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1 **Effect of pH on the uptake of arsenate and vanadate and the stability of these**
2 **anions in alkaline solutions – a Raman spectroscopic study**

3
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5
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9
10 **Hydrotalcites have been synthesised using three different pH**
11 **solutions to assess the effect of pH on the uptake of arsenate and**
12 **vanadate. The ability of these hydrotalcites to remove vanadate and**
13 **arsenate from solution has been determined by ICP-OES. Raman**
14 **spectroscopy is used to monitor changes in the anionic species for**
15 **hydrotalcites synthesised at different pH values. The results show a**
16 **reduction in the concentration of arsenate and vanadate anions that**
17 **are removed in extremely alkaline solutions. Hydrotalcites**
18 **containing arsenate and vanadate are stable in solutions up to pH**
19 **10. Exposure of these hydrotalcites to higher pH values results in the**
20 **removal of large percentages of arsenate and vanadate from the**
21 **hydrotalcite interlayer.**

22
23 **KEYWORDS:** Raman spectroscopy, hydrotalcite, vanadate, arsenate, ICP-OES

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25

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26 INTRODUCTION

27
28 Layered double hydroxides (LDH), also known as hydrotalcites or anionic clays have
29 received increasing attention in recent years due to their wide range of applications as
30 anion exchangers, adsorbents, ionic conductors, catalyst precursors and catalyst
31 supports.¹⁻³ Hydrotalcites are naturally occurring minerals derived from a brucite
32 structure ($\text{Mg}(\text{OH})_2$) in which Al^{3+} substitutes for Mg^{2+} . This substitution creates a
33 positive layer charge on the hydroxyl layers, which is compensated by interlayer
34 anions or anionic complexes.⁴ These anions may be any anion with a suitable negative
35 charge including arsenate and vanadate.

36
37 Hydrotalcites can be considered to be a large cation which is counterbalanced by
38 anions in the interlayer. A large variety of anions can be incorporated into the
39 interlayer region of LDH's using a range of methods: (1) anion-exchange; (2) co-
40 precipitation; (3) rehydration of a calcined LDH, and (4) thermal activation reaction.
41 This investigation utilised the co-precipitation method. Hydrotalcites intercalated with
42 other anions such as phosphate, molybdate, vanadate have been synthesised.⁵⁻⁷
43 Anion affinity in has been found to be based on the size of the anion and its associated
44 charge. Monovalent anions have lower affinities than divalent anions and are
45 therefore more likely to precipitate in anion exchange reactions. The ease of exchange
46 of monovalent anions is in the order $\text{OH}^- > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^-$ ⁸. Divalent anions
47 such as SO_4^{2-} and CO_3^{2-} have higher selectivity than monovalent anions.

48
49 This investigation studies the effect synthesis pH has on the intercalation of arsenate
50 and vanadate anions into the hydrotalcite interlayer. Optimisation of synthesis
51 conditions is essential for the use of these materials as adsorbent materials. The
52 stability of these materials in alkaline solutions, in relation to the hydrotalcite
53 interlayer, is also required for correct disposal and storage of these materials.

59 **EXPERIMENTAL**

61 *Synthesis of hydrotalcites*

62
63 The hydrotalcites were synthesised by the co-precipitation method, which utilises the
64 slow addition of a caustic solution containing the oxy-anion (1) and a mixed metal
65 solution (2). The concentrations of anions used are given in Table 2.1. Solution 1
66 contains 2M NaOH and a combination of either: 1) Na₂CO₃ and NaVO₃, or 2) NaVO₃,
67 or 3) Na₂CO₃ and Na₂HAsO₄·7H₂O, or 4) Na₂HAsO₄·7H₂O to give a combined
68 concentration of 0.2M, respectively. The mixed metal contained 0.75M Mg²⁺
69 (MgCl₂·6H₂O) and 0.25M Al³⁺ (AlCl₃·6H₂O). ICP-OES confirmed an average Mg,Al
70 ratio of 2.96 :1 for the synthesised hydrotalcites.

71
72 The caustic solution (2M) was added drop wise to the mixed metal solution and was
73 stirred at 400 rpm to ensure dissolution. After addition of the caustic solution was
74 complete, the pH was adjusted to pH 8, 10 and 13 and the mixture was allowed to stir
75 for two hours before the solid product was removed via vacuum filtration with a
76 Whatman 542 filter paper. The filtrate required two more filtrations to removal all the
77 solid product. The precipitate was washed twice with deionised water (250 mL
78 washing) before being vacuum dried and placed in an oven (85°C) overnight to dry.

80 *Inductively coupled plasma optical emission spectrometry (ICP-OES)*

81
82 Samples of the initial Bayer liquor and resulting solution after the SWN process were
83 analysed using a Varian ICP-OES instrument. The samples were not diluted before
84 analysis due to the low concentrations of anionic species. Standards containing
85 aluminium, arsenate, vanadate, and molybdate were prepared to establish a calibration
86 curve. Results were obtained using an integration time of 3 with 3 replications. The
87 relative amounts of each atom were recorded on Varian Liberty 2000 ICP–AES at
88 wavelengths of 394.400, 311.837, and 188.980 nm for Al, V, and As, respectively.
89 The results reported are an average of three replications for each sample.

93 *Fourier Transform Raman spectroscopy (FT-Raman)*

94

95 The FT-Raman analyses were performed on powder samples pressed in a sample-
96 holder suitable for the spectrometer using a Perkin Elmer System 2000 Fourier
97 transform spectrometer equipped with a Raman accessory comprising a Spectron
98 Laser Systems SL301 Nd:YAG laser operating at a wavelength of 1064 nm. Spectral
99 manipulation such as baseline correction, smoothing and normalisation was
100 performed using the GRAMS® software package (Galactic Industries Corporation,
101 Salem, NH, USA).

102

103 Band component analysis was undertaken using the Jandel ‘Peakfit’ software
104 package, which enabled the type of fitting function to be selected and allows specific
105 parameters to be fixed or varied accordingly. Band fitting was undertaken using a
106 Lorentz- Gauss cross-product function with the minimum number of component
107 bands used for the fitting process. The Lorentz- Gauss ratio was maintained at values
108 greater than 0.7 and fitting was undertaken until reproducible results were obtained
109 with squared correlations of r^2 greater than 0.995.

110

111 **RESULTS AND DISCUSSION**

112

113 This investigation will focus on the removal of arsenate and vanadate in different
114 synthesis conditions. The following results will look at the formation of hydrotalcite
115 from five solutions: 1) carbonate (0.1M) and vanadate (0.1M), 2) carbonate (0.1M)
116 and arsenate (0.1M), 3) vanadate (0.2M), 4) arsenate (0.2M), and 5) carbonate
117 (0.067M), vanadate (0.067M), and arsenate (0.067M). These hydrotalcites will be
118 referred to as: 1) HT(CO₃²⁻, VO₄³⁻), 2) HT(CO₃²⁻, AsO₄³⁻), 3) HT(VO₄³⁻),
119 4) HT(AsO₄³⁻), and 5) HT(CO₃²⁻, AsO₄³⁻, VO₄³⁻). The anion in bold or with a red box
120 around it for the mixed hydrotalcite is the anion that the results refer to. For example,
121 ICP-OES results for HT(CO₃²⁻, AsO₄³⁻, VO₄³⁻) refers to the percentage of arsenate
122 removed from solution.

123

124

125

126

127 *Effect of the synthesis pH*

128

129 In order to study the influence of the synthesis pH on the ability of hydrotalcite to
130 remove arsenate and vanadate from solution, hydrotalcites of formula
131 $Mg_6Al_2(OH)_{16}(A^{n-}) \cdot xH_2O$ were made at pH 8, 10 and 13 and were allowed to stir for
132 2 hours, Figure 1. Increasing the synthesis pH to 13 caused a significant reduction in
133 the removal of arsenate and vanadate from solution. At pH 8, essentially both anions
134 are completely removed from solution, whilst at pH 13 only 65-85 % of anions are
135 removed. A slight decrease in the amount of arsenate and vanadate removed from
136 solution is observed for the synthesis of hydrotalcite at pH 10. The removal
137 percentage of arsenate and vanadate remained greater than 85 %, except for
138 $HT(CO_3^{2-}, AsO_4^{3-}, VO_4^{3-})$, which only showed a vanadate removal percentage of 80 %.
139 Vanadate has the lowest affinity (compared to carbonate and arsenate), and therefore
140 is the most vulnerable to exchange reactions involving the increasing OH^-
141 concentration. The decrease in removal percentages at pH 13 is due to excess OH^-
142 anions in solution, which compete strongly with arsenate and vanadate anions for the
143 hydrotalcite interlayer.

144

145 Hydrotalcites with arsenate intercalated into the structure observed a much larger
146 decline in percentage removal (~10 %) when synthesised at pH 10, compared to the
147 vanadate hydrotalcites (~3 %). At pH 8 and 10 arsenate is present in solution as the
148 $HAsO_4^{2-}$ anion, while the vanadate anion exists as $H_2VO_4^-$ at pH 8 and as HVO_4^{2-} at
149 pH 10, Figures 2 and 3. The increase in anion charge, and a decrease in anion size,
150 increases the vanadate anions affinity. This means the vanadate anion has an increased
151 affinity for the interlayer, allowing it to compete more strongly for the interlayer with
152 the increased hydroxide concentration. The arsenate anion on the other hand still has a
153 -2 charge at pH 10. Therefore, its affinity is unchanged, which makes it more
154 vulnerable to the increased hydroxide concentration.

155

156 *Chemical stability of hydrotalcites synthesised over a 2, 24, and 48 hour period*

157

158 Fifteen hydrotalcites were prepared using solution with pH 8, using five different
159 anion mixtures, and allowing the hydrotalcites to age for 2, 24, and 48 hours.

160

161 The hydrotalcites synthesised with carbonate, arsenate, and vanadate are exposed to
162 solutions at pH 10 and 14 to determine the chemical stability of the
163 intercalated/adsorbed anions. ICP analysis showed the percentage of anions that are
164 re-dissolved back into solution through anion exchange reactions, at pH 10 and 14,
165 Table 2. After the hydrotalcite has been exposed to two different alkaline solutions,
166 the percentage of anions in solution indicates the stability of the anions in the
167 interlayer region. The lower the dissolution percentage, the more stable the
168 hydrotalcite structure.

169

170 The results indicate that the chemical stability of the hydrotalcites is relatively high,
171 with the majority of anions remaining in the hydrotalcite interlayer at pH 10.
172 Hydrotalcites prepared with an aging time of 2 hours had the lowest anion stability in
173 alkaline solutions.

174

175 pH 10

176

177 The following hydrotalcites were resilient to solutions of pH 10: HT(CO₃²⁻,VO₄³⁻),
178 HT(CO₃²⁻,AsO₄³⁻), HT(VO₄³⁻), and HT(AsO₄³⁻). The percentage of anions released
179 back into solution is insignificant. Therefore, arsenate and vanadate in the hydrotalcite
180 interlayer do not undergo exchange reactions with OH⁻ ions at pH 10. However, the
181 mixed anion hydrotalcite aged for 2 hours HT(CO₃²⁻,AsO₄³⁻,VO₄³⁻) did observe a 5.3
182 and 3.7 % release of arsenate and vanadate, respectively, back into solution. A limit to
183 the number of intercalation sites in the interlayer forces some of the anions to be
184 adsorbed to the external surface. The adsorbed arsenate and vanadate anions are more
185 susceptible to exchange reactions involving hydroxide ions. Minimal losses are
186 observed for the mixed hydrotalcite aged for 24 and 48 hours.

187

188 It is proposed that a higher percentage of arsenate and vanadate anions are adsorbed to
189 the external surface of hydrotalcites aged for 2 hours than there is after 24 and 48
190 hours. Due to immense competition between all the anions in solution, during
191 synthesis, only the anions with the highest affinity would be intercalated initially.
192 Therefore, the lower affinity anions (arsenate and vanadate) get adsorbed to the
193 external surface of the structure initially. Over longer periods of time, these low
194 affinity anions would be intercalated into the hydrotalcite interlayer as the hydroxyl

195 metal layers rearrange to form more aligned and ordered structures. The alignment of
196 the layers is believed to increase the interlayer distance and the number of
197 intercalation sites, thus allowing more anions to be removed from solution. As the
198 intercalation of anions in the hydrotalcite interlayer is more stable, less anionic
199 species will be released back into solution for hydrotalcites synthesised with greater
200 aging times.

201

202 pH 14

203

204 Exposing the fifteen hydrotalcites to a pH 14 solution significantly increased the
205 percentage of arsenate and vanadate anions that are released back into solution. The
206 hydrotalcites aged for 2 hours, showed the lowest interlayer stability, with the release
207 of 40 % and greater of arsenate and vanadate. The large influx of hydroxide ions in
208 solution competes very strongly with arsenate and vanadate in the hydrotalcite
209 interlayer, forcing arsenate and vanadate out of the interlayer via exchange reactions.
210 Again the disordered nature of the hydrotalcites after 2 hours contributes to the high
211 removal of arsenate and vanadate. Hydrotalcites containing arsenate showed lower
212 percentage dissolution percentages when synthesised over longer periods of time. This
213 is attributed to the slightly higher affinity of the arsenate anion compared with
214 vanadate anions. The vanadate hydrotalcites synthesised over a 24 hour period also
215 showed a large reduction in percentage dissolution. As the aging time increased to 48
216 hours, less vanadate anions are released back into solution. This increase in stability is
217 due to: 1) the re-arrangement of anions to form more ordered structure, and 2) a
218 network of hydrogen bonding involving the three anions and interlayer water.

219

220 *Raman spectra of hydrotalcites synthesised*

221

222 Hydroxyl stretching region (3800-2800 cm⁻¹):

223 The Raman spectra of hydrotalcites synthesised at pH 8 for 2 hours in the hydroxyl
224 stretching region, 4000 – 2500 cm⁻¹, are provided in Figure 4. The Raman spectra for
225 all the hydrotalcites synthesised, two bands are observed between 3670 and
226 3590 cm⁻¹. These bands are attributed to the OH stretching vibrations of the OH units
227 of –AlOH and –MgOH.⁹ Shifts in these bands for the different hydrotalcites are due to

228 slightly different bonding of the hydroxyl groups in each of the hydrotalcite structures
229 synthesised.

230

231 Bands between 2930 and 3100 cm^{-1} are due to strongly hydrogen-bonded water
232 molecules to interlayer anions such as arsenate, vanadate or carbonate.¹⁰ Bands at
233 lower wavenumbers, approximately 2900 cm^{-1} are believed to be due to the influence
234 of the carbonate anion. The intermediate region of the hydroxyl stretching region,
235 3300 – 3200 cm^{-1} , is attributed to water coordinated to the cation OH surface, M_3OH
236 units (where M might be Mg or Al or a combinational permutation of these metals).¹⁰
237 Bands at around 3400 cm^{-1} are believed to be due to water coordinated with other
238 water between the hydrotalcite layers.¹⁰

239

240 Carbonate vibrational region (1200-600 cm^{-1})

241

242 Band positions observed for carbonate, arsenate, and vanadate anions are given in
243 Tables 3 and 4. Four Raman bands, attributed to the carbonate anion, are observed in
244 $\text{HT}(\text{CO}_3^{2-})\text{-2h-pH8}$ between 1200 and 600 cm^{-1} , Figure 5. These bands are observed at
245 1084, 1061, 1058, and 1030 cm^{-1} , and are assigned to the symmetric stretching modes
246 of carbonate. The presence of four bands in this region suggests that the carbonate
247 anion is in different environments (slightly different bonding of the CO_3^{2-} anion). It is
248 proposed that carbonate is bonded to H_2O in the interlayer or other anions in the
249 hydrotalcite interlayer (1061 and 1058 cm^{-1}), and also bonded to the external surface
250 of the hydrotalcite structure (1030 cm^{-1}).¹⁰ The band at 1084 cm^{-1} is assigned to
251 carbonate in calcium carbonate species that form during the synthesis process,
252 aragonite and calcite.

253

254 The Raman spectra of the $\text{HT}(\text{CO}_3^{2-})\text{-48h-pH8}$ shows three bands at 1062, 1052 and
255 971 cm^{-1} , Figure 6, compared to the $\text{HT}(\text{CO}_3^{2-})\text{-2h-pH8}$, which showed four bands.
256 Calcium carbonate does not appear to have formed, indicated by the absence of a band
257 at 1080 cm^{-1} . The shift of the Raman band at 1030 to 971 cm^{-1} suggests that the
258 carbonate is non hydrogen bonded or only weakly hydrogen bonded, and is possibly
259 acting as a space-filler in the hydrotalcite interlayer.

260

261 The Raman spectrum for HT(VO_4^{3-})-2h-pH8 hydrotalcite, Figure 5, observed four
262 broad bands at 939, 907, 879 and 815 cm^{-1} , due to the A_1 stretching modes of
263 V-O.¹¹ The multiple V-O vibrational modes are believed to be due to different
264 bonding strengths of the V-O bond (i.e. it's in different environments). It is proposed
265 that the vibrational band at 939 cm^{-1} is due to the V-O symmetric stretching mode of
266 the tetrahedral vanadate anion. At pH 8, vanadate is most likely present as H_2VO_4^- .
267 The symmetry of the original tetrahedral vanadate structure is slightly obscured by the
268 hydrogen atoms bonded to O^- , and thus will show a shift to lower wavenumbers. It is
269 proposed that the lower wavenumber band at around 815 cm^{-1} is due to V-OH bonds,
270 which has a weaker bond strength compared to the other V-O bonds in the structure.
271 Within the hydrotalcite structure there may be numerous bands (slightly different) due
272 to this vibration, and this is shown by the broadness of the V-OH band at 815 cm^{-1} .
273 The bands at 907 and 879 cm^{-1} are believed to be due to the V- O^- stretching modes,
274 which are bonded to interlayer water, other anionic species, or to the hydroxyl surface
275 of the hydrotalcite. Synthesis of the same hydrotalcites but at pH 13, Figure 7, showed
276 a significant increase in the intensity and broadness of the band at around 870 cm^{-1} .
277 This indicates an increase in the number of V- O^- bonds, which correspond with the
278 change in vanadate specie as the pH increases to 13 (pH 8: H_2VO_4^- and pH 13: VO_4^{3-}).
279 The presence of a broad band at 835 cm^{-1} , (V-OH stretching mode), suggests that
280 there is still HVO_4^{2-} anions present at pH 13.

281

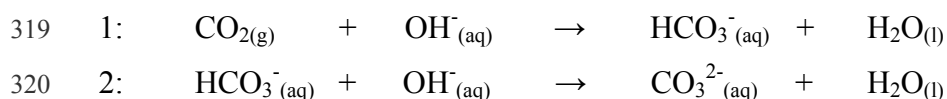
282 The Raman spectrum for HT(AsO_4^{3-})-2h-pH8, Figure 5, observed four bands at 911,
283 876, 841 and 808 cm^{-1} , due to A_1 stretching modes of As-O. As mentioned previously,
284 for the corresponding vanadate hydrotalcite, these different vibrational modes are
285 attributed to different bonding strengths of the As-O bond. It is proposed that the
286 strongest bond of the tetrahedral arsenate anion is As=O, and is assigned to the 876
287 cm^{-1} band. This band is assigned to the As=O symmetric stretching mode. At pH 8,
288 arsenate is predominantly present as HAsO_4^{2-} . It is proposed that the very broad band
289 at 841 cm^{-1} is attributed to the symmetric stretch of As- O^- , while at lower
290 wavenumbers, 808 cm^{-1} , is due to As-OH symmetric stretching vibrational modes.
291 The broadness of the band at 841 cm^{-1} is proposed to be due to the overlapping of
292 multiple As- O^- bands, which may be bonded in slightly different ways to other species
293 in the interlayer (water or cationic surface), which will result in a shift in band
294 position, and thus making the band appear broad. The relative areas under the bands at

295 876 and 808 cm^{-1} indicates that there are approximately the same number of As-OH
 296 bonds present in the hydrotalcite structure as there are As=O bonds, which suggests
 297 that the anion is in the HAsO_4^{2-} form (1:1 ratio of As-OH : As=O). Increasing the pH
 298 of solution to 13 results in AsO_4^{3-} being the primary arsenate species. This is clearly
 299 visible in Figure 7, as an extremely broad band at 830 cm^{-1} , assigned to the AsO^-
 300 vibration. The intensity of this band indicates a large number of multiple bands that
 301 are very similar, such as the three As-O $^-$ bonds in the AsO_4^{3-} anion. The broadness
 302 suggests that the arsenate anions are in slightly different environments, thus slightly
 303 shifting the individual bands to make one very broad band. The Raman spectra for the
 304 mixed hydrotalcite, $\text{HT}(\text{CO}_3^{2-}, \text{AsO}_4^{3-}, \text{VO}_4^{3-})\text{-2h-pH8}$, Figure 5, clearly shows the
 305 intercalation of all three anions into the hydrotalcite structure. Bands due to carbonate
 306 are observed at 1061 and 1055 cm^{-1} . Bands associated with vanadate are observed at
 307 942 and 912 cm^{-1} , while bands observed at 876 and 811 cm^{-1} are assigned to arsenate
 308 vibrational modes. The broad band at 859 cm^{-1} is attributed to a combination of
 309 arsenate and vanadate vibrational modes. The assignment of the bands is clearly
 310 shown in the stacked Raman spectra of the individual hydrotalcites and the mixed
 311 hydrotalcite. At pH 13 two very broad bands are observed for the mixed hydrotalcite
 312 synthesised at pH 13, Figure 7, due to the large number of As-O $^-$ and V-O $^-$ bonds.

313

314 The presence of the symmetric stretching CO_3^{2-} vibrational mode centred at
 315 1060 cm^{-1} observed for hydrotalcite structures synthesised in the absence of
 316 carbonate, is due to the dissolution of CO_2 from the atmosphere. It is proposed
 317 carbonate is introduced into the system via the following reactions:

318



321

322 At high pH, the concentration of OH^- anions greater, thus, the dissolution of CO_2 is
 323 more rapid. Therefore, the contamination of CO_3^{2-} is greater, as observed in the
 324 hydrotalcite structures prepared at pH 13.

325

326 There does not appear to be an effect on the Raman spectrum in the carbonate
 327 vibrational region over longer synthesis times. Comparison of hydrotalcites
 328 synthesised for 2 and 48 hours at pH 8, showed no real change in the overall band

329 positions of carbonate, vanadate, or arsenate, Figures 5 and 6. The only noticeable
330 change in the overall spectral profile is in the mixed hydrotalcite,
331 $\text{HT}(\text{CO}_3^{2-}, \text{AsO}_4^{3-}, \text{VO}_4^{3-})$ -48h-pH8, and this is due to a decrease in intensity of the
332 As-O⁻ vibrational mode for the arsenate anion. This decrease in intensity is believed to
333 be due to a reduction in the number of As-O⁻ symmetric vibrations, possibly due to
334 the arsenate anion being primarily in the HAsO_4^{2-} or even H_2AsO_4^- form.

335

336 **CONCLUSIONS**

337

338 Hydrotalcites have been synthesised at three different pH solutions to assess the effect
339 pH as on the uptake of arsenate and vanadate from solution. The influence of the
340 synthesis pH showed a reduction in the effectiveness of the removal of arsenate and
341 vanadate in highly alkaline solutions. Hydrotalcites containing both arsenate and
342 vanadate at pH 8 obtained percentage removal abilities greater than 95 %, while
343 hydrotalcites synthesised at pH 13 only obtained removal abilities of 70 %. This
344 decrease is believed to be due to excess OH⁻ anions in solution, which compete
345 strongly with arsenate and vanadate anions for the hydrotalcite interlayer.

346 Hydrotalcites containing vanadate and arsenate are stable in solutions up to pH 10,
347 however, exposure of these hydrotalcites to highly alkaline solutions does result in the
348 exchange of a considerable amount of vanadate and arsenate anions for hydroxyl
349 anions.

350

351 Raman spectroscopy confirmed the formation of hydrotalcite species and the presence
352 of vanadate and arsenate anions in different environments. The results also suggest
353 that the type of vanadate and arsenate anions intercalated do change with different pH
354 solutions.

355

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357

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362

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387

388

389

390 **List of Tables**

391

392 **Table 1:** Concentrations of Na_2CO_3 , $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, NaVO_3 , and Na_2MoO_4
393 used to synthesise hydrotalcites with different oxy-anions.

394 **Table 2:** Percentage dissolution of hydrotalcites formed over varying synthesis
395 periods in NaOH at pH 10 and pH 14. Note the results for the mixed
396 anion hydrotalcite are for the anion in bold.

397 **Table 3:** CO_3^{2-} bands.¹²

398 **Table 4:** VO_4^{3-} and AsO_4^{3-} bands from different sources.¹²

399

400

401 **List of Figures**

402

403 **Figure 1:** Percentage of anions removed from solution during the synthesis of
404 hydrotalcites at pH 8 (green), pH 10 (blue), and pH 13 (black).

405 **Figure 2:** Molecular shape of the vanadate anion in the pH range 7-14.

406 **Figure 3:** Molecular shape of the arsenate anion in the pH range 7-14.

407 **Figure 4:** Raman spectra of hydrotalcites synthesised at pH 8 for 2 hours in the
408 hydroxyl stretching region, $4000 - 2500 \text{ cm}^{-1}$.

409 **Figure 5:** Raman spectrum in the anionic stretching region, $1200-600 \text{ cm}^{-1}$, for
410 hydrotalcites prepared for 2 hours at pH 8.

411 **Figure 6:** Raman spectrum in the anionic stretching region, $1200-600 \text{ cm}^{-1}$, for
412 hydrotalcites prepared for 48 hours at pH 8.

413 **Figure 7:** Raman spectrum in the anionic stretching region, $1200-600 \text{ cm}^{-1}$, for
414 hydrotalcites prepared for 2 hours at pH 13.

415

416

417 **Tables**

418

419 **Table 1:** Concentrations of Na_2CO_3 , $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, NaVO_3 , and Na_2MoO_4
420 used to synthesise hydrotalcites with different oxy-anions.

Synthetic hydrotalcite	Na_2CO_3 (concentration)	Oxy-anion (concentration)	
	Na_2CO_3	-	
HT(CO_3^{2-})	0.20 M	-	
	Na_2CO_3	$\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$	
HT($\text{CO}_3^{2-}, \text{AsO}_4^{3-}$)	0.10 M	0.10 M	
HT(AsO_4^{3-})	-	0.20 M	
	Na_2CO_3	NaVO_3	
HT($\text{CO}_3^{2-}, \text{VO}_4^{3-}$)	0.10 M	0.10 M	
HT(VO_4^{3-})	-	0.20 M	
	Na_2CO_3	$\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$	NaVO_3
HT($\text{CO}_3^{2-}, \text{AsO}_4^{3-}, \text{VO}_4^{3-}$)	0.067 M	0.067 M	0.067 M

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423 **Table 2:** Percentage dissolution of hydrotalcites formed over varying synthesis
 424 periods in NaOH at pH 10 and pH 14. Note the results for the mixed
 425 anion hydrotalcite are for the anion in bold.

	% dissolution				% dissolution		
NaOH pH 10	2h	24h	48h	NaOH pH 14	2h	24h	48h
HT(CO ₃ ²⁻ ,VO ₄ ³⁻)	0.1	0.3	0.5	HT(CO ₃ ²⁻ ,VO ₄ ³⁻)	46.8	23.2	18.9
HT(VO ₄ ³⁻)	0.1	0.1	0.4	HT(VO ₄ ³⁻)	41.9	24.7	6.0
HT(CO ₃ ²⁻ ,AsO ₄ ³⁻)	0.6	0.1	0.0	HT(CO ₃ ²⁻ ,AsO ₄ ³⁻)	44.0	4.9	3.4
HT(AsO ₄ ³⁻)	0.3	0.1	0.0	HT(AsO ₄ ³⁻)	41.2	4.2	3.8
HT(CO ₃ ²⁻ , AsO₄³⁻ ,VO ₄ ³⁻)	5.3	0.9	0.1	HT(CO ₃ ²⁻ , AsO₄³⁻ ,VO ₄ ³⁻)	53.8	16.2	7.3
HT(CO ₃ ²⁻ ,AsO ₄ ³⁻ , VO₄³⁻)	3.7	1.0	0.5	HT(CO ₃ ²⁻ ,AsO ₄ ³⁻ , VO₄³⁻)	46.2	19.6	14.3

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432 **Table 3:** CO_3^{2-} bands.¹²

Wavenumber (cm^{-1})	Vibrational mode
1063	symmetric stretch $\nu_1 \text{CO}_3^{2-}$
1415	antisymmetric stretch $\nu_3 \text{CO}_3^{2-}$
879	out-of-plane bending $\nu_2 \text{CO}_3^{2-}$
680	in-plane bending $\nu_4 \text{CO}_3^{2-}$

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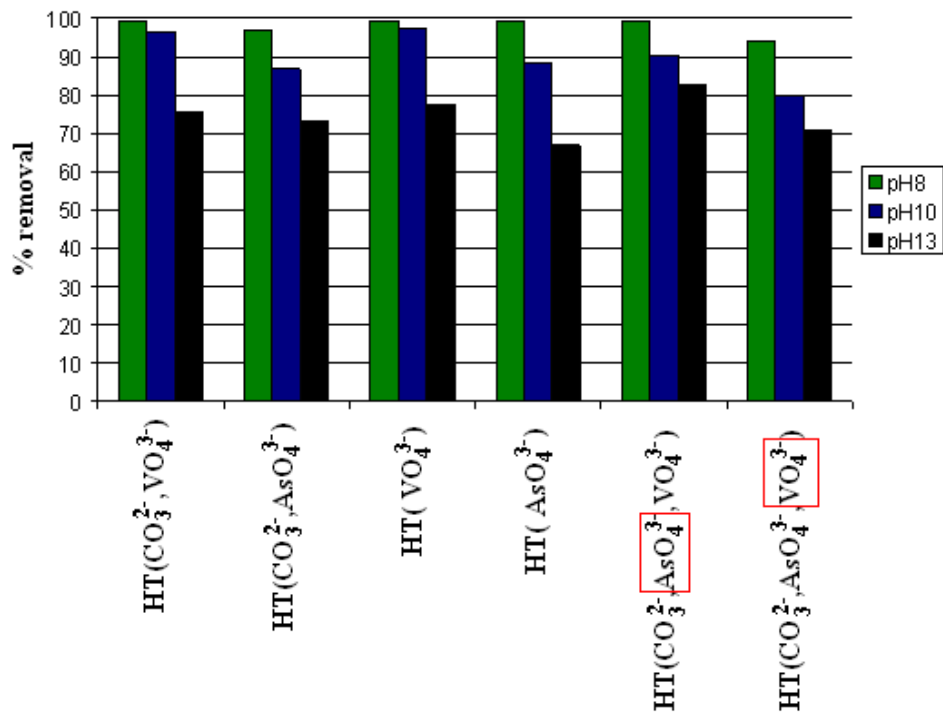
435 **Table 4:** VO_4^{3-} and AsO_4^{3-} bands from different sources.¹²

	ν_1 (A_1) symmetric stretch (cm^{-1}) (Raman active)	ν_2 (E) bend (cm^{-1}) (Raman active)	ν_3 (F_2) antisymmetric stretch (cm^{-1}) (IR and Raman active)	ν_4 (F_2) bend (cm^{-1}) (IR and Raman active)
VO_4^{3-}	824	340	790	340
	827	340	780	340
	870	328	825	480
	874	345	855	345
	824	305	790	340
AsO_4^{3-}	810	342	810	398
	837	349	878	463

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437 **Figures**

438



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440 **Figure 1:** Percentage of anions removed from solution during the synthesis of
441 hydrotalcites at pH 8 (green), pH 10 (blue), and pH 13 (black).

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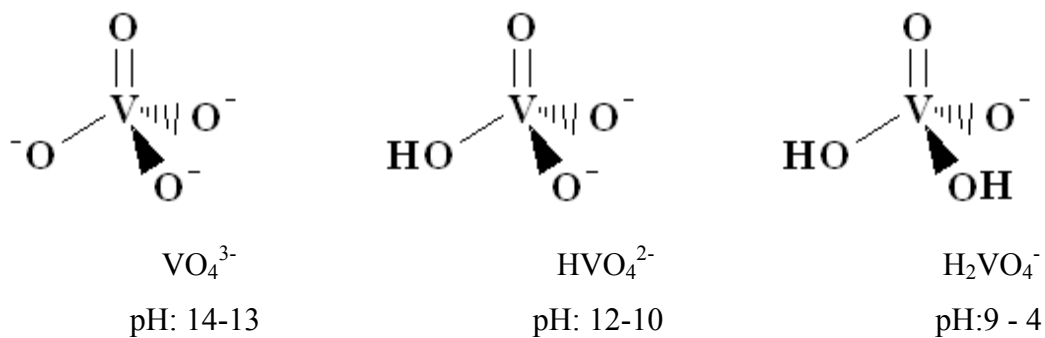
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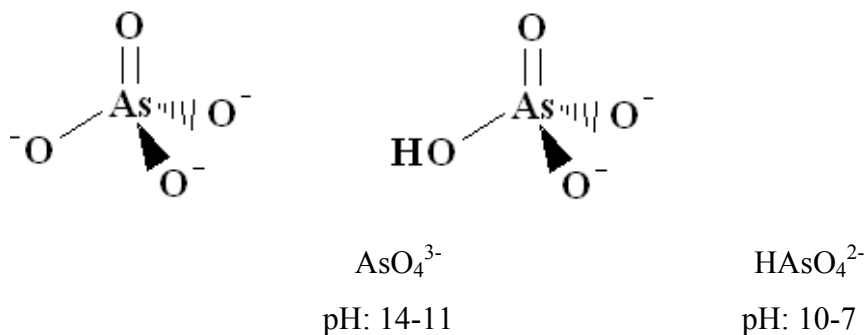


459 **Figure 2:** Molecular shape of the vanadate anion in the pH range 7-14.

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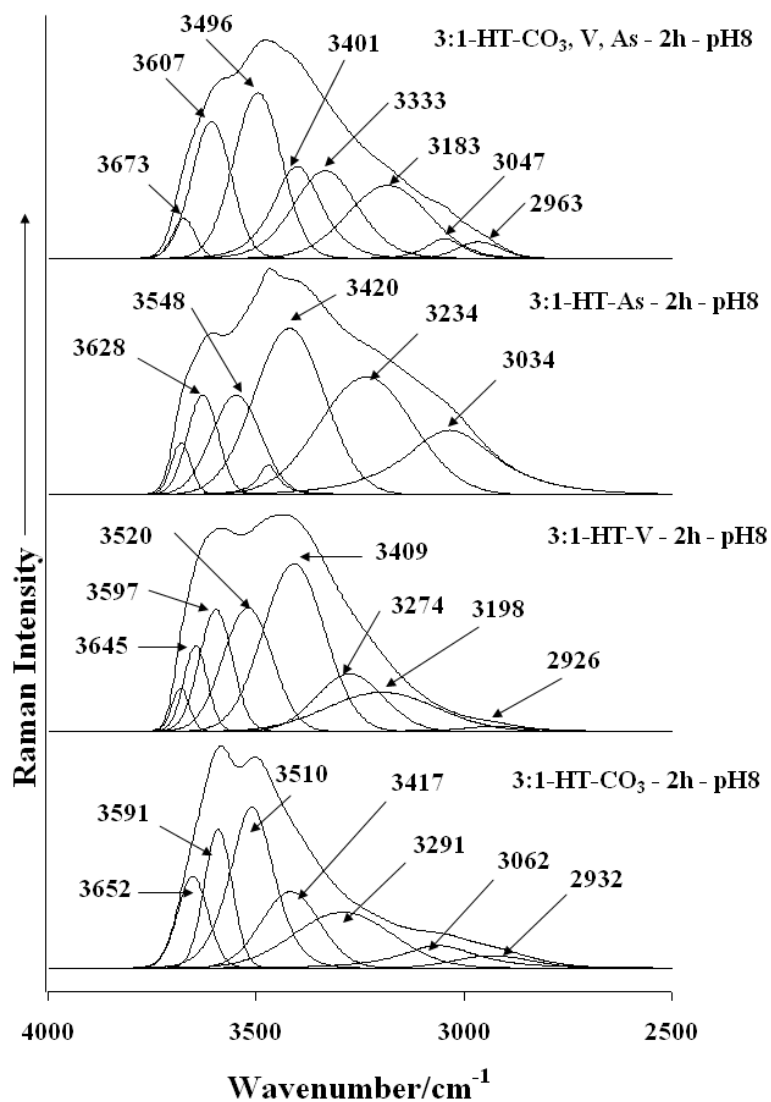
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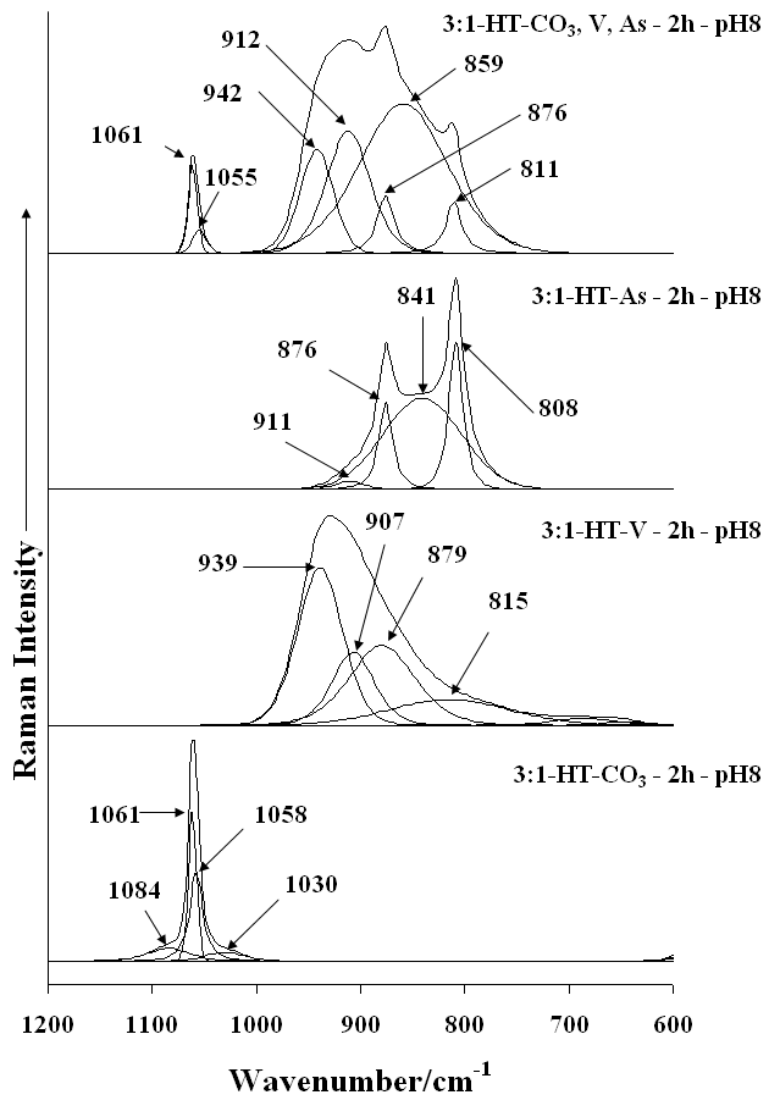
466 **Figure 3:** Molecular shape of the arsenate anion in the pH range 7-14.

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469 **Figure 4:** Raman spectra of hydroxalcalites synthesised at pH 8 for 2 hours in the
 470 hydroxyl stretching region, 4000 – 2500 cm⁻¹.

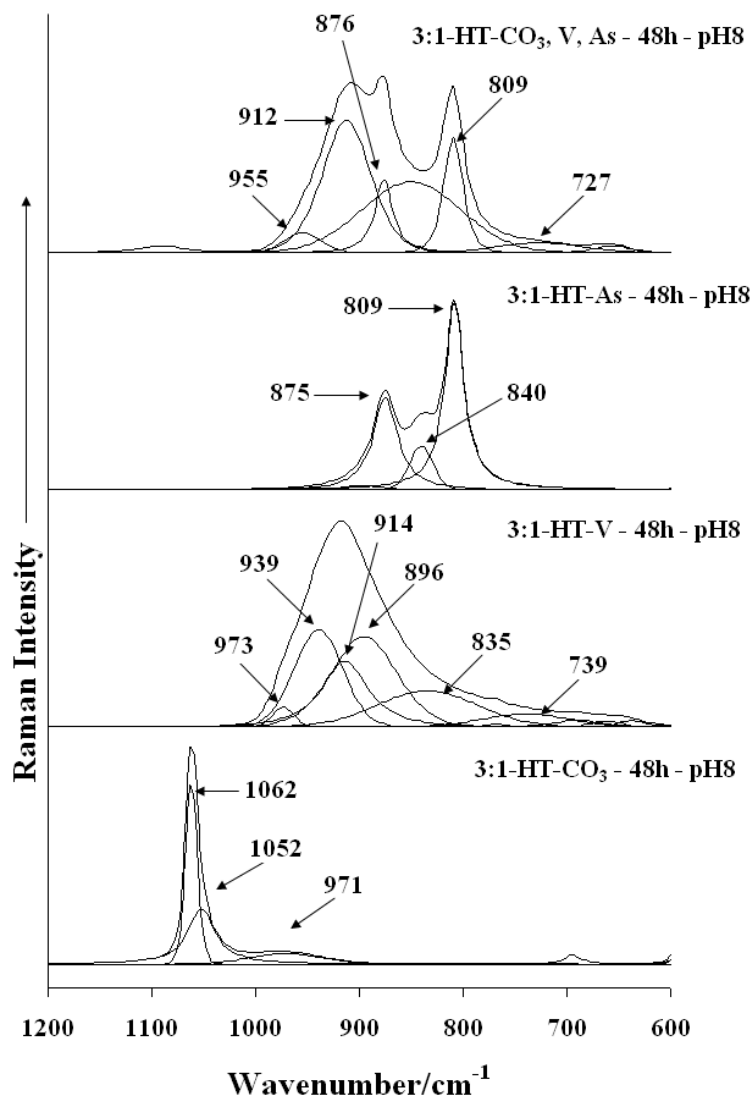


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473 **Figure 5:** Raman spectrum in the anionic stretching region, 1200-600 cm⁻¹, for

474 hydrotalcites prepared for 2 hours at pH 8.

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477 **Figure 6:** Raman spectrum in the anionic stretching region, 1200-600 cm⁻¹, for

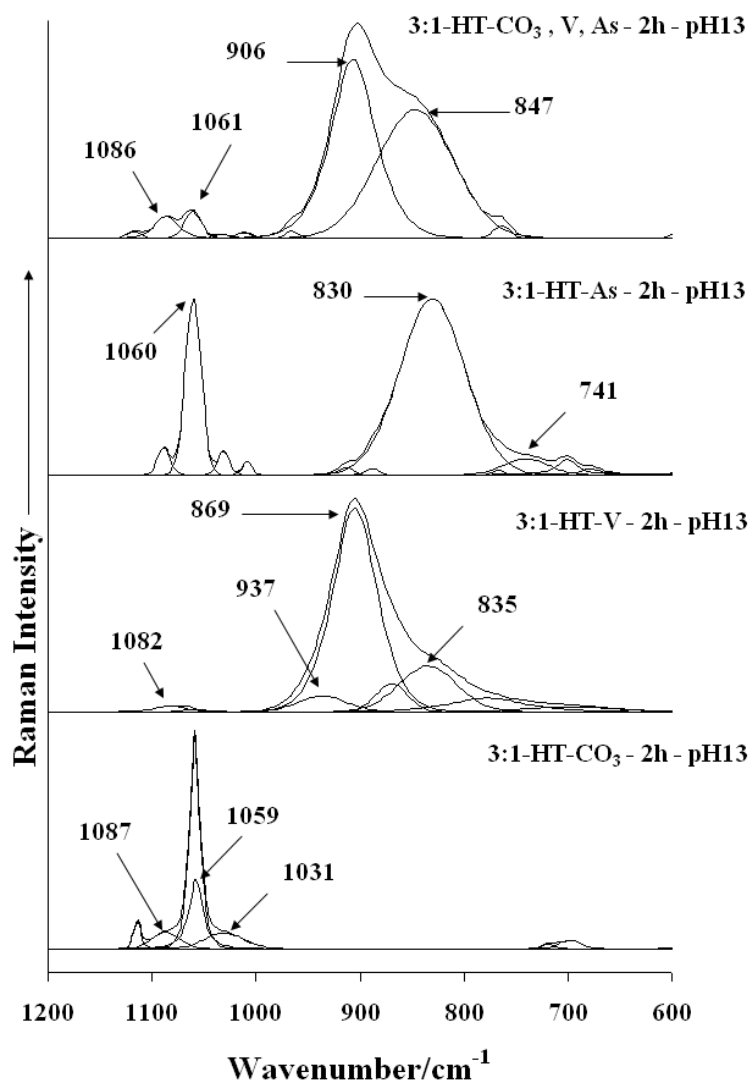
478 hydrotalcites prepared for 48 hours at pH 8.

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484 **Figure 7:** Raman spectrum in the anionic stretching region, 1200-600 cm⁻¹, for
 485 hydrotalcites prepared for 2 hours at pH 13.

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