

1 **Morphology dependent adsorption of methylene blue on**
2 **tritanate nanoplates and nanotubes prepared by the**
3 **hydrothermal treatment of TiO₂**
4

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17 **Abstract**

18 The adsorption properties of two nanomorphologies of tritanate, nanotubes (TiNT) and plates
19 (TiNP), prepared by the hydrothermal reaction of concentrated NaOH with different phases of TiO₂, were
20 examined. It was found that the capacity for both morphologies towards methylene blue (MB), an ideal
21 pollutant, was extremely high, with the TiNP having a capacity of 130 mg/g, higher than the TiNT, whose
22 capacity was 120 mg/g at 10 mg/L MB concentration. At capacity, the well-dispersed powders deposit on
23 the floor of the reaction vessel. The two morphologies had very different structural and adsorption
24 properties. TiNT with high surface area and pore volume exhibited exothermic monolayer adsorption of
25 MB. TiNP with low surface area and pore volume yielded a higher adsorption capacity through
26 endothermic multilayer adsorption governed by pore diffusion. TiNP exhibited a higher negative surface
27 charge of -23mV, compared to -12mV for TiNT. The adsorption process appears to be an electrostatic
28 interaction, with the cationic dye attracted more strongly to the nanoplates, resulting in a higher adsorption
29 capacity and different adsorption modes. We believe this simple, low cost production of high capacity
30 nanostructured adsorbent material has potential uses in wastewater treatment.

31
32 **Keywords:** tritanate nanotubes; adsorption; methylene blue

33 **Introduction**

34 Dye compounds are common and difficult to remove pollutants from several industries, including textiles
35 and printing. The removal of dye compounds from wastewater has therefore received considerable attention
36 in recent years and requires environmentally friendly materials and potentially easy separation or
37 regeneration techniques (Ramakrishna and Viraraghavan 1997, Crini 2006). Photocatalytic and biological
38 degradations of the dyestuffs can result in the production of toxic products due to the complex nature of the
39 aromatic dye molecules, therefore adsorption is a promising technique for the removal of dyes from water
40 (Zhao and Liu 2008). A wide variety of adsorbents have been employed for several different applications,
41 including activated carbon and mesoporous molecular sieves, however the operating and regeneration costs
42 are high, leading to a search for low cost, high capacity absorbants (Widjaja *et al.* 2004, Namane *et al.*
43 2005, Parida *et al.* 2006, Wang *et al.* 2006). Nanostructured materials are of great interest due to their
44 exceptional electronic and mechanical properties, as well as exhibiting high surface areas: a useful property
45 for adsorption. Research pertaining to inorganic nanotubes has been extensive (Tenne *et al.* 1992, Feldman
46 *et al.* 1995, Nakamuar and Matsui 1995, Hoyer 1996, Goldberger *et al.* 2001, Pu *et al.* 2001), with TiO₂
47 receiving a great deal of attention.

48 Titania nanotubes were first prepared by the hydrothermal treatment of TiO₂ with 10M NaOH
49 (Kasuga *et al.* 1998). The nanotubular material was produced by treating crystalline TiO₂ with 10 molar
50 NaOH. It was concluded that washing the alkali treated specimen with water followed by further reaction
51 with HCl are vital steps in the formation of nanotubes (Kasuga *et al.* 1999). Work has later shown (Chen *et*
52 *al.* 2002) that the nanotubes could be prepared via a single hydrothermal alkali treatment of crystalline
53 TiO₂.

54 We have shown that the reaction temperature and phase composition of the starting material are
55 important factors in determining the morphology of the product (Dawson *et al.* 2010). The anatase
56 component of the starting material is easily converted to trititanate nanotubes at 140 °C, where as the rutile
57 remains unreacted. After the temperature is increased to 170 °C the morphology is exclusively trititanate
58 nanoplates, with the tubular structure destroyed. The high adsorption capacity of trititanate nanotubes for
59 basic dyes has been reported (Lee *et al.* 2007, Hsieh *et al.* 2008), with the dye is adsorbed on the nanotube
60 via an ion exchange mechanism. Modification of the nanotube surface by dopamine imparts photocatalytic

61 properties on the composite material (Dawson *et al.* 2012, Liu *et al.*, 2016), however little is known about
62 the adsorption process and interaction.

63 In this study we have compared the adsorption properties of trititanate tubes and plates prepared by the
64 hydrothermal treatment of different phase TiO₂. It was found that nanotubes with high surface area and
65 pore volume exhibited exothermic monolayer adsorption of MB governed by external mass transport.
66 Nanoplates with low surface area and pore volume yielded a higher adsorption capacity through
67 endothermic multilayer adsorption governed by pore diffusion. We believe these nanostructured materials
68 have interesting potential applications in wastewater treatment and absorption.

69

70 **Experimental**

71 **Preparation of Nanostructures**

72 The two different nanostructures were prepared following our previously reported method (Dawson *et al.*
73 2010) at 140 °C for 72 hours for anatase (TiNT) and 170 °C for 7 days for rutile (TiNP).

74 **Characterisation**

75 The products morphologies were investigated using FESEM (FEI Quanta 400 FEG) and TEM (FEI Tecnai
76 F20 operating at 200 kV). Powder X-ray diffraction (XRD) was performed with Cu K α radiation on a
77 X'Pert Pro MPD operation at 40 kV and 30 mA. Zeta potentials were measured using a Colloidal Dynamics
78 Zeta Probe. Specific surface areas, pore size and pore volumes were determined by nitrogen adsorption at –
79 196 °C on a Micromeritics ASAP 2020 apparatus. The surface area was determined by the Brunauer-
80 Emmett-Teller (BET) method.

81 The adsorption capacity of the samples was investigated with methylene blue (MB) dye solution. Sample
82 powder (0.01g) was suspended in 100ml of methylene blue solution of the desired concentration. The
83 reaction mixture was placed in an incubator shaker equipped with a constant temperature controller at 100
84 rpm for 5 hours. After the adsorption period an amount of solution was centrifuged at 120,000 rpm for 20
85 minutes. The concentration of MB left in solution was determined using a UV spectrometer (Perkin Elmer
86 Lambda 25) at 665nm by comparing the absorbance against a standardised calibration curve. The amount

87 of dye adsorbed on the sample was calculated from the concentration of dye left in the solution using
88 equation 1:

$$89 \quad Q = V(C_i - C_e) / M \quad (1)$$

90

91 Where Q is the adsorption capacity (mg/g), C_i the initial concentration of methylene blue, C_e the
92 equilibrium concentration, V the volume of solution and M the mass of Ti sample in the reaction.

93

94 **Adsorption isotherms**

95 The equilibrium adsorption isotherms were analysed using the Langmuir and BET models.

96 The Langmuir model can be described by the following form:

$$97 \quad Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

98 where Q_e (mg/g) is the solid phase equilibrium concentration, Q_m (mg/g) the maximum adsorption capacity
99 K_L (L/mg) is the Langmuir constant and C_e (mg/L) is the liquid phase equilibrium concentration.

100 The model assumes that adsorption occurs on a homogenous surface of identical sites that are equally
101 available and energetically equivalent and each site carries equal numbers of molecules with no interaction
102 between adsorbate molecules. The linear form of the Langmuir equation can be represented as follows:

$$103 \quad \frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \quad (3)$$

104 Therefore, if the model is valid a linear plot of C_e/Q_e versus C_e will yield K_L and Q_m from the intercept and
105 slope.

106

107 The BET isotherm is given below in the linear form:

108

109
$$\frac{M.C}{(C_s - C)x} = \frac{1}{AX_m} + \frac{(A-1) C}{AX_m C_s} \quad (4)$$

110

111 where M is the mass of adsorber (mg), C_s is the saturation concentration, X_m is the BET monolayer
112 capacity and A is a constant.

113

114 For adsorption from the liquid phase the partial pressure term can be replaced by the saturation
115 concentration (Parker 1995). In this study we have used the initial concentration of MB, c_i, in accordance
116 with (El-Halwany 2010). Thus, plotting M.C/(C_s-c)x versus C/C_s will give rise to a straight line from whose
117 slope and intercept the BET monolayer can be calculated. The value of the correlation coefficient, r²,
118 determines which model is the best fit for the data.

119

120 **Thermodynamic parameters**

121 The adsorption isotherms were measured at three temperatures, so the heat of adsorption can be calculated.

122 The temperature dependency of the adsorption equilibrium constant K (Q_e/C_e) obeyed the van't Hoff
123 equation:

124

125
$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \quad (5)$$

126 Which, when integrated, gives:

127

128
$$\ln K = \ln K_0 + (-\Delta H / RT) \quad (6)$$

129

130 The value of ΔH can be determined from the slope of the plot of lnK versus 1/T, which produces a straight
131 line.

132

133 The Gibbs free energy, ΔG (J/mol), is an indication of the spontaneity of a chemical reaction. If the value
134 of ΔG has a negative value the reaction will proceed spontaneously. For an adsorption reaction it is given
135 by the following equation:

136

$$137 \quad \Delta G = -RT \ln K \quad (7)$$

138

139 The entropy change can also then be calculated using the following equation:

140

$$141 \quad \Delta G = \Delta H - T\Delta S \quad (8)$$

142 Kinetics

143 The kinetic data was analysed using the linear form of the pseudo second order kinetic model proposed by
144 Ho, which has been extensively used to predict dye adsorption kinetics (Ho and McKay 1999):

145 .

$$146 \quad \frac{t}{Q_t} = \frac{1}{k_{ps} Q_e^2} + \frac{t}{Q_e} \quad (9)$$

147 where k_{ps} (g/mg h) is the pseudo second order rate constant. A plot of t/Q_t versus time will yield a straight
148 line if the pseudo second order model is valid, with the values of k_{ps} and Q_e calculated from the slope and
149 intercept.

150

151 The adsorption was further investigated using the intraparticle diffusion model given below, which
152 examines the steps involved during adsorption:

153

$$154 \quad Q_t = k_d t^{1/2} \quad (10)$$

155

156 A two phase plot would suggest that the adsorption proceeds by external mass transfer, (boundary layer
157 diffusion) described by the curved section of the plot, and intraparticle, or pore, diffusion described by the
158 linear section.

159 **Results and Discussion**

160 **Structural Properties of nanotubes and nanoplates**

161

162 Two distinct morphologies of trititanate, nanotubes and nanoplates, were prepared from TiO_2 according to
163 our previous report. The morphological and structural properties are summarised in Fig. 1 and Table 1. A
164 detailed study of the morphology and synthesis can be found in our previous report (Dawson et al, 2010).

165

166 The specific surface area and pore volumes of the two samples were measured using the BET and BJH
167 methods respectively. The surface area of TiNT was found to be $250 \text{ m}^2/\text{g}$. The TiNP sample exhibited a
168 surface area of $40 \text{ m}^2/\text{g}$, much lower than the tube sample. In the TiNT sample the pore size peak at 3.4 nm
169 is attributed to the internal tube cavity, which is in agreement with the TEM observations (Fig. 1). The pore
170 distribution is wide, with the larger pores between 10 and 100 nm being attributed to voids formed between
171 nanotube aggregates. The distribution for the TiNP sample is also large, with small pore peaks at 2.1 and
172 3.7 nm . From the TEM shown in Fig. 1, we can see that there are no pores visible in the plate structures
173 themselves, so it can be concluded that the mesopores come from the aggregation and stacking of plates,
174 with the larger pores created in the voids between the particles. The pore volume for TiNT was high, 0.9
175 cm^3/g , but TiNP had a low pore volume of $0.19 \text{ cm}^3/\text{g}$.

176

177 The stability of the samples in aqueous solution was measured by zeta potential, and are shown in Table 1.
178 TiNT had a potential of -12 mV at a pH of 6.7 , and TiNP exhibited a value of -23 mV at pH 6.0 . TiNP
179 exhibit a higher $-ve$ zeta potential, and are therefore more stable in suspension.

180

181 The adsorption characteristics and kinetics of the two morphologies were compared and are detailed below.

182

183 **Liquid phase adsorption of MB**

184 The adsorption isotherms of TiNT and TiNP for MB uptake at different temperatures are shown in
185 Fig. 2. They were analysed according to the linear forms of the Langmuir and BET isotherms and the
186 parameters k_L and Q_e from the Langmuir model and A and X_m from the BET model were calculated and
187 listed in Table 2 along with the correlation coefficients, r^2 .

188 As can be seen, the Langmuir model is a good fit for the TiNT data, with all r^2 values >0.99 .
189 While the Langmuir model reflects monolayer adsorption, a good fit to the BET isotherm indicates
190 multilayer adsorption. The TiNP data is a good fit for the BET model, with a calculated monolayer capacity
191 of 15 mg/g, which is in keeping with the theoretically calculated value from the SSA data. The calculated
192 adsorption capacity maximums for the nanotubes using the Langmuir model were 122.65, 106.84 and
193 101.42 mg/g at 25, 40 and 60 °C respectively.

194 The experimental adsorption capacities measured in 100 ml of 10 mg/L MB solution at 25 °C were
195 found to be 120 mg/g for TiNT and 130 mg/g for TiNP samples. This is in good agreement with the
196 Langmuir calculated values for the TiNT sample. The Langmuir model gives lower capacities than
197 observed, however, this model is mostly suitable for monolayer adsorption.

198 The value of the zeta potential is a measure of the charge on the electric double layer, but can be
199 taken as the surface charge. Therefore, TiNP have a higher –ve surface charge, and attract the positively
200 charged MB ions more strongly. This stronger interaction, along with the flat plate structure compared to
201 the curved tube structure results in the formation of multilayers of MB, and only monolayers in the TiNT
202 adsorption. The lower surface charge may be a result of the scroll structure “hiding” some of the surface
203 within the tube, where it is balanced by H^+ and Na^+ ions and doesn't contribute to the surface negativity in
204 the zeta potential measurement. There may also be a contribution from the lowering of strain through layer
205 coupling in the scroll structure. However this will require further investigation.

206 As can be seen from Fig. 2a, the adsorbed amount for TiNT decreases with increasing
207 temperature, that is to say the reaction is an exothermic process. In the case of TiNP, the adsorbed amount
208 increases with increasing temperature, and therefore the adsorption reaction is endothermic in nature.
209 Physical adsorption is generally an exothermic process, however endothermic adsorptions of MB have been

210 reported on activated carbons and clays (Lin and Teng 2002, Hong *et al.* 2009). Because of this interesting
211 observation the adsorption was investigated further.

212 The heats of adsorption, ΔH , were calculated from the van't Hoff equation (Equation 5) and are –
213 39.83 kJmol⁻¹ for TiNT and +25.98 kJmol⁻¹ for TiNP. These values indicate a physical adsorption, which is
214 generally of the range <40 kJmol⁻¹ (Lin and Teng 2002). The Gibbs free energy was calculated from
215 Equation 10, and was –ve for both morphologies, indicating a spontaneous reaction in both cases. The
216 values of ΔG at different temperatures are listed in Table 3. The change in entropy for both systems was
217 also calculated as –86 and 130 JK⁻¹mol⁻¹ for TiNT and TiNP respectively. The different signs of the entropy
218 for both reactions is interesting. The numerical values are both relatively small, and around the order of
219 values seen for phase changes. Both reactions are spontaneous, as shown by the negative values of the
220 Gibbs energy. A decrease in entropy for an adsorption process would be expected, as is seen for the TiNT,
221 where the negative entropy change is accounted for by the increase in order of the system through
222 adsorption as the condensed state is more ordered than in bulk solution. The exothermic nature of the
223 adsorption overcomes the increase in order to give a negative value of Gibbs energy, and a spontaneous
224 reaction. The positive value of ΔS for TiNP overcomes the exothermic value of ΔH , resulting in a negative
225 Gibbs energy and a spontaneous reaction. This entropy change reflects the affinity of the plates for the dye
226 and suggests some structural changes in the system. The adsorption of MB will result in a negative change
227 in entropy, however each MB will replace several water molecules, resulting in an overall positive entropy
228 change for the system (Hong *et al.* 2009).

229 Assuming that MB molecules can occupy the entire surface area, we can calculate the maximum
230 amount of MB adsorbed in a monolayer (Hong *et al.* 2009) . Rather than lying flat on the surface,
231 methylene blue has been shown to adsorb onto clay surfaces at a tilted angle (Krishna *et al.* 2004). The
232 dimensions of a MB molecule are given as 1.65 nm by 0.77 nm wide and 0.4 nm thick. Therefore the area
233 that one molecule of MB takes up on a surface can therefore vary from 1.27 nm² for flat lying cations to
234 0.66 nm² for molecules perpendicular to the surface. These values correspond to a capacity of 102-240
235 mg/g for TiNT and 16.4-38.6 mg/g for TiNP. From these figures we can conclude that MB is adsorbed on
236 the nanotube surface in a monolayer at low tilting angle, whereas the adsorption mode for the nanoplates

237 appears to be multilayered adsorption, with not enough surface layer available to provide the high capacity
238 observed in a monolayer configuration.

239 The adsorption capacities of the TiNT and TiNP were compared with similar complex
240 nanomaterials in the literature, shown in Table 4. Both materials showed a favourable adsorption capacity.

241 **Kinetics of adsorption**

242 The kinetics of the adsorption process for both morphologies was examined using the linear form of the
243 pseudo second order model, shown in Fig. 3. The suitability of the model to the data was determined from
244 the correlation coefficients of the linear regression, r^2 . In both cases the coefficients are >0.99 , indicating a
245 good fit. The kinetic parameters are listed in Table 5. Fig. 4 shows the plots of the adsorption process using
246 the intraparticle diffusion model. For TiNT the two-phase plot suggests that the adsorption proceeds by
247 external mass transfer or boundary layer diffusion, which is described by the curved section of the plot, and
248 intraparticle or pore diffusion described by the linear section. TiNP exhibits a linear plot, indicating that
249 pore diffusion governs the process. The slope of the linear portion of the plot is defined as the intraparticle
250 diffusion parameter, k_i . The values are listed in Table 5. The value for TiNP is higher than for TiNT,
251 indicating the intraparticle diffusion occurs faster for the TiNP sample.

252 After the capacity of adsorption was reached the particles aggregated and deposited on the base of
253 the beaker. This is an interesting property for applications of water treatment, where separation of the
254 adsorbant is an issue. This occurs because the adsorption is an electrostatic interaction, and repulsion
255 between the particles helps in stabilising the suspension. When the charge is neutralized by MB adsorption,
256 the particles aggregate and deposit on the base of the vessel. The adsorption capacities of macrosized bulk
257 TiO_2 and $\text{H}_2\text{Ti}_3\text{O}_7$ was also measured and found to be negligible. During the measurements of adsorption
258 the sample was suspended in the MB solution by sonication. After adsorption the particles aggregated
259 together to form m sized clumps and deposited on the bottom of the vessel. As a comparison, TiNT
260 dispersed in water aggregate and deposit over hours, but TiNT after MB adsorption aggregate and deposit
261 within 5 minutes.

262

263 **Conclusions**

264 Two distinct trititanate nanomorphologies were prepared by the hydrothermal treatment of TiO₂
265 with strong base. The two morphologies, plates and tubes, had very different structural and adsorption
266 properties. Nanotubes with high surface area and pore volume exhibited exothermic monolayer adsorption
267 of MB. Nanoplates with low surface area and pore volume nanoplates yielded a higher adsorption capacity
268 through endothermic multilayer adsorption governed by pore diffusion. The stronger electrostatic
269 interaction between the TiNP surface and the MB molecules results in multilayer adsorption, and the
270 different modes of adsorption of the two morphologies result in the exothermic and endothermic character
271 for TiNT and TiNP respectively.

272 The morphology dependent adsorption characteristics of two materials prepared by a facile and
273 low cost production method have interesting potential applications in wastewater treatment. It is also
274 interesting and informative to observe such different adsorption properties within the same material phase
275 of different nanomorphologies.

276

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350

351

352 **Fig. 1** SEM and TEM images of TiNT (a and b) and TiNP (c and d)

353

354

355 **Fig. 2** Liquid phase adsorption isotherms of MB on (a) TiNT and (b) TiNP.

356

357 **Fig. 3** Pseudo second order kinetics of MB onto TiNP and TiNT.

358 **Fig. 4** Diffusion model plots for TiNT and TiNP adsorption of MB. Conditions: 10mg/L

359 25 °C

360

361 Table 1 Surface properties for TiNT and TiNP

Sample	BET surface area (m ² /g)	Pore Volume (cm ³ /g)	Average Pore Size (nm)	Zeta Potential (mV)	Experimental Adsorption Capacity (mg/g)
TiNT	249.4	0.945	13.1	-12	120
TiNP	40.1*	0.19*	18.1*	-23	130

362 * from ref [17]

363

364 Table 2 Adsorption isotherm data for MB on TiNT and TiNP

Morphology	T (°C)	Langmuir Isotherm			BET Isotherm		
		K _L	Q _m	r ²	X _m	A	r ²
TiNT	25	11.74	122.25	0.999			
	40	9.18	106.84	0.999			
	60	4.16	101.42	0.997			
TiNP	25	37.08	138.69	0.999	12.21	-3297.47	0.997
	40	-185.13	151.98	0.999	13.51	-1.325 × 10 ⁶	0.998
	60	25.16	193.05	0.998	15.69	-842	0.998

365

366

367

368 Table 3 Thermodynamic parameters for adsorption of MB on TiNT and TiNP

Morphology	ΔH (kJmol ⁻¹)	T (°C)	ΔG (kJmol ⁻¹)	ΔS (kJmol ⁻¹)
TiNT	-39.83	25	-14.04	-86.68
		40	-12.7	-86.68
		60	-10.97	-86.67
TiNP	25.98	25	-12.965	130.7
		40	-15.34	132.0
		60	-17.56	130.75

369

370

371 Table 4 Comparison of adsorption capacities of complex nanomaterials for methylene
372 blue

373

Adsorbent	Experimental adsorption capacity (mg/g)	Reference
Carbon nanotubes	35.4 – 64.7	Yao <i>et al.</i> 2010
Magnetite loaded carbon nanotubes	48.06	Ai <i>et al.</i> 2011
Carbon nanotube aerogels	62.5	Tabrizi and Yavari 2015
Halloysite nanotubes	84.32	Zhao and Liu 2008
NiO/MCM-41 composite	23.26	Xiao <i>et al.</i> 2015
TiNT and TiNP	120, 130	This study

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377 Table 5 Kinetic data for the adsorption of MB on TiNT and TiNP

	TiNT	TiNP	378
Pseudo second order			
Q_e , mg/g	106.61	257.07	
k_{ps} , g/mg min	7.05×10^{-4}	1.67×10^{-4}	
r^2	0.999	0.995	
Intraparticle			
diffusion			
k_i (mg/(gmin ^{0.5}))	2.54	10.37	