Morphology dependent adsorption of methylene blue on trititanate nanoplates and nanotubes prepared by the hydrothermal treatment of TiO$_2$

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Abstract

The adsorption properties of two nanomorphologies of trititanate, nanotubes (TiNT) and plates (TiNP), prepared by the hydrothermal reaction of concentrated NaOH with different phases of TiO$_2$, were examined. It was found that the capacity for both morphologies towards methylene blue (MB), an ideal pollutant, was extremely high, with the TiNP having a capacity of 130 mg/g, higher than the TiNT, whose capacity was 120 mg/g at 10 mg/L MB concentration. At capacity, the well-dispersed powders deposit on the floor of the reaction vessel. The two morphologies had very different structural and adsorption properties. TiNT with high surface area and pore volume exhibited exothermic monolayer adsorption of MB. TiNP with low surface area and pore volume yielded a higher adsorption capacity through endothermic multilayer adsorption governed by pore diffusion. TiNP exhibited a higher negative surface charge of –23mV, compared to –12mV for TiNT. The adsorption process appears to be an electrostatic interaction, with the cationic dye attracted more strongly to the nanoplates, resulting in a higher adsorption capacity and different adsorption modes. We believe this simple, low cost production of high capacity nanostructured adsorbent material has potential uses in wastewater treatment.

Keywords: trititanate nanotubes; adsorption; methylene blue

Introduction

Dye compounds are common and difficult to remove pollutants from several industries, including textiles and printing. The removal of dye compounds from wastewater has therefore received considerable attention in recent years and requires environmentally friendly materials and potentially easy separation or regeneration techniques (Ramakrishna and Viraraghavan 1997,Crini 2006). Photocatalytic and biological degradations of the dyestuffs can result in the production of toxic products due to the complex nature of the aromatic dye molecules, therefore adsorption is a promising technique for the removal of dyes from water (Zhao and Liu 2008). A wide variety of adsorbents have been employed for several different applications, including activated carbon and mesoporous molecular sieves, however the operating and regeneration costs are high, leading to a search for low cost, high capacity absorbants (Widjaja *et al.* 2004, Namane *et al.* 2005, Parida *et al.* 2006, Wang *et al.* 2006). Nanostructured materials are of great interest due to their exceptional electronic and mechanical properties, as well as exhibiting high surface areas: a useful property for adsorption. Research pertaining to inorganic nanotubes has been extensive (Tenne *et al.* 1992, Feldman *et al.* 1995, Nakamuar and Matsui 1995, Hoyer 1996, Goldberger *et al.* 2001, Pu *et al.* 2001), with TiO_2 receiving a great deal of attention.

Titania nanotubes were first prepared by the hydrothermal treatment of TiO_2 with 10M NaOH (Kasuga *et al.* 1998). The nanotubular material was produced by treating crystalline TiO_2 with 10 molar NaOH. It was concluded that washing the alkali treated specimen with water followed by further reaction with HCl are vital steps in the formation of nanotubes (Kasuga *et al.* 1999). Work has later shown (Chen *et al.* 2002) that the nanotubes could be prepared via a single hydrothermal alkali treatment of crystalline TiO_2.

We have shown that the reaction temperature and phase composition of the starting material are important factors in determining the morphology of the product (Dawson *et al.* 2010). The anatase component of the starting material is easily converted to trititanate nanotubes at 140 ℃, where as the rutile remains unreacted. After the temperature is increased to 170 ℃ the morphology is exclusively trititanate nanoplates, with the tubular structure destroyed. The high adsorption capacity of trititanate nanotubes for basic dyes has been reported (Lee *et al.* 2007, Hsieh *et al.* 2008), with the dye is adsorbed on the nanotube 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 TiO_2. 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 Kα 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                       $Q = V(C_i - C_e)/M$ (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
$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}$$
    (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
$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m}$$
    (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 $$\frac{M.C}{(C_s - C)x} = \frac{1}{AX_m} + \frac{(A-1)}{AX_m}\frac{C}{C_s}$$ (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, r^2,

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

126 Which, when integrated, gives:

127

128 $$\ln K = \ln K_0 + (-\Delta H / RT)$$ (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        $$\Delta G = -RT \ln K \qquad (7)$$

138

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

140

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

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

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

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 summerised 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 BHJ

167 methods respectively. The surface area of TiNT was found to be 250 m^2/g. The TiNP sample exhibited a

168 surface area of 40 m^2/g, much lower than the tube sample. In the TiNT sample the pore size peak at 3.4nm

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 100nm 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 cm^3/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 –23mV 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 ^{o}C respectively.

194   The experimental adsorption capacities measured in 100 ml of 10 mg/L MB solution at 25 ^{o}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^{-1}mol^{-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 nm^2 for flat lying cations to

234   0.66 nm^2 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 multilayed 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 stabalising 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 $H_2Ti_3O_7$ 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

Conclusions

Two distinct trititanate nanomorphologies were prepared by the hydrothermal treatment of TiO_2 with strong base. The two morphologies, plates and tubes, had very different structural and adsorption properties. Nanotubes with high surface area and pore volume exhibited exothermic monolayer adsorption of MB. Nanoplates with low surface area and pore volume nanoplates yielded a higher adsorption capacity through endothermic multilayer adsorption governed by pore diffusion. The stronger electrostatic interaction between the TiNP surface and the MB molecules results in multilayer adsorption, and the different modes of adsorption of the two morphologies result in the exothermic and endothermic character for TiNT and TiNP respectively.

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

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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 (^{o}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

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366

367

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

Morphology	ΔH (kJmol^{-1})	T (^{o}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

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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 *et al.* 2010
Magnetite loaded carbon nanotubes	48.06	Ai *et al.* 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 *et al.* 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

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