from theory. Thus, the model
264 represents the initial stages where rapid adsorption occurs but cannot be applied for
265 the entire adsorption range (McKay and Ho, 1999). This confirms that the pseudo-
266 first-order model does not adequately describe the adsorption kinetics for BY by
267 stevensite. The calculated parameters are presented in Table 3.

268 According to Ho and McKay (1999), the pseudo-second-order model (Eq (6))
269 agrees with the complexation reaction:

270
$$\frac{dq_t}{dt} = k_s(q_e - q_t)^2 \quad (6)$$

271 where k_s (g/mg·min) is the pseudo-second-order rate constant. Integrating and noting
 272 that $q_t = 0$ at $t = 0$, results in:

273
$$q_t = \frac{t}{\frac{1}{k_s q_e^2} + \frac{t}{q_e}} \quad (7)$$

274 The linear form of which is:

275
$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{1}{q_e} t \quad (8)$$

276 The initial adsorption rate, h (mg/g·min), is defined as:

277
$$h = k_s q_e^2 \quad (9)$$

278 Then, Eqs (7) and (8) become

279
$$q_t = \frac{t}{\frac{1}{h} + \frac{t}{q_e}} \quad (10)$$

280 and

281
$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (11)$$

282 Table 3 abridges the results of the constant rate calculations for different initial
 283 dye concentrations according to the pseudo-second-order and pseudo-first-order
 284 adsorption models, and both linear fittings of t/q_t vs. t are plotted in Fig. 5.

285

286 **Fig. 5.**

287

288 A good fitting of this kinetic model (continuous lines in Fig. 3) with the
 289 experimental data is obtained. These facts suggest that the pseudo-second-order

290 adsorption mechanism was predominant, similar to what was previously proposed for
291 crystal violet and brilliant green adsorption in kaolin (Nandi et al., 2009).

292

293

Table 3.

294

295 Finally, if we consider the maximum adsorption capacity estimated by the fitting,
296 that is, $q_e = 526$ mg/g and the SSA of the adsorbent (104 g/m²), we can conclude the
297 maximum surface dye density obtained is 5.06 mg/m², or ~ 9 BY molecules/nm².
298 Considering the proposed BY molecule size of 1.4 nm x 0.7 nm x 0.4 nm (Wu et al.,
299 2011), a columnar arrangement of the adsorbed dye cations surrounding the surface of
300 the stevensite is concluded.

301

302

303 4. Conclusions

304 The high efficiency of the natural raw stevensite for the cationic dye basic
305 yellow 87 removal from an aqueous solution was confirmed. Adsorption equilibrium
306 was practically achieved within 20 min, being this equilibrium time independent of
307 the dye concentration. The adsorption capacity was affected by the initial dye
308 concentration; the uptake increased with increasing initial dye concentration, above
309 the monolayer adsorption capacity derived from Langmuir isotherm model. The
310 Freundlich model confirmed that adsorption processes of basic yellow on stevensite
311 were favourable, and adsorption sites appeared above the Langmuir theoretical
312 monolayer capacity. In addition, the adsorption is governed by the electrostatic
313 interaction between negatively sites of stevensite and cationic dye, and therefore it is
314 favoured by alkaline pH. Finally, the pseudo-second-order kinetic model was

315 successfully fitted to the kinetic studies, and a very high adsorption capacity of 526
316 mg/g of basic yellow onto stevensite was measured.

317

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450 Table captions

451

452 Table 1. Chemical composition of clay.

453 Table 2. The Langmuir and Freundlich fitting parameters for the adsorption of BY

454 by stevensite.

455

456 Table 3. Pseudo-first-order and pseudo-second-order adsorption parameters of BY

457 dye. Pseudo-second-order function can be plotted and compared with experimental

458 results in Fig. 3.

459

460 Figure captions

461 Fig. 1. X-ray diffraction pattern of natural stevensite. Black line was obtained by
462 smoothing original data (gray line). S: stevensite-15A (PDF: 00-025-1498); Q: quartz-
463 α (PDF: 01-089-8936); D: dolomite (PDF: 01-083-1530).

464

465 Fig. 2. a) Effect of adsorbent dose on the adsorption of BY dye by stevensite; b)
466 Effect of pH on the adsorption of BY dye by stevensite. Lines are guides for the eye
467 only.

468

469 Fig. 3. Variation of adsorption capacity with time, for three different initial dye
470 concentrations. The calculated value of monolayer capacity of the Langmuir
471 adsorption model q_{max} is indicated by a dashed line (see discussion in section
472 3.4). Solid lines are fittings of the simplified kinetic the pseudo-second-order
473 model, as obtained in section 3.5.

474

475 Fig. 4. Top: Langmuir plot and linear fitting for the adsorption of BY onto stevensite;
476 q_e and C_e were considered in mg/l and g/l, respectively. Bottom: Freundlich plot and
477 linear fitting for the adsorption of BY onto stevensite. Red lines are linear fittings.

478

479 Fig. 5. Pseudo-second-order kinetic plots for the experimental data shown in Fig. 3.

Table 1[Click here to download Table: Table1.doc](#)

Elements	Percentage present (w/mass- %)
SiO ₂	57.94
Al ₂ O ₃	1.47
Fe ₂ O ₃	0.43
MgO	32.46
CaO	0.34
Loss of ignition	7.36

Table 2[Click here to download Table: Table2_err.doc](#)

Langmuir			Freundlich		
q_{max} (mg/g)	K_L (ml/mg)	R^2_L	$1/n$	K_F (l/g)	R^2_F
455±2	210±9	0.9993	0.64±0.03	81.5±0.6	0.9913

Table 3[Click here to download Table: Table3_err.doc](#)

Initial dye concentration C_0 (mg/l)	Pseudo-first-order			Pseudo-second-order			
	$q_{e,F}$ (mg/g)	k_F (10^{-3} min)	R_F^2	$q_{e,s}$ (mg/g)	k_s (10^{-3} min)	h (mg/g.min)	R_s^2
250	200±10	180±10	0.78	250±3	3.8±0.2	238±9	0.999
500	290±10	120±10	0.95	454±4	1.6±0.1	330±10	0.999
1000	280±30	130±20	0.83	526±4	2.40±0.07	670±10	0.999

Figure 1

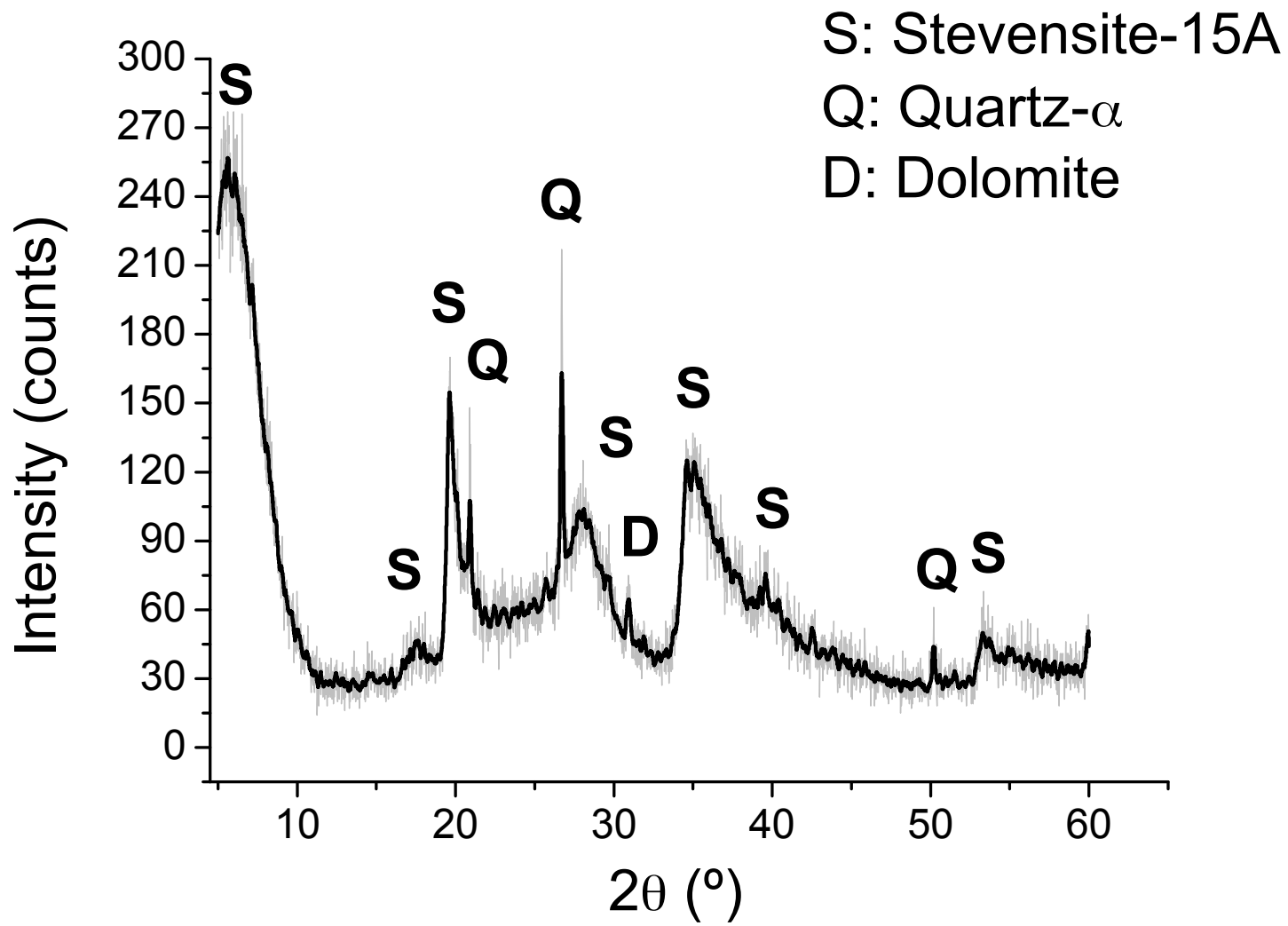


Figure 2

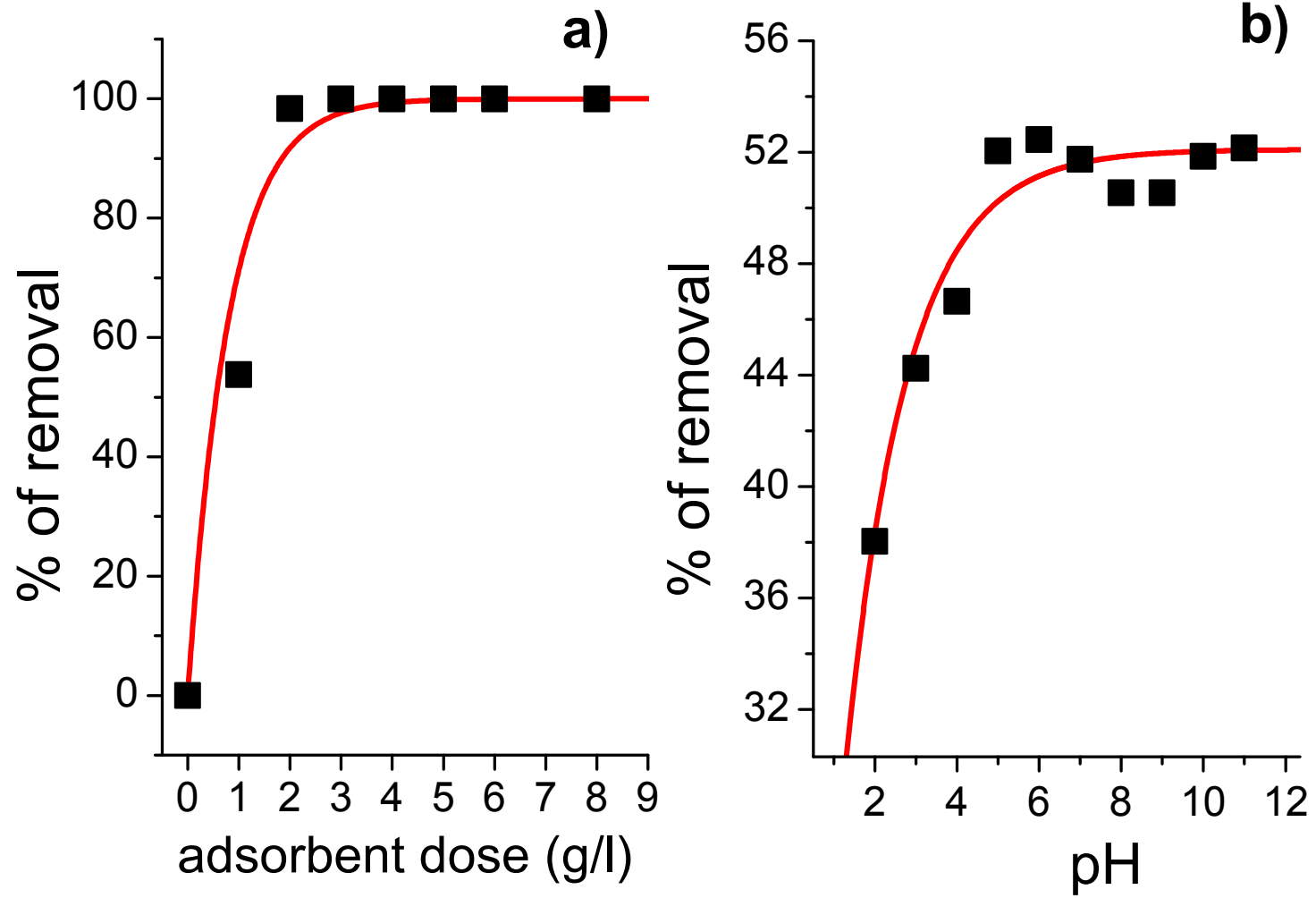


Figure 3

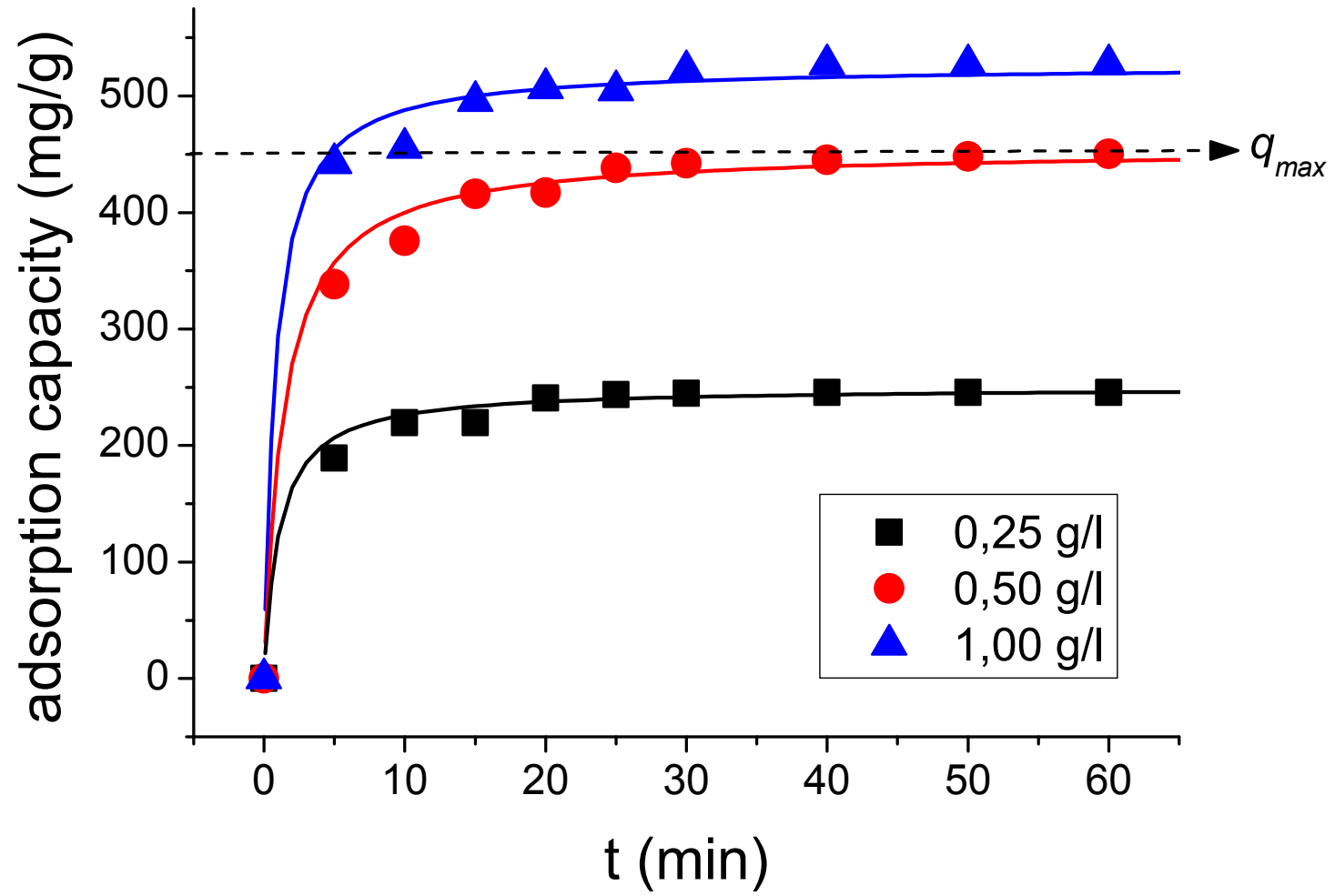


Figure 4

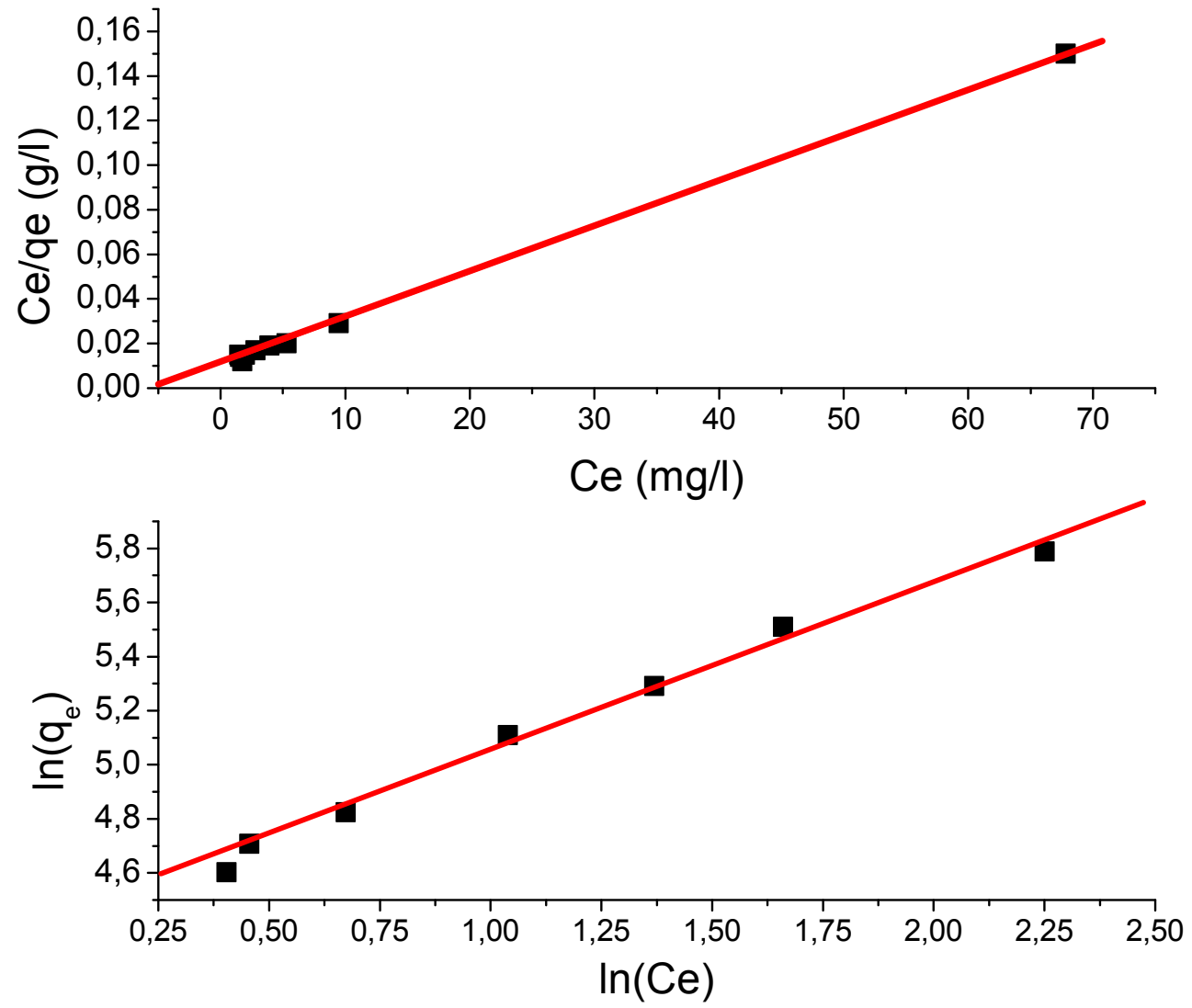


Figure 5

