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1 **Graphene oxide chemically reduced and functionalized with KOH-PEI for**
2 **efficient Cr(VI) adsorption and reduction in acidic medium**

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5 Yasmine Tadjenant,^{1,2} Nahed Dokhan,² Alexandre Barras,¹ Ahmed Addad,³ Roxana Jijie,¹
6 Sabine Szunerits¹ and Rabah Boukherroub^{1*}

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9 ¹ *Univ. Lille, CNRS, Centrale Lille, Univ. Polytechnique Hauts-de-France, UMR 8520 -*
10 *IEMN, F-59000*

11 *Lille, France*

12 ² *Research Unit, Materials, Processes and Environment (URMPE), University of Boumerdes,*
13 *Algeria*

14 ³ *Univ. Lille, CNRS, UMR 8207 – UMET, F-59000 Lille, France*

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24 *To whom correspondence should be addressed: Rabah Boukherroub
25 (rabah.boukherroub@univ-lille.fr; Tel: +333 62 53 17 24)

26 **Abstract**

27 In this study, graphene oxide (GO), polyethyleneimine (PEI) and potassium hydroxide (KOH)
28 were used to synthesize reduced graphene oxide (rGO/PEI-KOH) nanocomposite. The
29 presence and grafting of PEI molecules on the reduced GO surface were assessed by X-ray
30 photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) analyses. The
31 rGO/PEI-KOH nanocomposite was successfully applied for hexavalent chromium, Cr(VI),
32 wastewater elimination. The resulting rGO/PEI-KOH adsorbent was found to be highly
33 effective for Cr(VI) removal at low pH values and achieved a maximum capacity of
34 experimental adsorption of 398.9 mg/g, which is one of the highest sorption capacity of most
35 GO- and PEI-based adsorbents reported in the literature up to date. Studying the adsorption
36 mechanism, the sorption isotherm revealed that the modified-Langmuir model was the best fit
37 and Cr(VI) removal follows a pseudo-second-order kinetics, with the predominance of
38 intraparticle diffusion during the first step of adsorption. XPS analysis indicated the presence
39 of appreciable amount of Cr(III) on the adsorbent surface, which suggests that the adsorbed
40 Cr(VI) ions were effectively reduced to Cr(III) on the rGO/PEI-KOH adsorbent surface
41 (~70% of the total adsorbed Cr). Cr(VI) adsorption and subsequent reduction to Cr(III) both
42 contributed to the Cr(VI) removal. The results of the present study highlight the benefits of
43 rGO/PEI-KOH like low cost, environmentally friendly, large toxic Cr(VI) ions adsorption
44 capacity and its effective reduction to less-toxic Cr(III).

45

46 **Keywords:** *Reduced graphene oxide; Polyethylenimine; Cr(VI) adsorption; High adsorption*
47 *capacity; Cr(VI) reduction.*

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50

51 **1. Introduction**

52 Chromium is one of the most toxic heavy metals discharged into the environment and
53 constitutes one of the main causes of environmental pollution associated with a non-negligible
54 health problem. It commonly originates from diverse industrial wastewaters, derived from
55 factories of electroplating, tanning, textile dyeing, stainless steel production, water cooling,
56 and other industries ([Barnhart, 1997](#)).

57 Chromium is usually found in trivalent (III) as well as hexavalent (VI) states. While
58 Cr(VI) is highly toxic and can lead to severe illnesses such as dermatitis, kidney failure, lung
59 cancer and even death, Cr(III) is less toxic and represents an important element for the proper
60 functioning of living organisms ([Zhou et al., 2016](#)). Therefore, Cr(VI) is viewed as a critical
61 polluting agent and is listed by the US Environmental Protection Agency as class A human
62 carcinogen (US-EPA1998). Hence, eliminating Cr(VI) from wastewater or reducing it to
63 Cr(III) prior to discharge into the environment is imperative.

64 Several methods have been developed for the removal of Cr(VI) from aqueous media,
65 including physical (washing or electrical enrichment), biological (plant enrichment), and
66 chemical (adsorption and reduction) approaches. However, most of these methods and
67 particularly the physical and biological processes experience several limitations such as
68 complexity of operation and elevated costs, and require long periods of time, which has
69 significantly impeded their use in Cr(VI) treatment. In contrary, the chemical method is a
70 favored technique because of its flexibility, high efficiency, design and operational simplicity
71 for the elimination of Cr(VI) and thus it is attracting increasing attention ([Zhou et al., 2016](#);
72 [Wang et al., 2017](#)).

73 In chemical methods, various adsorbents have been identified to withdraw Cr(VI) from
74 polluted water, such as activated carbon ([Sandhya and Tonni, 2004](#)), KOH-modified
75 carbonized eucalyptus sawdust ([Zhang et al., 2018a](#)), PEI-modified biomass ([Deng and Ting,](#)

76 2005), mesoporous carbon microspheres (Zhou et al., 2016), iron nanoparticle-decorated
77 graphene (Jabeen et al., 2011), etc. However, biosorbents have often low surface area and
78 limited mechanical resistance, causing additional potential secondary emissions in extreme
79 conditions. On the other hand, bare metallic nanoparticles are readily oxidizable and can
80 easily agglomerate, while carbon-based adsorbents display a relatively low adsorption
81 capacity. Such forms of disadvantages have impeded their use for Cr(VI) elimination from
82 wastewater (Ma et al., 2012; Zhang et al., 2018b). Therefore, the development of new
83 materials with a large surface area, high removal efficiency, stability in extreme conditions
84 and easy separation procedure is very attractive.

85 Most recently, chemical methods for the synthesis of adsorbents exhibiting high
86 performance for simultaneous adsorption and reduction of Cr(VI) turns to an applicable
87 research hotspot (Ma et al., 2012; Wang et al., 2017; Zhang et al., 2018b). Graphene oxide
88 (GO), consisting of a monolayer of carbon atoms covalently bonded, forms one of the
89 currently most investigated two-dimensional nanomaterial. GO displays an ultra large active
90 surface area and plentiful of oxygen containing functional groups (e.g., -OH, -C=O, -COOH).
91 Reduced GO (rGO), obtained from GO reduction using different means, has been investigated
92 as an efficient adsorbent for Cr(VI) thanks to its high capacity of adsorption (He et al., 2017;
93 Pakulski et al., 2018).

94 KOH reduction of GO was firstly reported by Fan et al. (Fan et al., 2008) who noticed that
95 a chemically stable suspension of graphene can be easily prepared by a simple heating of
96 exfoliated graphite oxide at mild temperatures (50-90°C) in strongly alkaline conditions. But
97 no noticeable works has been reported on the Cr(VI) adsorption/reduction by GO treated with
98 KOH.

99 Polyethyleneimine (PEI) with plenty of primary and secondary amine groups present in a
100 macromolecular chain can partially reduce and simultaneously functionalize GO (Shao et al.,

101 2016). PEI-functionalized GO exhibits interesting adsorption ability for removing toxic
102 cations (Pakulski et al., 2018).

103 Compared with chemical reduction using strong and toxic agents like hydrazine and
104 sodium borohydride, chemical reduction with KOH or PEI is less efficient for completely
105 eliminating the oxygen-containing functional groups on GO, but they have the advantage of
106 being environmentally friendly. Additionally, their simultaneous use may be interesting as in
107 chemical reduction processes of GO, elimination of oxygen groups is generally selective
108 depending on the reducing reagent used (Hayes et al., 2014; Nia et al., 2017). Hence,
109 combining two soft reducing chemicals may represent an efficient manner to optimize
110 deoxygenation of GO sheets, while simultaneously functionalizing the resulting rGO.

111 In the present work, a strong KOH solution containing PEI as a reducing and
112 functionalizing agent is proposed to prepare a nanocomposite material, rGO/PEI-KOH, under
113 mild reaction conditions. The resulting rGO/PEI-KOH was investigated for Cr(VI)
114 elimination. The rGO/PEI-KOH not only exhibited high adsorption capacity, but it was able
115 to effectively reduce the adsorbed Cr(VI) to low toxic Cr(III) ions.

116

117 **2. Experimental**

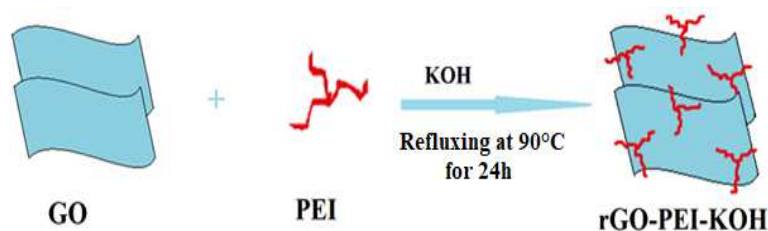
118 **2.1. Materials**

119 Polyethylenimine (PEI, MW~25,000), potassium hydroxide (KOH), potassium dichromate
120 ($K_2Cr_2O_7$), and hydrogen chloride (HCl) were purchased from Sigma-Aldrich. Graphene
121 oxide (GO) powder was obtained from Graphenea-Spain. Milli-Q water (resistivity: 18.2
122 $M\Omega.cm$) was utilized throughout this work.

123 **2.2. Preparation of rGO/PEI-KOH nanocomposite**

124 An easy preparation technique of rGO/PEI-KOH was established in this work. In short, 20 mg
125 of GO was added to 18 mL of water and sonicated for 1 h to form a homogeneous solution.

126 Then, 2 mL of PEI aqueous solution (1 mg/mL) was added. The resulting suspension was
127 mixed under vigorous stirring for 5 h at room temperature. Thereafter, 40 mg of KOH was
128 added to the mixture and stirred at 90°C for 24 h. The color of the dispersion changed from
129 yellow-brown to black, signifying the transformation of GO to reduced graphene oxide (rGO).
130 The obtained black precipitate was isolated by centrifugation (4600 rpm) and washed
131 copiously with water and ethanol to remove excess of PEI and KOH. Finally, the rGO/PEI-
132 KOH was obtained and dried at 80°C for overnight (**Scheme 1**).



134 **Scheme 1.** Schematic illustration of rGO/PEI-KOH preparation.

135

136 2.3. Cr(VI) removal experiments

137 A stock solution of Cr(VI) (20 mg/mL) was obtained by dissolving $K_2Cr_2O_7$ in Milli-Q
138 water. The stock solution was diluted to prepare different concentrations. We varied the initial
139 concentration of Cr(VI) from 50 to 700 mg/L, the pH from 2 to 9, the dosage of adsorbent
140 from 0.5 to 2.5 mg/mL, and the contact time from 10 to 1440 min. 0.1 M HCl or 0.1 M NaOH
141 aqueous solution was used to adjust the pH value. All adsorption experiments were performed
142 at ambient temperature. Adsorption experiments were performed by adding 2 mg of rGO/PEI-
143 KOH into 2 mL of Cr(VI) aqueous solution. After being shaken for 24 h, the solution was
144 subjected to centrifugation at 13,500 rpm during 5 min and finally UV-vis spectrophotometry
145 was used to determine the residual concentration of Cr(VI) in the supernatant at the maximum
146 absorption wavelength of 348 nm in acidic pH and at 372 nm in alkaline pH.

147 The effect of initial Cr(VI) amount, pH, and contact time on the efficiency of Cr(VI)
148 elimination was investigated. Afterwards, the percentage of removal R (%) and the capacity
149 of adsorption (Q_e , mg/g) of Cr(VI) were calculated using equations (1) and (2), respectively:

$$150 \quad R(\%) = \left(\frac{C_0 - C_e}{C_0} \right) \times 100 \quad (1)$$

$$151 \quad Q_e = (C_0 - C_e)V/M \quad (2)$$

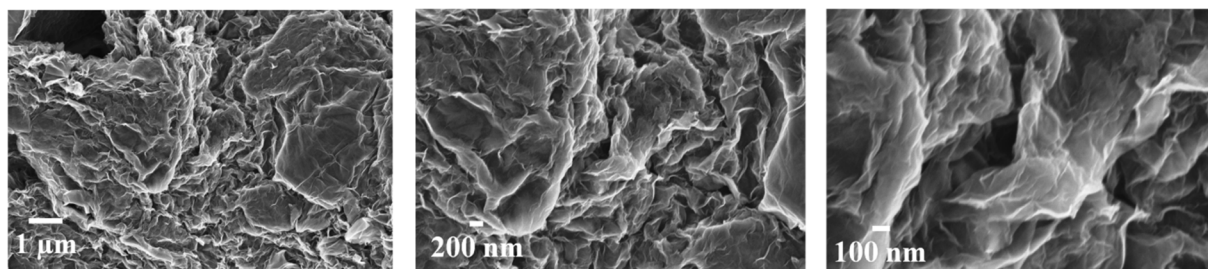
152 Where C_0 (mg/L) is the initial concentration of Cr(VI) ions, C_e (mg/L) is the equilibrium
153 concentration of Cr(VI) ions, Q_e (mg/g) is the capacity of adsorption, V (L) is the initial
154 volume of Cr(VI) solution, and M (g) is the mass of the as-elaborated rGO/PEI-KOH.

155

156 3. Results and discussion

157 3.1. Morphological and chemical analysis

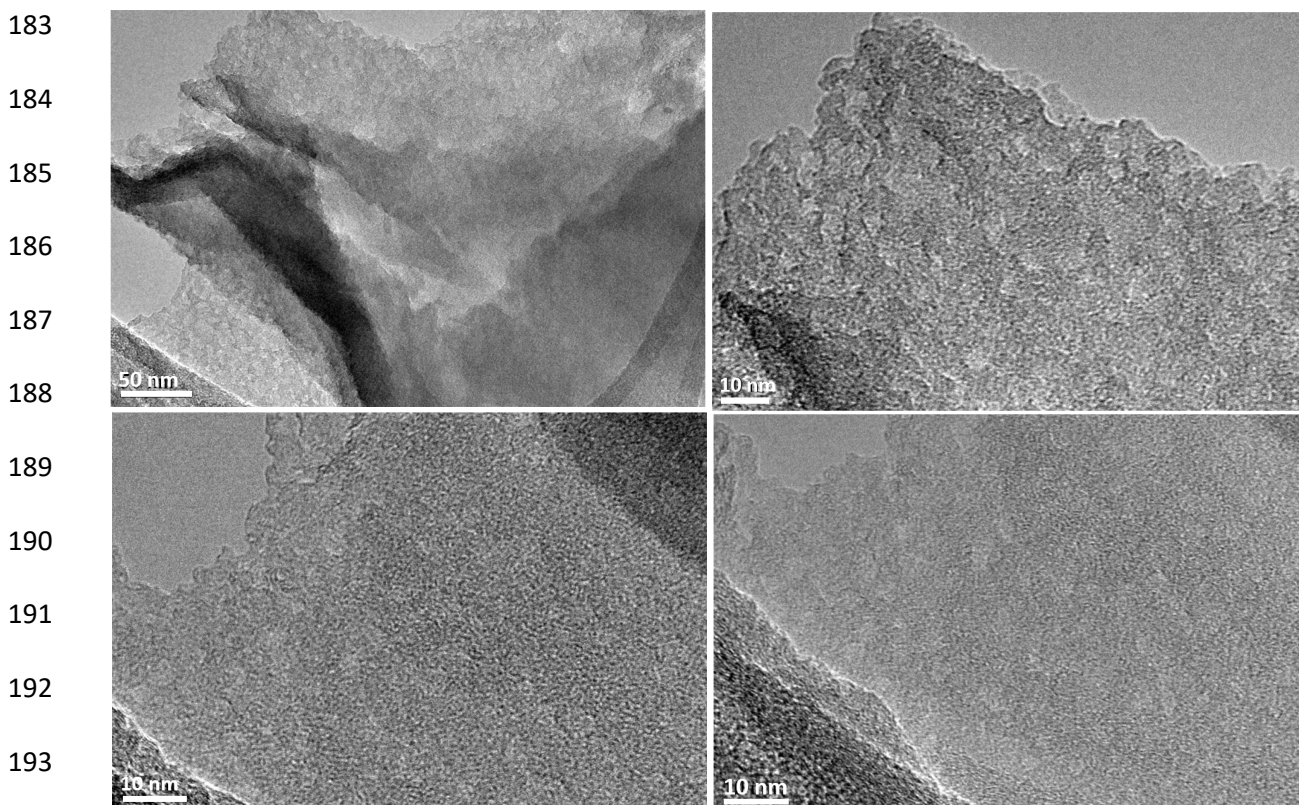
158 **Figure 1** depicts the SEM images of rGO/PEI-KOH at different magnifications. It reveals
159 wrinkled flakes aspect of thin and random rGO/PEI-KOH sheets; the nanosheets are visibly
160 crumpled in an agglomerated phase. The presence of these many wrinkles is most likely due
161 to the suppression of the large quantities of negatively charged functional oxygen groups
162 previously covering the GO during the thermal reaction with PEI-KOH. Indeed, the reduction
163 of GO, as suggested by the UV-Vis, FTIR and XPS analyses (discussed in the next section),
164 led to the partial reconstruction of the graphenic network; the sheets then tend to aggregate in
165 order to diminish the free energy ([Huang et al., 2018](#)). Additionally, hydrogen bonding
166 between the remaining oxygen and the amine groups of PEI might result in these crumpled
167 rGO sheets.



168

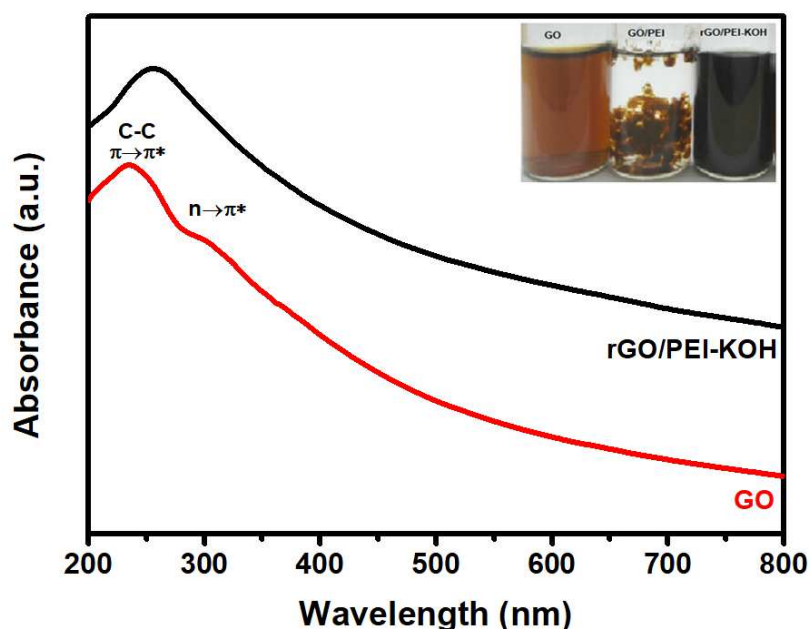
169 **Figure 1.** SEM images of rGO/PEI-KOH composite at low and high magnifications.

170 On the transmission electron microscopy (TEM) images of **Figure 2**, wrinkled graphene
171 sheets (dark areas) are visible. The images also indicate that the graphene sheets were etched
172 during the hydrothermal reduction-functionalization of GO; traces of nanopores can be seen
173 in **Figure 2** (Lu et al., 2012; Sun et al., 2012). The nanopores formation is not fully clarified
174 in this work as usually GO becomes porous during a process where strong radicals like
175 hydroxyl radicals (OH[•]) are produced locally in the vicinity of rGO surface; these radicals are
176 known to have ability to break the C–C (sp²) bonds in the graphene sheet, causing its porosity
177 and could even break GO into ultra-small graphene oxide of zero dimensions (Zhao et al.,
178 2017). Many oxidation processes are able to produce these highly reactive hydroxyl radicals,
179 such as photocatalysis, Fenton reactions, ozone, radiolysis, electron beam irradiation,
180 sonolysis (Wu and Shi, 2010) and high voltage electrical discharge (Sahni and Locke, 2006).
181 However, these strong radicals could also intervene during elaboration under hydrothermal
182 conditions in basic media, as reported by Feng *et al.* (Feng et al., 2016).



194 **Figure 2.** TEM images of rGO/PEI-KOH sheets at low and high magnifications.

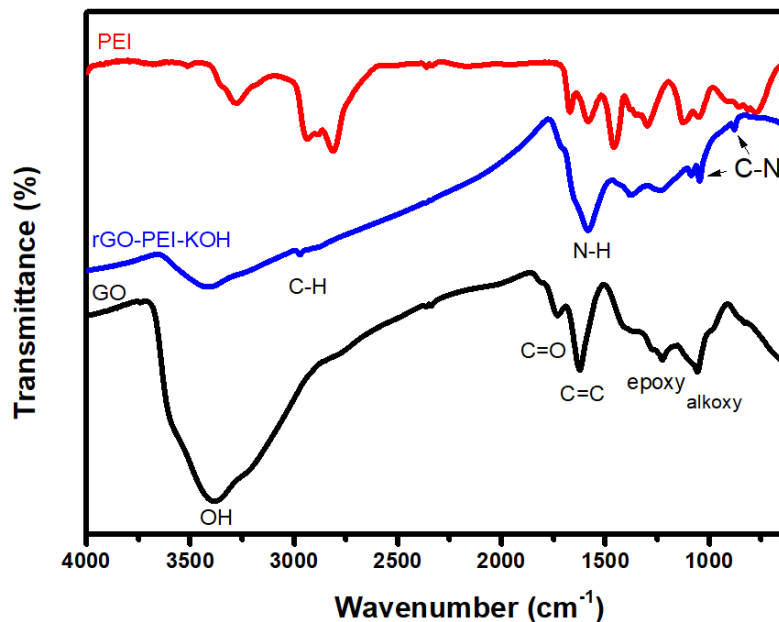
195 The reduction of GO was monitored by UV-vis spectrophotometry. As shown in **Figure 3**,
196 GO displays two bands at 235 nm due to the $\pi-\pi^*$ transition of aromatic C=C bonds, and 310
197 nm ascribed to the $n-\pi^*$ transition of C=O bonds (Fellahi et al., 2011). After PEI-KOH
198 reduction-functionalization for 24 h, the peak related to the $\pi-\pi^*$ transition initially at 235 nm
199 shifted to 258 nm; this red-shift in absorption peak takes place when the π electron
200 conjugation is restored within the sheets of graphene. Furthermore, the shoulder in the
201 spectrum disappears, signifying an important decrease of C=O bonds; these two features
202 indicate the partial reduction of GO during the hydrothermal process.



203
204 **Figure 3.** UV-vis spectra of GO and rGO/PEI-KOH in water. The inset exhibits the digital
205 photographs of GO, GO-PEI and rGO/PEI-KOH dispersion in water.
206

207 **Figure 4** shows the FTIR spectra of GO, PEI and rGO/PEI-KOH FTIR. The following
208 functional groups were established in the FTIR spectrum of GO sample: O-H stretching
209 vibrations in COOH group and/or intercalated water (3381cm^{-1}), C=O stretching vibration

210 (1736 cm^{-1}), aromatic stretching vibration of C=C bonds (1623 cm^{-1}), and C-O vibrations of
211 epoxy and alkoxy groups at 1228 and 1056 cm^{-1} , respectively (Budimir et al., 2019).
212 After reduction-functionalization by PEI-KOH treatment, peak intensities associated with
213 oxygen containing groups (O-H and C-O stretching vibrations) diminished significantly,
214 which is a signature of effective GO reduction. In addition, the typical absorption features of
215 the PEI at 2898 and 2970 cm^{-1} corresponding respectively to symmetric and asymmetric C-H
216 stretching from the $-\text{CH}_2$ group of PEI were visible (Budimir et al., 2019). Moreover, the band
217 at 1736 cm^{-1} nearly disappeared, and a new band attributed to the stretching vibration of N-H
218 (in the C-NH group) appeared at 1575 cm^{-1} (Ramanathan et al., 2005; Budimir et al., 2019).
219 Other observed peaks at around 1085 and 876 cm^{-1} are assigned to C-N bond stretching
220 vibrations and CH_2 rock + N-H bending, respectively (York et al., 2003). These results
221 clearly confirm that the GO was effectively reduced during the hydrothermal process and the
222 PEI molecules were attached to the rGO sheets.



223
224
225

Figure 4. FTIR spectra of GO, PEI, and rGO/PEI-KOH.

226 The elemental composition of the as-elaborated PEI-KOH reduced-functionalized GO was
 227 examined using X-ray photoelectron spectroscopy (XPS). **Figure 5(a)** depicts the XPS
 228 spectra of GO and rGO/PEI-KOH. The spectrum of GO essentially comprises the C_{1s} and O_{1s}
 229 peaks at ~285 and ~532 eV, respectively. The peaks in the rGO/PEI-KOH XPS wide scan
 230 located at 285, 400 and 531 eV are ascribed to C_{1s}, N_{1s} and O_{1s}, respectively. The occurrence
 231 of tiny peaks attributable to K_{2p} and K_{1s} in the XPS spectrum originates most likely from
 232 potassium adsorption. Furthermore, the intensity of the oxygen peak was greatly reduced in
 233 the rGO/PEI-KOH as compared to GO, indicating an efficient reduction of GO by KOH-PEI
 234 treatment. The presence of a peak at 400 eV due to N_{1s} proves the successful grafting of PEI
 235 on the rGO sheets (Liu et al., 2013; Budimir et al., 2019). The atomic percentages of each
 236 element (C, O and N) in GO and rGO/PEI-KOH are summarized in **Table 1**.

237 The core level of the C_{1s} of GO can be deconvoluted into three distinct peaks centered at
 238 284.8, 286.8 and 288.3 eV, which correspond to unoxidized graphite carbon skeleton (C–C),
 239 hydroxyl/epoxide groups (C–O) and carboxyl groups (C=O), respectively (**Figure 5b**) (Li et
 240 al., 2001; Liu et al., 2013). The reduction of GO is mainly indicated by three peaks in the C_{1s}
 241 core-level spectrum (**Figure 5c**) showing the same functional groups, but with decreased
 242 intensities of the groups containing oxygen: the sp²-hybridized carbon atoms of graphene (C-
 243 Csp²) at 284.6 eV, the carbon in hydroxyl and epoxide groups (C-O) at 286.5 eV, the
 244 carbonyl groups (C=O) at 287.8 eV, and the carboxyl (OH-C=O) groups at 288.9 eV (Liu et
 245 al., 2013). The band at 285.3 eV is assigned to C-N of the PEI molecules (Shao et al., 2016).

246 The N_{1s} high resolution peak showed a single component after fitting due to amine groups
 247 from PEI (**Figure 5d**).

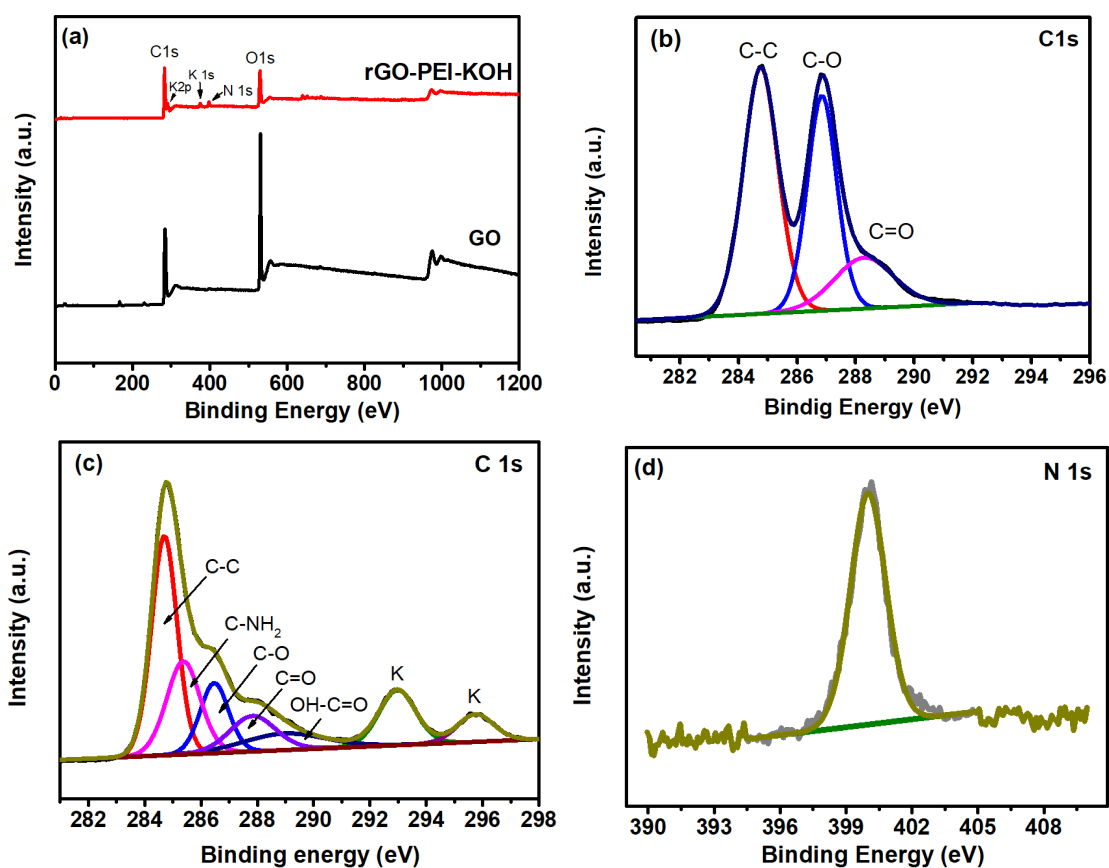
248

249 **Table 1.** Elemental atomic percentage determined using the XPS spectra.

Composite	C _{1s} at. %	O _{1s} at. %	N _{1s} at. %
-----------	-----------------------	-----------------------	-----------------------

GO	69.93	30.07	-
rGO/PEI-KOH	80.13	16.68	3.19

250



251

252

253 **Figure 5.** (a) XPS survey spectra of GO and rGO/PEI-KOH; core level spectra of (b) C_{1s} of
 254 GO, (c) C_{1s} and (d) N_{1s} of rGO/PEI-KOH.

255

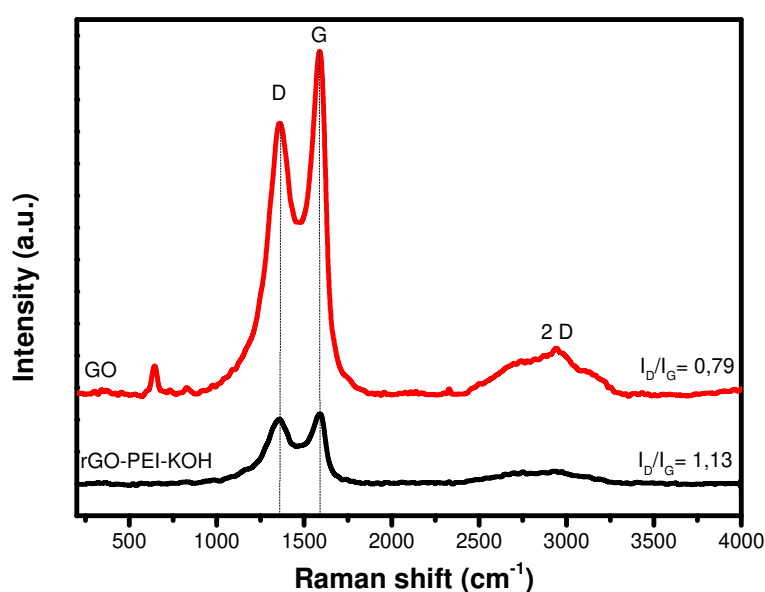
256 The existence of a significant amount of K was identified by the presence of imposing peaks
 257 at 292.9 and 295.7 eV in **Figure 5c**. Since the binding energy discrepancy between these two
 258 peak components is ca. 2.8 eV, and their intensity ratio is ca. 2:1, they are attributed to the
 259 spin-orbit-split doublet K_{2p1/2} and K_{2p3/2}, respectively of potassium cations and oxides (Li et
 260 al., 2001). This suggests that potassium ions probably bind to the remaining oxygen atoms or
 261 are intercalated within rGO sheets.

262 Raman spectroscopy is a powerful and widely employed technique for characterizing
263 graphene based structures involving disorder and defects (Fang et al., 2013). The Raman
264 spectra of GO and rGO/PEI-KOH are depicted in **Figure 6**. They indicate important structural
265 changes in graphene sheets before and after treatment with PEI-KOH. It can be seen that the
266 D peaks (disorder induced symmetry A_{1g} mode) of GO and rGO/PEI-KOH are located at
267 1360 and 1357.3 cm^{-1} , respectively, while the G bands (due to the E_{2g} mode associated with
268 the bond stretching of sp^2 -bonded carbon atoms in hexagonal, two-dimensional lattices) are at
269 1589.4 and 1590 cm^{-1} , respectively.

270 It is worth noting that the chemical changes in graphene-based materials are marked by
271 variations in the D and G band ratios; these variations in the relative intensities of the D and G
272 bands (D/G) reflect modifications in GO electronic conjugation state during the reduction-
273 functionalization phase. Commonly, the ratio I_D/I_G serves to quantify the disorder level in
274 graphene and rGO; this disorder can be related to vacancies, impurities, dislocation, dangling
275 bonds at the edges of the rGO sheets and to the decrease of the average size of the sp^2
276 domains, but can also be the signature of an augmentation of the C sp^3 hybridization caused
277 by molecules grafted to the 2-D hexagonal carbon lattice. After the reduction-
278 functionalization of GO with PEI-KOH, the intensity ratio I_D/I_G rises from 0.79 for GO to
279 1.13 for rGO/PEI-KOH. Usually, reducing GO consists mainly in the elimination of the
280 oxygen functional groups (these later are known to induce sp^3 hybridization of the carbon
281 atoms) from the graphene sheet; when the GO is reduced, sp^3 hybridization diminishes, and
282 the graphene sheet is more or less restored, which is generally accompanied by a diminution
283 in the I_D/I_G ratio. This is not the case in this work as a non-negligible augmentation of I_D/I_G is
284 observed despite the fact that oxygen functionalities have been significantly eliminated as it
285 was proven by XPS and FTIR analyses. We can speculate two reasons for this increase in
286 I_D/I_G ratio: either it highlights the large presence of sp^3 carbon atoms on GO due the grafting

287 of PEI molecule, a signature of the mesoporosity and/or a decrease in the average size of the
288 sp^2 domains in rGO sheets (Fang et al., 2013; Liu et al., 2013; Tong et al., 2015; Singh et al.,
289 2017; Pakulski et al., 2018).

290 Also the red-shift of the D-band (from 1360 to 1357.3 cm^{-1}) testifies the actual
291 functionalization of reduced GO (Budimir et al., 2019). Such results confirm that PEI was
292 effectively grafted on the rGO layer during the reduction-functionalization process; these
293 results are well consistent with the FTIR and XPS data.



294

295 **Figure 6.** Raman spectra of GO and rGO/PEI-KOH.

296

297 The thermal behavior of the rGO/PEI-KOH was evaluated by thermogravimetric and
298 differential thermogravimetric (TG/DTG) analysis. **Figure S1** exhibits the TG analysis curve
299 of the as-prepared rGO-PEI-KOH, displaying different weight losses within the temperature
300 range tested. The initial weight drop (15.4%) between ambient temperature and 150°C is
301 more possibly caused by the evaporation of adsorbed water molecules. A second weight loss
302 (7.4%), observed in the range 150-270°C, is related to the removal of oxygen-containing
303 functional groups. Finally, the weight loss (12.8%) in the 270–550°C temperature range
304 corresponds to the covalently bonded PEI molecules pyrolysis, suggesting that the rGO

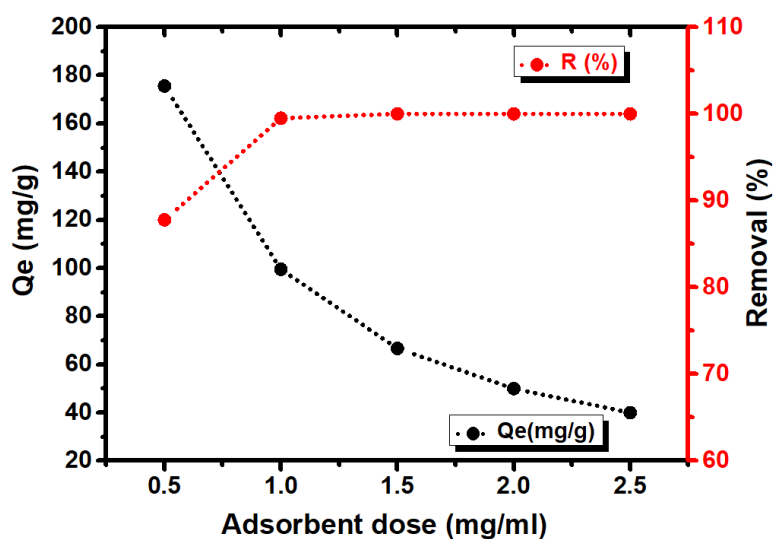
305 surface was modified by PEI (Liu et al., 2013). The results confirm again the surface grafting
306 of PEI molecules on rGO sheets.

307

308 3.2. Cr(VI) elimination performance of the rGO/PEI-KOH composite

309 3.2.1 Effect of adsorbent dosage

310 The effect of adsorbent dosage on the Cr(VI) removal, for a fixed pollutant concentration
311 of 100 mg/L, was investigated and the results are displayed in **Figure 7**. The percentage of
312 removal increases from 87.78 to 100% by increasing the adsorbent dosage from 0.5 to 2.5
313 mg/mL. For adsorbent dosage from 0.5 to 1 mg/mL, the removal efficiency increases until
314 reaching ~100%; this means that the more adsorbent in the solution, the higher the availability
315 of exchangeable sites for metal ions (Sandhya and Tonni, 2004).



316

317 **Figure 7.** Effect of rGO/PEI-KOH dosage on the capacity of adsorption (Q_e) and removal

318 efficiency (R) (initial Cr(VI) concentration: 100 mg/L, pH 2, room temperature, contact time:

319 24 h).

320 On the other hand, the adsorption capacity Q_e shows a clear decrease, suggesting a possible

321 formation of microscopic agglomerates of rGO/PEI-KOH sheets that would reduce the access

322 to all adsorption sites. Exceeding the adsorbent dosage of 1 mg/mL, the removal efficiency

323 remains roughly at ~100%, while the adsorption capacity continues dropping; this is expected
324 given the presence of more adsorbent than what is necessary to remove all the pollutant.

325

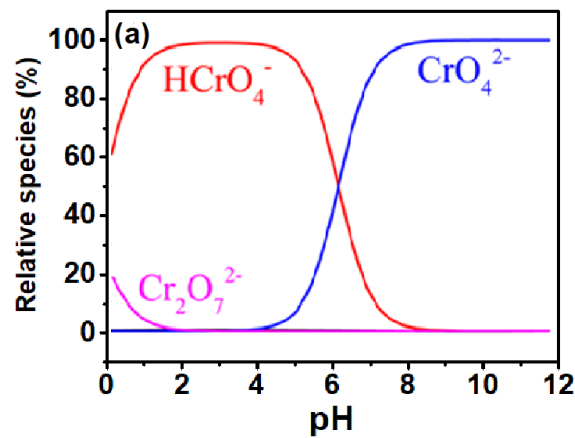
326 3.2.2 pH effect

327 The adsorption tests were carried out at an initial concentration of Cr(VI) of 100 mg/L, a
328 24 h contact time, an adsorbent dosage of 1 mg/mL, in the pH range from 2 to 9 at room
329 temperature. The solution pH greatly affects the stability of Cr(VI) species and the adsorbent
330 charge, thereby affecting the adsorption efficiency. **Figure 8a** illustrates the predominance
331 diagram of $K_2Cr_2O_7$ in water at different pH values. It indicates that the prevailing forms of
332 Cr(VI) ion in solution are chromate (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$), and hydrogen chromate
333 ($HCrO_4^-$) and predominant ions are related to the solution pH and overall concentration of
334 chromate. Cr(VI) is in the form of anionic species, like $HCrO_4^-$ (pH range 2.0–7.0) and
335 CrO_4^{2-} (pH range 7.0–10.0) (Fan et al., 2012) are the dominant species.

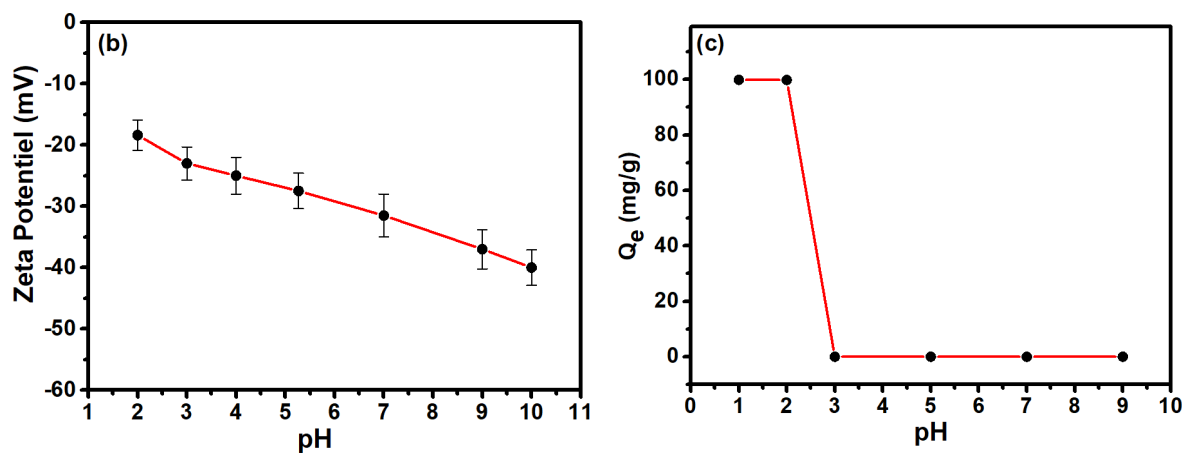
336 **Figure 8b** displays the zeta potential of rGO/PEI-KOH at different pH values. The
337 rGO/PEI-KOH sheets are globally negatively charged even they are grafted with PEI
338 molecules, which are positively charged at low pH. Indeed, the amine groups are protonated
339 under strong acidic conditions, which is beneficial for the Cr(VI) anions adsorption through
340 electrostatic interactions. In contrast, uncharged ($-NH_2$) or deprotonated ($-NH^-$) groups,
341 occurring under basic conditions, will repel these anions thus inhibiting their adsorption. On
342 the other hand, the overall negative charge of the adsorbent sheets remains beneficial, and
343 even necessary, as it will supply the adsorbent with H^+ ions necessary for the Cr(VI)
344 reduction, as we will be seen in the last section (Luo et al., 2017; Wang et al., 2017).

345 **Figure 8c** depicts the adsorption capacity at different pH values. We can notice the
346 absence of Cr(VI) removal by rGO/PEI-KOH for a pH value higher or equal to 3. Indeed,
347 upon increasing the pH from 3 to 9, the divalent CrO_4^{2-} amount rises by gradual conversion of

348 HCrO_4^- ; also the protonation degree of the surface is weakened under weak-acidic/basic
 349 conditions, resulting in greater electrostatic repulsion between ions charged negatively and the
 350 adsorbent surface (Zhou et al., 2016). Nevertheless, strong acid conditions corresponding to
 351 pH lower or equal to 2 is beneficial for Cr(VI) elimination by rGO/PEI-KOH as it promotes
 352 more positive amine groups and less negative Cr(VI) species.
 353 Hence, the pH of the solution, which greatly influences the stability of Cr(VI) species and the
 354 electrostatic charge of the adsorbent, impacts significantly the adsorption efficiency. The pH
 355 2, being the optimal one, was used for all subsequent experiments.



356



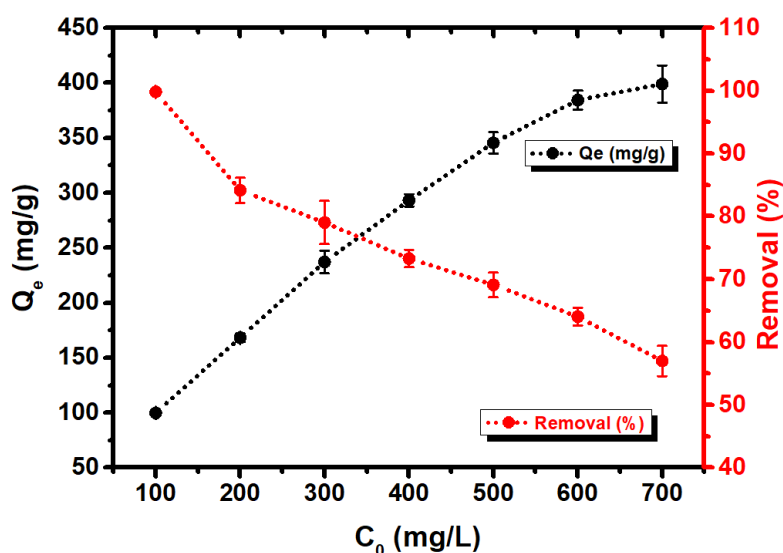
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358 **Figure 8.** (a) Cr(VI) species predominance diagram as a function of pH; (b) Zeta potential of
 359 rGO/PEI-KOH; (c) Adsorption capacity at different pH (initial Cr(VI) concentration:
 360 100 mg/L, adsorbent dosage: 1 mg/mL, room temperature, contact time: 24 h).

361

362 3.2.3 Initial concentration effect

363 The influence of the initial Cr(VI) concentration on adsorption capacity of rGO/PEI-KOH
364 is depicted in **Figure 9**; the Cr(VI) ions are adsorbed favorably on the rGO/PEI-KOH surface
365 at pH 2. The adsorption capacity of rGO/PEI-KOH increases rapidly with increasing the
366 initial concentration of Cr(VI) from 100 to 700 mg/L, implying that there are enough
367 adsorption sites on the adsorbent and attesting the attraction effectiveness between the
368 protonated adsorbent and the hydrochromate anion. The results revealed that the Cr(VI)
369 maximum adsorption capacity of rGO/PEI-KOH is $(398.9 \pm 16.9 \text{ mg/g})$ at room temperature,
370 which is greater than the capacity of PEI-modified graphene (324 mg/g), as shown in the last
371 section.



372
373 **Figure 9.** Effect of initial Cr(VI) concentration on the adsorption capacity (black) and the
374 removal efficiency (red) of rGO/PEI-KOH (pH 2, adsorbent dosage: 1 mg/mL, room
375 temperature, contact time: 24 h).
376 On the other hand, the removal efficiency decreases with the increase of Cr(VI) concentration.
377 This is most likely related to the total available adsorption sites, since they are limited for a
378 fixed adsorbent dose and consequently we approach saturation at a higher Cr(VI)
379 concentration.

380

381 3.2.4 Adsorption isotherm study

382 The adsorption equilibrium data give very important information needed to understand the
383 adsorption process correctly. The understanding of adsorption isotherms is important for
384 optimizing the adsorption process pathways and implementing adsorption systems effectively
385 (Ayawei et al., 2017). Hence, the linear and nonlinear forms of modified-Langmuir, Temkin,
386 Freundlich and Dubinin-Radushkevich isotherm models were used to fit experimental data; C_e
387 (mg/L) and Q_e (mg/g) are the equilibrium Cr(VI) concentration and adsorption capacity,
388 respectively; the initial concentration of Cr(VI) is represented by C_0 (mg/L).

389 The classic Langmuir adsorption isotherm was derived for the gas phase adsorption
390 process. It supposes a homogeneous surface where the binding sites have the same energy and
391 affinity (equivalency of the adsorption sites) and where adsorption occurs in a monolayer;
392 also it assumes that adsorbed molecules do not interact with each other (Langmuir, 1918; Luo
393 et al., 2017). Recently, a modified Langmuir equation has proved to be more applicable for
394 modeling liquid adsorption data. This model is given according to the following equations
395 (Azizian et al., 2018):

$$396 \frac{C_e}{Q_e} = \frac{(K_{ML}-1)C_e}{K_{ML}Q_m} + \frac{C_s}{K_{ML}Q_m} \quad (3)$$

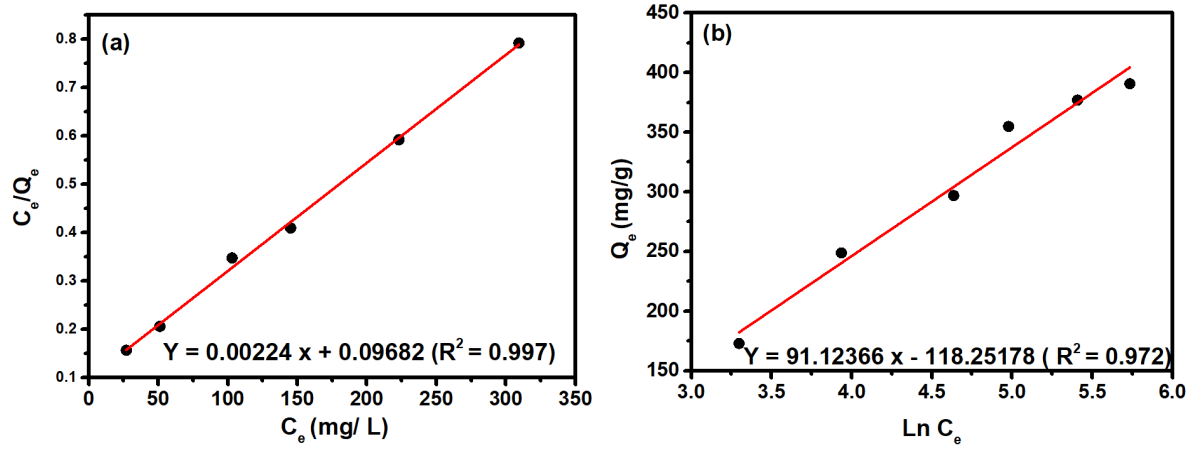
$$397 Q_e = \frac{Q_m K_{ML} C_e}{(C_s - C_e) + K_{ML} C_e} \quad (4)$$

398

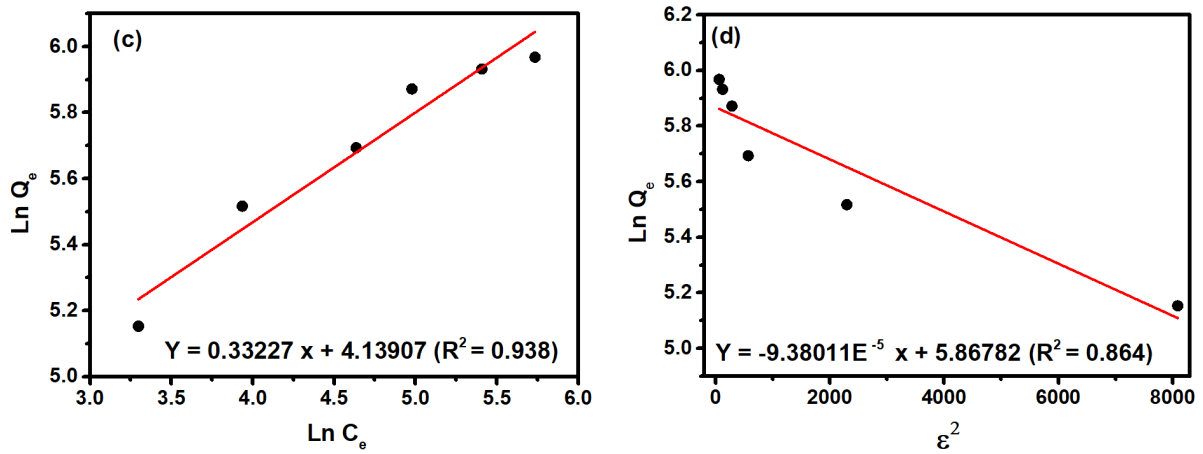
399 Where Q_m is the maximum adsorption capacity, C_s is the saturation concentration of Cr(VI) in
400 liquid-phase (45,000 mg/L) and K_{ML} is the constant of modified Langmuir.

401 By linear and nonlinear fittings, the Q_m capacity and K_{ML} constant are extracted from
402 experimental data (Figure 10a and 10e) and presented in Table 2; Q_m obtained is close to the
403 experimental value (398.9 ± 16.9 mg/g).

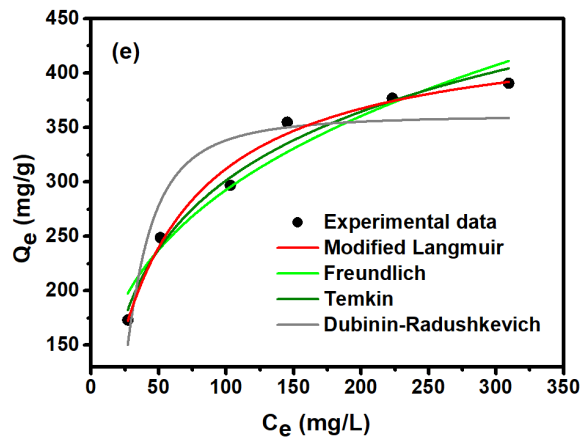
404 The modified-Langmuir isotherm parameters as well as the regression coefficient obtained
 405 (Table 2) suggest Adsorptive Interaction Effectiveness between the protonated rGO/PEI-
 406 KOH adsorbent and the hydrochromate anion.



407



408



409

410 **Figure 10.** Linear fitting of (a) modified-Langmuir, (b) Temkin, (c) Freundlich, (d) Dubinin-
 411 Radushkevich and (e) nonlinear fitting of adsorption isotherm models (pH 2, adsorbent
 412 dosage: 1 mg/mL, room temperature, contact time: 24 h).

413

414 The Temkin model of isotherm takes into-account the effects of the interaction between
 415 adsorbed molecules in the adsorption process. The adsorption energy (ΔH_{ads}) in this model
 416 displays a linear decrease when surface coverage rises, due to adsorbent–adsorbate
 417 interactions (Ayawei et al., 2017; Darabi et al., 2018). The following equations give the
 418 nonlinear and linear forms of the Temkin isotherm model (Temkin, 1941):

$$419 \quad Q_e = ALn(K_T C_e) \quad (5)$$

$$420 \quad Q_e = A lnK_T + A lnC_e \quad (6)$$

$$421 \quad A = \frac{RT}{b} \quad (7)$$

422 Where A is related to the Temkin constant b corresponding to the adsorption heat, K_T is the
 423 Temkin isotherm equilibrium binding constant, R is the gas constant and T is the temperature
 424 (Darabi et al., 2018). K_T and A are extracted from the linear and nonlinear fittings (**Figure**
 425 **10b and 10e**), whose values are reported in **Table 2**. The positive sign of b indicates an
 426 exothermic process (Ferrandon et al., 1995), and its value (27.19 kJ/mol) suggests that
 427 chemisorption may be an important part of the adsorption process (Ho et al., 2002).

428 The isotherm of Freundlich (Freundlich, 1906) is used when adsorption occurs on surfaces
 429 that are heterogeneous, showing a non-uniform adsorption heat distribution. The expression
 430 describing this isotherm encompasses the heterogeneity of the surface and the active sites (and
 431 their energy) exponential distribution. The Freundlich sorption isotherm is given by the
 432 equations (8, 9) (Ayawei et al., 2017; Darabi et al., 2018):

$$433 \quad Q_e = K_F C_e^{1/n} \quad (8)$$

$$434 \quad lnQ_e = \frac{1}{n} lnC_e + lnK_F \quad (9)$$

435 Where the constant K_F is related to the relative adsorption capacity of the adsorbent and n is a
 436 constant indicating the adsorption intensity (the lower the $1/n$ value the stronger the
 437 adsorption intensity (Darabi et al., 2018)). The linear and nonlinear fittings allow obtaining
 438 easily these constants (Figure 10c and 10e) whose values are summarized in Table 2. The
 439 isotherm of Freundlich is extensively used in heterogeneous systems, the value of $(1/n)$
 440 ranging from 0 to 1 may be an indicator of the degree of surface heterogeneity, surface being
 441 more heterogeneous as $(1/n)$ approaches zero (Foo and Hameed, 2010). The $1/n$ value
 442 obtained here (0.33) is closer to zero than to unity and may imply a chemisorption process
 443 (Foo and Hameed, 2010).

444 The Dubinin–Radushkevich (D-H) isotherm is usually used to describe the mechanism of
 445 adsorption onto a heterogeneous surface with a Gaussian energy distribution. Generally, this
 446 isotherm is expressed as follows (Ho et al., 2002; Foo and Hameed, 2010):

$$447 \quad Q_e = Q_D \exp(-B_D \varepsilon^2) \quad (10)$$

$$448 \quad \ln Q_e = \ln Q_D - B_D \varepsilon^2 \quad (11)$$

449 where Q_D is the maximum adsorption capacity, the activity coefficient B_D is related to mean
 450 sorption energy, ε^2 is Polanyi potential. By fitting (Figure 10d and 10e), B_D is extracted from
 451 the slope of the fitting and Q_D from the intercept.

452 The ε is estimated using Eq.12:

$$453 \quad \varepsilon = RT \ln \left[1 + \frac{1}{C_e} \right] \quad (12)$$

454 where R , T and C_e represent the gas constant, absolute temperature and adsorbate equilibrium
 455 concentration, respectively.

456 The mean sorption energy E necessary to detach a molecule from its position in the sorption
 457 space to the infinity, which is a measure of the nature of adsorption (physical or chemical) is
 458 expressed as:

$$459 \quad E = \frac{1}{\sqrt{2B_D}} \quad (13)$$

460 The E value, determined using equation (13), is 73 kJ/mol. The Q_D value (353.47 mg/g) is
 461 consistent with both the Q_{max} value (446 mg/g) previously determined with the modified-
 462 Langmuir isotherm and the experimental one (398.9±16.9 mg/g).

463 The results provided in **Table 2** show that the regression coefficient R^2 in the Dubinin-
 464 Radushkevich (0.864) is lower than that of modified-Langmuir, Temkin and Freundlich
 465 fittings, indicating that D-H data do not correlate as well as for the previous isotherms. The
 466 Cr(VI) removal simulation data using the modified-Langmuir model ($R^2 = 0.997$) are better
 467 than those obtained by the Freundlich ($R^2 = 0.938$) and the Temkin ($R^2 = 0.972$) models,
 468 demonstrating that Cr(VI) adsorption process on rGO/PEI-KOH is best fitted by the modified-
 469 Langmuir model; this result indicates that Cr(VI) sorption onto rGO/PEI-KOH is not
 470 exceeding a monolayer coverage on a homogeneous surface with active sites well distributed
 471 throughout.

472 **Table 2.** Isotherm rate constants and regression coefficients for different models.

Models	Parameters	Linear	Nonlinear
Langmuir	Q_{max} (mg/g)	446.00	445.97
	K_{ML} (L/mg)	1042.10	1047.11
	R^2	0.997	0.982
Temkin	A (unitless)	91.12366	91.11
	K_T (L/mg)	0.27	0.27
	b (kJ/mol)	27.1891	27.1
	R^2	0.972	0.972
Freundlich	K_F (mg/g) (L/mg) ^{1/n}	62.74	73.30
	n	3	3.32
	R^2	0.938	0.933
Dubinin- Radushkevich	Q_m (mg/g)	353.47	361.96
	B (mol ² /kJ ²)	9.38011E ⁻⁵	6.6496E ⁻⁵

E (kJ/mol)	73	86.71
R ²	0.864	0.829

473

474 3.2.5 Effects of contact time and adsorption kinetics study

475 Cr(VI) kinetics of adsorption on rGO/PEI-KOH are estimated with the pseudo-first and
 476 second order models by fitting kinetic experimental data. Thereby, the influence of the contact
 477 time on Cr(VI) adsorption was studied (Cr(VI) concentration: 100 mg/L at pH 2.0). **Figure**
 478 **11a** reveals that the capacity of adsorption rises rapidly within the first 4 h; afterward, it
 479 continues to raise slowly and approaches equilibrium at around 24 h. Both the kinetic models,
 480 pseudo-first-order and second-order, are given by the following equations (Ho and Mckay,
 481 1999; Azizian, 2004):

482 Pseudo-first-order:

$$483 \quad Q_t = Q_e(1 - e^{-K_1 t}) \quad (14)$$

484 Pseudo-second-order:

$$485 \quad Q_t = \frac{Q_e^2 K_2 t}{1 + Q_e K_2 t} \quad (15)$$

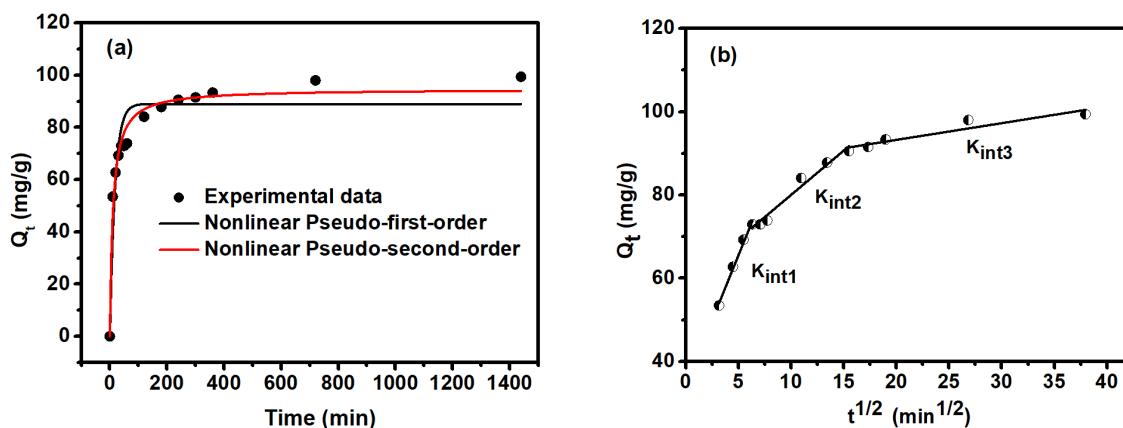
486 Where Q_e is the quantity of adsorbed pollutant at equilibrium, Q_t is the amount of adsorption
 487 at t time, and K_1 and K_2 are the pseudo-first order and pseudo-second order rate constant,
 488 respectively.

489 The nonlinear fitting of the kinetic data is presented in **Figure 11a** and the obtained kinetic
 490 parameters are listed in **Table 3**. The comparison of the regression coefficient (R^2) values
 491 revealed that the adsorption kinetics of Cr(VI) onto rGO/PEI-KOH are well-described with
 492 the pseudo-second-order model. In addition, the absorption capacity ($Q_{e.cal}=94.67$ mg/g),
 493 calculated from the pseudo-second order kinetic model, is closer to that obtained
 494 experimentally ($Q_{e.exp}= 99.38$ mg/g). This result is predictable, because this model is adequate
 495 for a concentration of solute not too high as it is the case in this work (Azizian, 2004).

496 In order to investigate the mechanism of mass transfer during the adsorption process, the
 497 Weber-Morris model for intraparticle diffusion (Ho and Mckay, 1999; El Ouardi et al., 2019)
 498 was used. Weber-Morris stated that if intra-particle diffusion is the rate-controlling factor
 499 during an adsorption process, uptake of the adsorbate varies with the square root of time
 500 (equation (16)).

$$501 \quad Q_t = K_{int}t^{1/2} + C \quad (16)$$

502 Where K_{int} is the intraparticle diffusion rate constant. **Figure 11b** shows that the plots of Q_t
 503 *versus* $t^{1/2}$ are multi-linear, indicating that Cr(VI) adsorption mechanism occurs in three
 504 distinct stages. The first stage with the largest slope (K_{int1}) is due to an important diffusion of
 505 Cr(VI) anions from the solution to the intraparticle regions; the R^2 value indicates that at this
 506 first step of the adsorption process, the intraparticle diffusion is the predominant factor. The
 507 second linear stage, with lower K_{int} and R^2 values, suggest that the intraparticle diffusion
 508 becomes less predominant, this is probably linked both to the decrease in the Cr (VI)
 509 concentration gradient between the intraparticle regions and the solution, as well as a
 510 diminution of the available adsorption sites (intraparticle). For the final stage, with the lowest
 511 K_{int} and R^2 , the process evolution ultimately resulted in a non-predominant intraparticle
 512 diffusion as the system approaches equilibrium. This is presumably due to a drop in the
 513 concentration gradient (between solution and intraparticle regions) as well as the almost-
 514 saturation of the intraparticle adsorption sites.



515

516 **Figure 11.** (a) Pseudo-first-order and pseudo-second-order nonlinear fitting and (b)
 517 intraparticle diffusion linear fitting for Cr (VI) adsorption onto rGO/PEI-KOH (pH: 2,
 518 concentration of Cr(VI): 100 mg/L, adsorbent dosage 1 mg/mL, room temperature, time of
 519 contact 24 h).

520

521

522 **Table 3.** Cr(VI) kinetic adsorption parameters onto rGO/PEI-KOH.

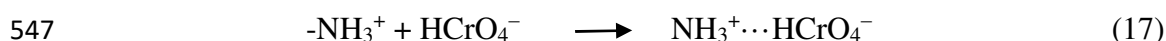
Kinetic models	Parameters	
Pseudo-first-Order		
	K_1 (min^{-1})	0.056
	$Q_{e,\text{cal}}$ (mg/g)	88.96
	R^2	0.898
Pseudo-second-Order		
	K_2 (g/mg min)	0.0009
	$Q_{e,\text{cal}}$ (mg/g)	94.67
	R^2	0.975
Intraparticle diffusion		
	K_{int1} ($\text{mg/g min}^{1/2}$)	6.24
	C_1	34.25
	R^2	0.991
	K_{int2} ($\text{mg/g min}^{1/2}$)	2.13
	C_2	58.70
	R^2	0.973
	K_{int3} ($\text{mg/g min}^{1/2}$)	0.40
	C_3	85.19
	R^2	0.892

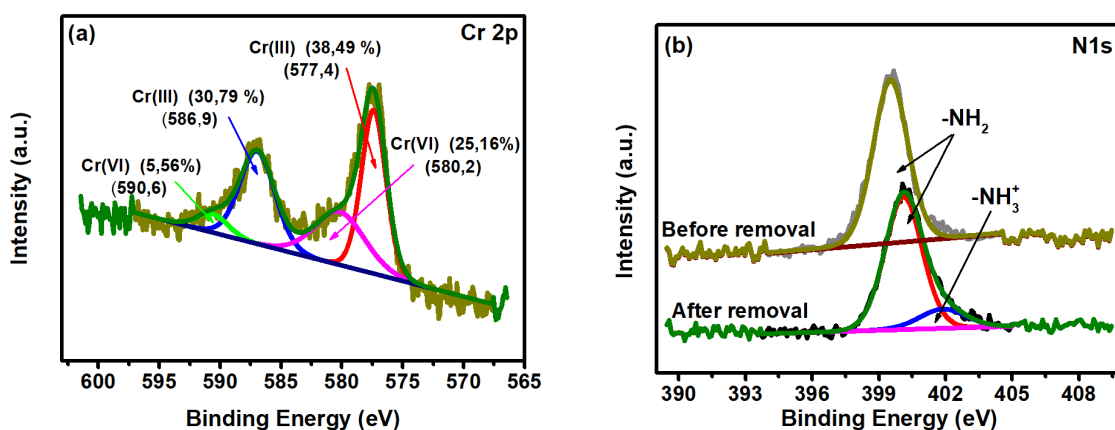
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524 **3.2.6 Cr(VI) adsorption-reduction mechanism**

525 To further analyze the Cr(VI) elimination mechanism by rGO/PEI-KOH, XPS was used to
526 examine the elemental composition after the adsorption of Cr(VI). As shown in **Figure 12a**,
527 the peaks of Cr_{2p} appear in the solid material, confirming that Cr(VI) is adsorbed successfully
528 onto the material. The XPS spectrum of the Cr_{2p} further indicates that there are four
529 components at 577.4, 580.2, 586.9 and 590.6 eV. The peaks at 577.4 and 580.2 eV represent
530 Cr_{2p3/2} orbitals, while the components at 586.9 and 590.6 eV are due to Cr_{2p1/2} orbitals. The
531 577.4 and 586.9 eV peaks are ascribed to Cr(III), while 580.2 and 590.6 eV peaks are related
532 to Cr(VI) (Ma et al., 2012; Zhang et al., 2013; Nezar et al., 2019). These results clearly
533 indicate that both Cr(VI) and Cr(III) ions coexist on the rGO/PEI-KOH surface with 70.3 at%
534 of Cr(III) of the total amount of adsorbed chromium, signifying a good reduction of the
535 adsorbed pollutant.

536 **Figure 12b** displays the high-resolution N_{1s} XPS spectrum of rGO/PEI-KOH composite
537 prior to and after Cr(VI) elimination. Before adsorption, the spectrum consists of one peak
538 corresponding to N_{1s} of the amine group. After adsorption process in acidic conditions (pH 2),
539 the N_{1s} can be deconvoluted into two peaks: a preponderant peak related to the amine group
540 slightly shifted to higher binding energy, and a second peak at 401.4 eV due to the protonated
541 amine groups (-NH₃⁺). As explained above, at this pH value and K₂Cr₄O₇ concentration used,
542 the chromium predominant species is the hydrochromate anion, HCrO₄⁻, and it is worth
543 noting that at this acidic pH, the PEI molecule is known to present a maximum protonation of
544 amine groups, almost all these groups become positively charged (Curtis et al., 2016).
545 The HCrO₄⁻ anions are electrostatically attracted to the protonated amine groups where they
546 will be adsorbed, as illustrated by equation (17) (Wang et al., 2017):





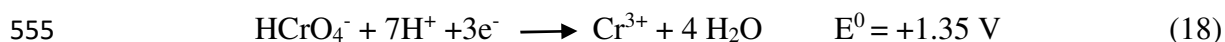
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549 **Figure 12.** Core level XPS spectra of (a) Cr_{2p} and (b) N_{1s} of the rGO/PEI-KOH adsorbent

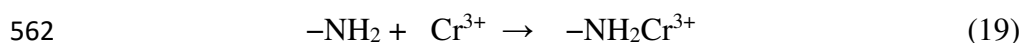
550 before and after adsorption of Cr(VI).

551

552 Afterwards, Cr(VI) reduction takes place resulting in Cr(III) formation thanks to π -electrons
 553 of rGO, which serves as a donor of electrons in the Cr(VI)/Cr(III) reduction process (Ho et al.,
 554 2002; Ma et al., 2012; Darabi et al., 2018), according to equation (18):



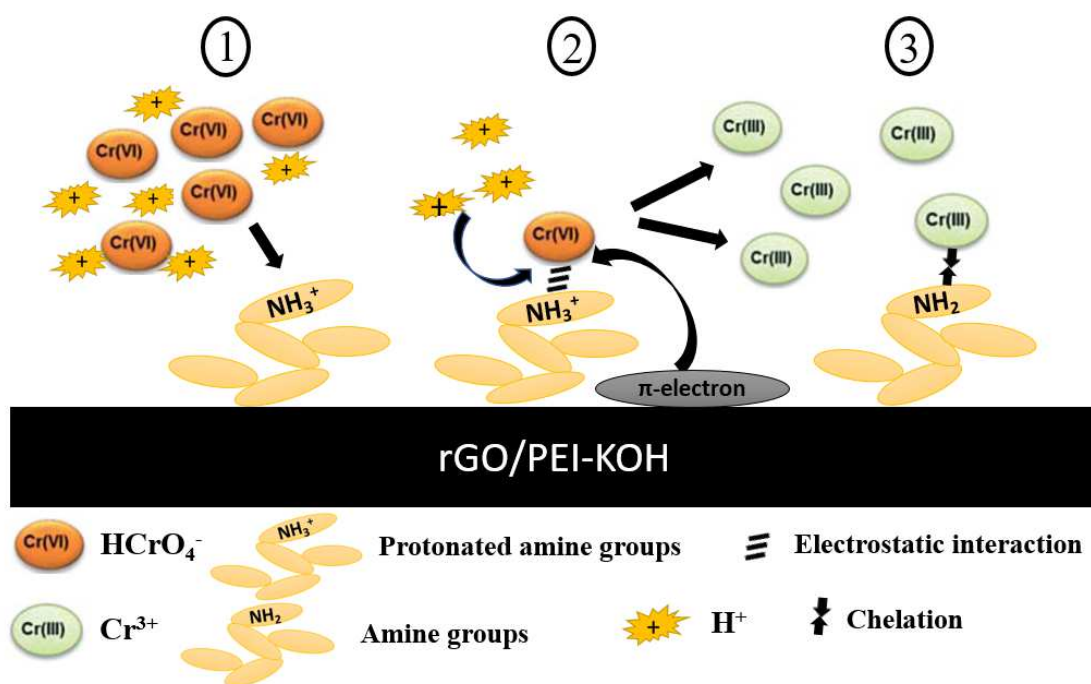
556 This E^0 positive value indicates that Cr(VI) is a strong oxidant at this low pH. Also, it can be
 557 noticed from equation (18) that the reduction of Cr(VI) is concomitant with an important
 558 consumption of protons; we presume that this property may explain that most amine groups
 559 are deprotonated after adsorption (Figure 11b), but it does not explain why they are not
 560 reprotonated as it is expected in this still relatively acidic medium (Curtis et al., 2016). A
 561 possible response is given by the equation (19) (Deng and Ting, 2005; Zhao et al., 2016):



563 This equation illustrates the chelation between Cr(III) species and the deprotonated amine
 564 groups (-NH₂), thus preventing an ulterior reprotonation; a chelated complex may be formed
 565 by coordination between newly formed Cr(III) and -NH₂ group thanks to the fact that Cr(III)
 566 cation has an empty orbital and the amine group has a lone pair of electrons (Dai et al., 2012).

567 On the other hand, we speculate that the blue shift observed for the N_{1s} of the amine group
568 after chromium adsorption is related to this chelation.

569 **Scheme 2** illustrates the adsorption/reduction process, and **Table 4** depicts the values of some
570 other adsorbent capacities for Cr(VI) reported in the literature. We can clearly see that the
571 adsorption capacity of 398.9 ± 16.9 mg/g at ambient temperature is among the highest recorded
572 values.



573
574 **Scheme 2.** Schematic illustration of the mechanism of Cr(VI) removal by rGO/PEI-KOH.

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Table 4. The maximum adsorption capacity of Cr(VI) compared with some indicative reported works.

Adsorbent	Q _{max} (mg/g)	Reference
Mesoporous carbon microspheres	156.3	(Zhou et al., 2016)
RGO/PEI/Fe ₃ O ₄	266.6	(Wang et al., 2017)
Commercial activated carbon (CAC)	15.47	(Sandhya and Tonni, 2004)
KOH-modified carbonized Eucalyptus sawdust	45.88	(Zhang et al., 2018a)
PEI-modified-biomass of <i>Penicillium chrysogenum</i>	279.2	(Deng and Ting, 2005)
Iron nanoparticle decorated graphene	162	(Jabeen et al., 2011)
P(TA-TEPA)-PAM-RGO	397.5(35°C)	(Zhang et al., 2018b)
3-aminopropyltriethoxysilane-functionalized graphene oxide (AS-GO)	215.2	(He et al., 2017)
Magnetic β-cyclodextrin/graphene oxide nanocomposite (MCGN)	120.1	(Fan et al., 2012)
ED/DMF/rGO	92.15	(Zhang et al., 2013)
Amino functionalized graphene oxide decorated with Fe ₃ O ₄ nanoparticles (AMGO)	123.4	(Zhao et al., 2016)
Reduced graphene oxide–montmorillonite (GCM)	12.86	(Zhang et al., 2015)
Polyethyleneimine modified eggshell membrane (PEI–ESM)	160	(Liu and Huang, 2011)
Ionic liquid modified reduced graphene oxide (IL-rGO)	232.55	(Nasrollahpour et al., 2017)
Sulfonated magnetic graphene oxide (SMGO)	222.22	(Alizadeh et al., 2017)
Graphene/MgAl-layered double hydroxides	172.55	(Yuan et al., 2013)

(G–MgAl-LDH)		
Triethylenetetramine modified graphene oxide/ chitosan composite (TGOCS)	219.5	(Ge and Ma, 2015)
rGO-PEI-KOH	398.9 (25°C)	This work
rGO-PEI	324.0 (25°C)	This work

590

591

592 **4. Conclusion**

593 A graphene-based adsorbent was elaborated by reacting graphene oxide (GO) with
594 polyethylenimine (PEI) and potassium hydroxide (KOH) at 90°C. Under these experimental
595 conditions, GO sheets were partially reduced while being at the same time functionalized with
596 PEI moieties. XPS, Raman, FTIR and TGA characterization proved an appreciable
597 deoxygenation of GO as well as the effective grafting of PEI on the rGO sheets. The as-
598 prepared rGO/PEI-KOH adsorbent exhibits an adsorption capacity of 398.9 mg/g for Cr(VI)
599 at room temperature. Compared to other works in the literature, this value is among the
600 highest reported. This adsorption is mainly attributable to the electrostatic interactions
601 between the chromium anion species and the low pH induced protonation of amine groups.
602 The isotherm plots suggest that during Cr(VI) sorption process rGO/PEI-KOH shows a
603 homogeneous surface where active sites are well distributed throughout; also, the results
604 suggest that chemisorption may play a non-negligible role in this process. Investigating the
605 adsorption kinetics, we found that it follows pseudo-second order model, which is consistent
606 with the Cr(VI) concentration range used. In addition, by applying the Weber-Morris model,
607 we noticed that intraparticle diffusion phenomena play a predominant role in the initial phase
608 of Cr (VI) adsorption. The subsequent Cr(VI) reduction to Cr(III), which attained 70.3% of
609 the total adsorbed chromium, is related to the oxidative action of the hydrochromate anion on
610 the rGO/PEI-KOH sheet, since this later acts as electron donor (π electrons). The results of

611 this work represent an interesting way to eliminate Cr(VI), while offering the advantages of
612 reduced cost, high capacity of adsorption and respect for the environment. Therefore, it could
613 be a promising adsorbent in environmental applications.

614

615 **Acknowledgment**

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617 Recherche Scientifique (CNRS), the MESRS-Algeria, the University of Lille and the Hauts-
618 de-France region.

619

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