1 **Adsorption and photocatalytic degradation of Methylene Blue over Hydrogen-Titanate**

2 **nanofibres produced by a peroxide method**

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17

18 **Abstract**

19

20 In this study, Degussa P25 TiO_2 was partially dissolved in a mixture of hydrogen peroxide

21 and sodium hydroxide at high pH. The fabrication of nanofibres proceeded by the

22 hydrothermal treatment of the solution at 80 °C. This was followed by acid wash in HCl at

23 pH 2 for 60 min, which resulted in the formation of hydrogen-titanate nanofibres. The

24 nanofibres were annealed at 550 °C for 6 h to produce crystalline anatase nanofibres. The

25 nanofibres were characterised for physico-chemical modifications and tested for the

26 adsorption and photocatalytic degradation of methylene blue as a model water pollutant. An

27 average specific surface area of 31.54 m^2/g, average pore volume of 0.10 cm^3/g and average

28 pore size of 50 Å were recorded. The nanofibres were effective adsorbents of the model

29 pollutant and adsorbents and good photocatalysts under simulated solar light illumination. No

30 reduction in photocatalytic activity was observed over three complete treatment cycles, and

31 the effective separation of nanofibres was achieved by gravity settling resulting in low

32 residual solution turbidity.

33

1. Introduction

The use of titania nanoassemblies in the treatment of contaminated water have provided a solution to the problem encountered during the separation of nanoparticles from water. Even though "traditional" nanoparticles showed better apparent photocatalytic activity, their separation from the suspension remains the major challenge for process up-scaling. Therefore, the use of relatively large titanate nanoassemblies has become more popular because they can be easily removed from the solution.

The production of titanate nanostructures using a peroxo-titanate solution has been discussed by several authors (Mao et al., 2006; Nyman and Hobbs, 2006), and the application of Na-titanates in the adsorption and photocatalytic removal of Methylene Blue (MB) was recently reported (El Saliby et al., 2011a). Titanate nanostructures can effectively adsorb dye molecules due to their high surface area and special characteristics (Lee et al., 2007; Baiju et al., 2009; Xiong et al., 2010). The effect of synthesis temperature (Lee et al., 2008a), and sodium content (Lee et al., 2008b) on the cation exchange capacity of titanate nanotubes were reported. It was found that the increase of sodium content in the nanotubes increases the adsorption of dye through cationic exchange. Na^+ can be replaced by H^+ in the nanostructure framework by washing the Na-titanates in an HCl solution (Wei et al., 2004; Zhu et al., 2004; Mao et al., 2006; Bela et al., 2010). Belaet al. (2010) reported that the ion exchange in the titanate nanobelts was highly dependent on the duration of acid wash. The authors found that the acid wash of titanate nanobelts in a 0.1 M HCl solution for 72 h was enough to completely exchange Na^+ for H^+.

The adsorption of MB on TiO_2 nanoparticles from aqueous solution was studied by Fetterolf et al. (2003). The authors found that the Langmuir adsorption model is adequate for representing the adsorption of MB, which was attributed to electrostatic attractions. Similarly, Xiong et al. (2010) studied the adsorption of MB on titanate nanotubes and reported that the Langmuir model was appropriate for describing the monolayer adsorption mechanism.

67 In a recent study, MB adsorption on titanate nanostructures has been found to significantly

68 affect the degradation of the dye under UV light (Xiong et al., 2011). Better photocatalytic

69 decomposition was achieved in the adsorption/photocatalysis system compared to the

70 adsorption followed by photocatalysis system under UV irradiation.The adsorption of dye

71 molecules onto titanate nanostructures can be of significant importance in terms of initiating

72 the dye sensitization mechanism. This can be used in solar light treatment systems that treat

73 dye contaminated wastewater.Thus, the objectives of this study were to:

74 ➢ Synthesise H-titanates nanofibres by a peroxide method and study their morphology

75   and physico-chemical characteristics.

76 ➢ Investigate the kinetics of MB adsorption on the nanofibres and carry out

77   photocatalytic degradation of MB under simulated solar light.

78 ➢ Test the photocatalytic stability and the ease of separation of the produced

79   nanofibres.

80

81 **2. Experimental Investigations**

82 **2.1.   Synthesis**

83

84 H-titanate nanofibres were fabricated by the same method described elsewhere (El Saliby et

85 al., 2011b). In a typical synthesis, 2 g of Degussa P25 powder was dispersed in 12 mL of

86 H_2O_2 (50%) under alkaline conditions by adding 4 g of NaOH (final pH 13). Later on, the

87 mixture was placed in a Teflon cell at 80 °C for 24 h. After hydrothermal treatment, the pH

88 of the Na-titanates suspension was decreased to pH 2 by using 1 N HCl, at which ion

89 exchange (Na^+ and H^+) was carried out for 60 min under magnetic stirring. This was followed

90 by washing with Milli Q (MQ) water until a pH of 7. The as-prepared nanofibres were dried

91 in oven at 100 °C for 12 h and annealed at 550 °C for 6 h to obtain anatase nanofibres. H-

92 titanate anatase nanofibres will be named hereafter as HTNF.

93

94 **2.2.   HTNF Characterisation**

95

96 Morphology and elemental composition analyses of HTNF were carried out using the Zeiss

97 Supra 55VP SEM/EDS operating at 20 kV. X-ray diffraction (XRD) patterns were generated

98 on MDI Jade 5.0 X-ray diffractometer. Brunauer, Emmet and Teller (BET) surface area

99 analyses were performed on an automated surface area analyser (Micromeritics Gemini 2360,

100 USA) by means of nitrogen adsorption-desorption. The zeta potential of as-prepared and

3

calcined powders was determined by dispersing the nanofibres in MQ water under variable pH (adjusted by 0.1 N HCl or NaOH) and measured using the Malvern nano-series (Nano-zs, Malvern Instruments Limited, UK) analyser.

2.3.   MB Adsorption Experiments

MB powder was dissolved in MQ water to prepare a stock solution of 1 g/L concentration. All experimental MB solutions were prepared from the stock solution by dilution. The dark adsorption experiments were performed in 250 mL conical glass Erlenmeyer flasks containing 100 mL of the desired MB solution. The flasks were enwrapped in aluminium foil to prevent the illumination of slurries by ambient light. The homogeneity of suspensions was maintained by placing the flasks in an orbital shaking incubator (Thermoline, TU400) at a set temperature of 25 °C and a shaking speed of 150 rpm unless otherwise stated. Samples were collected at designated time intervals, filtered through 0.45 μm polytetrafluoroethylene (PTFE) membrane syringe filters, and analysed for colour removal by measuring absorbance at the maximum absorbance wavelength of MB ($\lambda = 664$ nm) using a Shimadzu UV-Vis 1700 spectrophotometer. The concentration of MB (mg/L) was calculated by the following equation:

$$C_t = \frac{Abs_t}{Abs_0} C_0$$

(Eq. 1)

where, C_t (mg/L) is the concentration of MB at time t, C_0 (mg/L) is the initial concentration of MB, Abs_t and Abs_0 are absorbance values for $\lambda = 664$ nm at time t and 0, respectively.

2.3.1. Effect of HTNF Loading

In this experiment, five different powder loadings (0.1, 0.2, 0.5, 1 and 2 g/L) were selected to study the adsorption of MB molecules onto HTNF. The experimental conditions were: MB concentration 10 mg/L, pH = 9 (after adding the powder no pH adjustment was done) and T = 25 °C.

2.3.2. Effect of MB Concentration

134   After optimising the HTNF loading, three MB concentrations (5, 10 and 20 mg/L) were
135   selected to study the kinetics of adsorption. The experiment was performed under the
136   following conditions: HTNF = 0.5 g/L, pH = 9 and T = 25 °C.
137
138   ### 2.3.3. Effect of pH
139
140   The pH of the solution is known to affect the surface charge of the nanofibres, and
141   consequently the adsorption of dye molecules. The experiment was conducted at the pH
142   values of 3, 5, 7 and 9 while all other factors were kept constant at HTNF = 0.5 g/L, MB = 20
143   mg/L and T = 25 °C.
144
145   ### 2.3.4.   Effect of Solution Temperature
146
147   The temperature of the solution was changed to study its effect on the adsorption process. In
148   these experiments the selected temperatures were 25, 35, and 45 °C. The experimental
149   conditions were: HTNF = 0.5 g/L, MB = 20 mg/L, and pH = 9.
150
151   ### 2.3.5.   Adsorption Equilibrium and Isotherms
152
153   The amount of dye adsorbed at equilibrium was calculated from the following equation:
154

$$q_e = (C_0 - C_e)\frac{V}{m}$$

155   (Eq. 2)
156
157   where, C_0 and C_e (mg/L) are the initial and equilibrium concentration of MB in solution, V
158   (L) is the solution volume and m (g) is the mass of the HTNF.
159
160   Sorption equilibrium data were fitted to the Langmuir, Freundlich, and Toth models using
161   both linearised and nonlinear parameter estimations. The Langmuir isotherms showed good
162   correlations, while the Toth model showed significantly low fit ($R^2 = 0.70$) for HTNF loading
163   data. The Freundlich model poorly predicted the effect of MB concentration ($R^2 = 0.48$), and
164   was inappropriate ($R^2 = 0.09$) for HTNF loading data. Therefore, in this study the Langmuir
165   isotherm model was employed for data analysis, using a simple yet sufficiently accurate
166   linearised form (Langmuir, 1918):

167

168

$$\frac{C_e}{q_e} = \frac{1}{kq_m} + \frac{1}{q_m}C_e$$

(Eq. 3)

170

171 where, C_e is the equilibrium concentration, q_e (mg/g) is the amount of adsorbate adsorbed on

172 unit mass of adsorbent, q_m (mg/g) and k (L/mg) are the Langmuir adsorption constants related

173 to adsorption capacity and rate of adsorption, respectively. The q_m and k values were

174 calculated from the slope and intercept of the straight line obtained after plotting C_e/q_e against

175 C_e, respectively.

176

177 **2.4.   Photocatalytic Degradation under Simulated Solar Light**

178

179 The photocatalytic activity of HTNF (0.5 g/L) was assessed using 200 mL volume of MB

180 solution (20 mg/L). The HTNF loading and MB concentration were selected based on the

181 results obtained in the adsorption experiments. The effect of solution pH (3, 5, 7 and 9) and

182 solar light intensity (5000, 15000 and 28000 lx; measured by a digital power meter AR 823)

183 on the removal of MB were studied. MB molecules were adsorbed on HTNF in dark after

184 mixing at 450 rpm for 30 min. The solution was then placed in the Solar Simulator (SolSim,

185 Luzchem Research, Canada) and photocatalysis was carried out for 180 min at a stable

186 temperature of 26 ºC. The Luzchem Research SolSim Xenon photoreactor featured an

187 enclosed exposure chamber, an exhaust system and thermostatic control to maintain the

188 chamber temperature close to ambient temperature. The principal light source was a Xenon

189 lamp (300 W) and a complex filter system ensured emission to closely match the AM1.5

190 spectrum. Air sparging was adjusted at 0.6 L/min to provide adequate dissolved oxygen to the

191 reaction. MB degradation was monitored by collecting samples (filtered by 0.45 μm PTFE

192 syringe filters) at fixed time intervals and analysed for colour removal at λ = 664 nm using a

193 Shimadzu UV-Vis 1700 spectrophotometer. Samples were also analysed for dissolved

194 organic carbon (DOC) removal using a Multi N/C 3100, Analytik Jena instrument. The

195 kinetics of the photocatalytic discolouration (MB removal) and mineralisation (DOC

196 removal) reactions were analysed by nonlinear data fitting (OriginPro v8 software,

197 OriginLab) to the equation:

198

199 $$C_t = C_0 \cdot e^{-k_a \cdot t}$$

(Eq. 4)

where, C_t (mg/L) is the concentration of MB or DOC at time t, C_0 (mg/L) is the initial concentration of MB or DOC, t is time, and k_a is the apparent pseudo first order constant.

2.5. Photocatalytic Stability

The photocatalytic stability of HTNF (0.5 g/L) was examined over three successive cycles using 200 mL volume of MB solution (20 mg/L). The pH of the solution was 9 and air sparging was adjusted to a rate of 0.6 L/min at a light intensity of 28000 lx. At the end of each cycle (for 8 h to ensure complete regeneration), HTNF were recovered and washed with MQ water before being used in the next degradation cycle. Samples were also analysed for changes in absorbance at 254 nm and 664 nm wavelengths, and for DOC removal.

2.6. Photocatalyst Separation by Settling

The separation of HTNF in MQ water by gravity settling was studied in 200 mL beaker by collecting samples from 5 cm below the water surface (HTNF = 0.5 g/L, pH = 9). Sample turbidity was logged over time and measured using the Hach HI 93414 turbidity and chlorine meter.

3. Results and Discussion

3.1.1. Characteristics of H-titanate Nanofibres

Figure 1 shows the zeta potential of the as-prepared and calcined HTNF. The calcination shifted the PZC towards higher pH due to the evaporation of peroxo groups (O_2^-, adsorbed H_2O_2 etc). While the properties of the as-prepared titanate will not be discussed in this study, its zeta potential characteristics are useful to elucidate the noticed shift of pH after calcination.

SEM images of HTNF revealed fibrous nanostructures of randomly dispersed nanofibres with an average diameter of 40-70 nm and few hundred nanometers in length (Figure 2). The length and width of nanofibres were averaged from twenty measurements recorded after image capture using a measuring tool provided by the Zeiss Supra 55VP SEM/EDS instrument software. It has been discussed previously (El Saliby et al., 2011a) that the Na-titanate nanofibres were arranged in microspheres of few micrometres in diameter. In contrast, the acid wash at low pH (ion exchange) affected the aggregation of nanofibres but the nanofibres conserved their typical morphology; the latter has also been observed by several researchers (Wei et al., 2004; Zhu et al., 2004; Bela et al., 2010).

Figure 1

Figure 2

The characteristic peaks in the EDS spectrum of HTNF (Figure 3) reveal the presence of only titanium and oxygen. This result indicates the effective exchange of Na^+ for H^+ prior to calcination.. The XRD analysis showed that the nanofibres were mainly anatase (data not shown). The calculated surface area of nanofibres was 31.54 m^2/g, the average pore volume 0.10 cm^3/g and average pore size 50 Å.

Figure 3

3.1.2. Effect of Operating Conditions on MB Adsorption

3.1.2.1. Effect of HTNF Loading

253 The effect of HTNF loading on the removal of MB from the solution was studied using

254 photocatalyst loadings of 0.1, 0.2, 0.5, 1 and 2 g/L. The results of experiments carried out at

255 25 °C and 10 mg/L of MB are shown in Figure 4. The adsorption of MB increased with

256 photocatalyst loading until equilibrium was reached after 30 min. An increase in HTNF

257 dosage from 0.1 to 0.5 g/L increased the adsorption of MB from 11% to a remarkably high

258 90%. The increase in the adsorption efficiency can be explained by the increase in the surface

259 area available for adsorption. However, no significant increase in adsorption was recorded

260 after increasing the loading to 1 and 2 g/L (92% and 93%, respectively). This could be

261 attributed to the attainment of adsorption equilibrium between MB and HTNF, or reaching

262 the adsorption saturation point. The photocatalyst loading of 0.5 g/L was considered optimum

263 and was adopted for the next optimisation process.

264

265 **Figure 4**

266

267 3.1.2.2. Effect of Initial MB Concentration

268

269 Figure 5 shows the adsorption of MB onto HTNF using initial MB concentrations of 5, 10

270 and 20 mg/L. It is evident that the initial MB concentration played a significant role in the

271 adsorption process, where 97%, 89% and 42% of MB were removed at MB concentrations

272 equal to 5, 10 and 20 mg/L, respectively. The HTNF removed almost all the dye at relatively

273 low initial concentration. In industrial applications, high MB removal at low concentrations is

274 considered to be of a great importance. The amount of MB adsorbed increased with time until

275 the equilibrium was attained at 30 min for high MB concentrations (10 and 20 mg/L), while

276 almost all MB molecules were adsorbed within 5 min at 5 mg/L of MB. The initial uptake

277 (first few minutes) for MB was high because a large number of adsorption sites were

278 available for adsorption. Later on, the adsorption decreased as the repulsive forces between

279 the adsorbed MB molecules (on HTNF) and the MB molecules in the solution increased

280 (Fetterolf et al., 2003; Xiong et al., 2010). In order to study the effect of other parameters in

281 the adsorption process such as pH and temperature, 20 mg/L MB concentration was selected

282 and will be discussed in the following sections.

283

284 **Figure 5**

285

286 3.1.2.3. Effect of Solution pH

287

288 The adsorption of MB was studied in a suspension of 0.5 g/L of HTNF and 20 mg/L of MB

289 using different pH values (3, 5, 7 and 9). The results of adsorption are shown in Figure 6. MB

290 is a cationic dye which is favourably adsorbed on negatively charged surfaces (Feetrolf et al.,

291 2003). The zeta potential measurements of HTNF revealed that the surface charge of the

292 nanofibres was negative over a wide pH range, and that the PZC was around pH 3.2. At pH 3,

293 the repulsive forces between the HTNF and MB molecules dominated the adsorption process,

294 leading to a low overall adsorption (7% after 30 min). In contrast, when the pH was increased

295 to 5, 7, and 9, MB adsorption increased to 28%, 32% and 42%, respectively. This was mainly

296 due to electrostatic attraction between the HTNF surface and MB molecules. This finding

297 was in agreement with previous studies on the adsorption of MB onto titania (Fetterolfet al.,

298 2003), titanate nanotubes (Xiong et al., 2010) and different organic and inorganic adsorbent

299 (Ai et al., 2011).

300

301 **Figure 6**

302

303 3.1.2.4. Effect of Solution Temperature

304

305 The effect of different solution temperatures on the adsorption is shown in Figure 7. The

306 adsorption of MB increased with temperature increase, indicating an endothermic adsorption

307 process (Bulut and Aydin, 2006; Hong et al., 2009). The total adsorption at equilibrium (30

308 min) was found to increase from 42% to 52% for an increase in the solution temperatures

309 from 25 to 45 °C.

310

311 **Figure 7**

312

313 3.1.2.5. Adsorption Equilibrium and Isotherms

314

315 Figures 8A and 8B show the amount of MB adsorbed at equilibrium (30 min) using different

316 HTNF loadings and MB concentrations, respectively. The adsorption of dye increased with

317 HTNF loading to a maximum of 17.8 mg/g at 0.5 g/L and then decreased to 9.18 and 4.64

318 mg/g at 1 and 2 g/L, respectively. The increase in the adsorption capacity (q_e) reached a

319 maximum at 0.5 g/L of HTNF loading while further increase in the mass of HTNF

320 (denominator in Eq.2) with $(C_0-C_e)*V$ (Eq. 1) remaining constant caused the decrease in q_e.

10

321   The effect of initial MB concentration revealed that the increase of MB concentration at a

322   constant HTNF loading increased the adsorption mainly because of high driving force for

323   mass transfer (Bulut and Aydin, 2006). The data plotted in Figure 8B showed some decrease

324   in q_e after increasing the concentration of MB from 10 to 20 mg/L (data collected after 30

325   min of contact). However, the experiments were continued for 3 h and no significant

326   difference in q_e at MB concentrations of 10 mg/L and 20 mg/L was found (q_e for both

327   concentrations varied from 16.5 to 17.8 mg/g).

328

329   **Figure 8**

330

331   During adsorption, the adsorption capacity is highly influenced by the pH variations of the

332   solution (Wang et al., 2005). The plot of pH variation against the adsorption capacity is

333   shown in Figure 9A. The adsorption capacity increased from 2.55 mg/g at pH 3 to 16.57

334   mg/g at pH 9 after 30 min of contact. As discussed earlier, the surface charge of HTNF

335   changed from positive to negative at pH 3 and 9, respectively. This played an important role

336   in adsorbing more cationic MB molecule at high pH.

337

338   Increasing the temperature of the solution enhanced the adsorption of MB molecules onto

339   HTNF (Figure 9B). The adsorption capacity increased from 16.57 mg/g at 25 °C to 19 mg/g

340   at 45 °C. It has been discussed earlier in this study that the process of adsorption is

341   endothermic. The heat of adsorption can describe the physical or chemical adsorption of gas

342   molecules into solid surfaces (Sircar, 2005). Nevertheless, the use of endothermic and

343   exothermic adsorption terminologies to explain adsorption in water has been widely accepted.

344

345   To further describe the equilibrium of adsorption, the most commonly used adsorption model

346   (Langmuir) has been used to fit the data obtained under different operating conditions. The

347   data was fitted using Eq. 3 and the results are shown in Table 1. Our data fitted well the

348   Langmuir model. The goodness of fit was shown with R^2 equal to 0.99, 0.91, 0.89 and 0.99

349   for experiments on HTNF loading, MB concentration, pH and temperature, respectively.

350   These findings indicated that the monolayer adsorption of MB on HTNF was the dominant

351   mechanism of adsorption. The Langmuir model has fitted well the adsorption data of MB

352   onto titanate nanotubes (Xiong et al., 2010). It has been reported that uniform nanotubular

353   structure and homogenous distribution of active sites on the walls favoured this adsorption

354   mechanism.

Figure 9

Table 1

The Langmuir isotherm was further evaluated by the dimensionless constant separation factor R_L (Hall et al., 1966; Weber and Chakravorti, 1974):

$$R_L = \frac{1}{1+kC_0}$$

(Eq. 5)

With k Langmuir constant (L/mg) and C_0 initial MB concentration (mg/L). The value of R_L indicates the shape of the adsorption isotherm and values between 0 and 1 indicate favourable adsorption (McKay et al., 1982). The calculated R_L from our data showed values between 0 and 1 suggesting that the adsorption between MB and HTNF was favourable (Table 2). Moreover, low R_L values (<0.04) indicated that the interaction between MB and HTNF was relatively strong (Xiong et al., 2010).

3.1.3. Photocatalytic Decolourisation and DOC Removal of MB

3.1.3.1. Effect of Solution pH

The variation of solution pH directly influenced the adsorption of MB molecules onto HTNF through electrostatic interactions. The adsorption was favoured at high pH between different surface charges and decreased with pH decrease. Figure 10 shows the discolouration and the DOC removal of MB solution after 30 min adsorption and 180 min of light irradiation. The discolouration of the solution was almost complete after 90 min for pH values of 5, 7 and 9. In contrast, only 89% of MB was removed after 180 min of light irradiation at pH 3. The decrease in DOC was slower being 48%, 75%, 78% and 78% for pHs of 3, 5, 7 and 9. The results of regression analysis between MB discolouration and DOC removal are presented in Table 3.

The effect of solution pH on the discolouration of MB solution was reported in the literature (Shimizu et al., 2007; Tayade et al., 2009). Shimizu et al. (2007) found that the change of pH between 3 and 10 did not influence the solution colour in the absence of the photocatalyst.

12

388   However, significant decrease in colour was reported at pH above 10. In this study, the pH

389   range was between 3 and 9, thus it can be assumed that the initial concentration of MB was

390   constant. Moreover, photodegradation data collected in different experiments were

391   normalised to the initial MB absorbance measured at pH values of 3, 5, 7 and 9. Lachheb et

392   al. (2002) studied the adsorption of several dyes, including MB, onto TiO_2 under different pH

393   values ranging from 3 to 9. In agreement with the present findings, they also reported low

394   MB adsorption at low pH but little influence of pH variations upon the kinetics of colour

395   disappearance under UV light. In another study on MB photodegradation, Wu and Chern

396   (2006) showed that increasing the pH above the PZC of TiO_2 (PZC $\approx$ 4.5 according to

397   authors' measurements) has dramatically impacted the dispersion of particles in solution,

398   leading to coagulation and sedimentation. Consequently, the decomposition of MB was

399   decreased because of the decrease in TiO_2 surface area. In this study, no coagulation of

400   HTNF was observed but the decrease of adsorption (at pH 3) retarded the discolouration.

401   This observation indicates that the decomposition of MB molecules was due to the attack by

402   the $OH^{\bullet}$ radicals near the HTNF surface under these conditions. In contrast, surface

403   degradation was the dominating degradation mechanism at high solution pH.

404

405   **Figure 10**

406

407   **Table 3**

408

409   3.1.3.2. Effect of Light Intensity

410

411   The effect of light intensity on the photodegradation of MB was studied and the results are

412   shown in Figure 11. The light intensity of the system can affect the electron/hole formation,

413   their separation and recombination rate. However, this can also be affected by the emitted

414   wavelength of the lamp and the type of photocatalyst. In the reactor used in the present

415   experiments, the decrease of light intensity from 28000 lx to 15000 lx did not significantly

416   decrease the degradation rate of MB after 180 min of light irradiation. However, a further

417   reduction in light intensity to 5000 lx resulted in 25% decrease in discolouration efficiency of

418   the system (adsorption + photodegradation). DOC removal of the system was high (78%) for

419   the maximum intensity (28000 lx), decreasing to 73% at 15000 lx and to 64% at 5000 lx.

420

13

The pseudo-first order apparent constants are shown in Table 4. These were calculated by using the decrease in MB concentration (k^1_a) and the decrease of solution DOC (k^2_a) over time. k^1_a values increased from 0.011 min^{-1} at pH 3 to 0.034 min^{-1} at pH 9. Similarly, k^1_a increased from 0.0037 min^{-1} to 0.034 min^{-1} with the increase in light intensity. The photodiscolouration of MB over HTNF followed the pseudo-first order reaction kinetics, noting that similar finding was reported by Houas et al. (2001) for photodegrading MB over Degussa P25.

Figure 11

k^2_a was calculated from the DOC concentration decrease over time (Table 4). DOC removal kinetics were slower than those observed for MB discolouration and this could be attributed to the formation of photodegradation intermediates (Herrmann, 1999; Houas et al., 2001; Lachheb et al., 2002). The apparent rate constant increased with pH and light intensity increase. The adsorption of MB onto HTNF favoured its photocatalytic removal from the solution at basic pH (Houas et al., 2001).

Table 4

3.1.4. Photocatalytic Stability of HTNF

The photocatalytic stability of HTNF was also tested by adopting the experimental model of Xiong et al. (2011). The experiments consisted of running photocatalytic degradation reactions without the dark adsorption of MB onto HTNF. A 200 mL beaker containing 0.1 g of HTNF suspended in 20 mg/L MB solution was placed in the solar simulator at 28000 lx and at a temperature of 26 °C.

Figures 12 and 13 show the normalised photocatalytic degradation data obtained from the absorbances at $\lambda = 254$ nm and 664 nm. The MB solution changed to colourless after 2 h of photoreaction, then turned to humic-like water colour between 2 h to 6 h before becoming colourless at the end (after almost 8 h). These findings suggest that the photocatalytic degradation of MB in this system has occurred in three stages:

14

- Stage 1: Concurrent adsorption of MB and photocatalytic degradation to positively charged intermediates (surface reaction) (Houas et al., 2001; Orendorz et al., 2008).

- Stage 2: Desorption of intermediate compounds, (mainly negatively charged phenolic or aromatic organics) from HTNF surface (Houas et al., 2001).

- Stage 3: Degradation of aromatic intermediates by OH$^{\bullet}$ attacks.

The experiments were repeated using the recycled photocatalyst over three degradation cycles, with no significant changes in photocatalytic activity (Figure 14).

Figure 12

Figure 13

Figure 14

3.1.5. Settling Characteristic of HTNF

The high cost associated with the separation of titania at commercial scale has seriously retarded the use of industrial photocatalysis. At the end of photocatalysis, the facile recovery of the photocatalyst is very important for its reuse. A low cost catalyst separation process can be achieved by settling of particles. Accordingly, the settling characteristics of HTNF were also evaluated by comparing the sedimentation of HTNF to Degussa P25 in aqueous suspensions (Figure 15). The catalyst concentration was 0.5 g/L at a pH of 9. Rapid HTNF sedimentation was recorded by measuring the turbidity of decanted solution at fixed time intervals. About 80% turbidity removal was achieved after 30 min of settling that increased up to 90% after 2 h settling time. In contrast, the turbidity of P25 suspension did not change significantly. In a similar study, Xiong et al. (2011) reported 72% decrease in turbidity within 180 min settling time for titanate nanotubes (0.5 g/L titanate loading in a 300 mL square photoreactor). The rapid sedimentation of HTNF is another advantage for their industrial application in wastewater photocatalysis.

Figure 15

4. Conclusions

H-titanate nanofibres were synthesised by an aqueous peroxide route at high pH. The HTNF were characterised for changes in morphology by observing SEM images which revealed randomly dispersed nanofibres with an average diameter of 40-70 nm and few hundred nanometers in length. The nanofibres were negatively charged over a wide pH range and their PZC was found at pH 3.2. H^+ successfully replaced Na^+ in the nanofibres by ion exchange as confirmed by EDS measurements. The HTNF were mainly anatase with a surface area of 31.54 m^2/g, average pore volume of 0.10 cm^3/g and average pore size of 50 Å.

The adsorption of MB onto HTNF was examined by investigating the effect of HTNF loading, MB concentration, solution pH, and temperature on the adsorption capacity. The results showed that the adsorption of MB was promoted by high catalyst loadings, high pH (greater than the PZC) and temperature. The adsorption capacity increased from 2.55 mg/g at pH 3 to 16.57 mg/g at pH 9 after 30 min of contact, and from 16.57 mg/g at 25 °C to 19 mg/g at 45 °C. The adsorption data fitted well the Langmuir model for all operational conditions. The optimum operational conditions for the adsorption of MB onto HTNF were found at 0.5 g/L of photocatalyst, 10 mg/L MB, pH 9 and temperature of 45 °C.

The photocatalytic degradation of MB was studied under simulated solar light to study the effect of pH and light intensity. No significant differences were found for the discolouration of MB at pHs greater than the PZC. However, at pH 3, the decrease in MB adsorption significantly reduced its consecutive photocatalytic degradation. The increase in light intensity from 5000 lx to 28000 lx was found to increase 10 folds the discolouration of MB, according to the apparent degradation constant (k^1_a) obtained from the L-H model. In contrast, the DOC removal at the highest light intensity was only twice as good as the DOC removal found at the lowest light intensity (k^2_a).

The photocatalytic activity of the nanofibres was found stable after 3 degradation cycles using the adsorption/photocatalysis model. Moreover, the fibres were easily separated from the solution by settling at room temperature.

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648   **Figure 1**

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Figure 2

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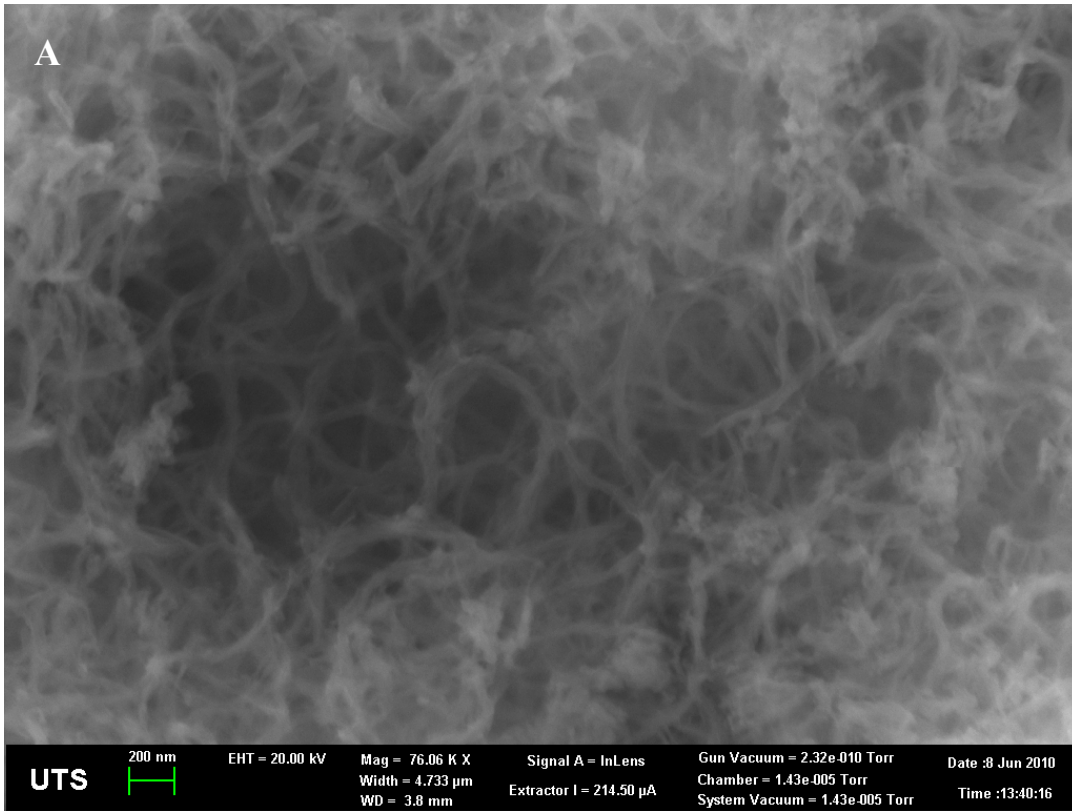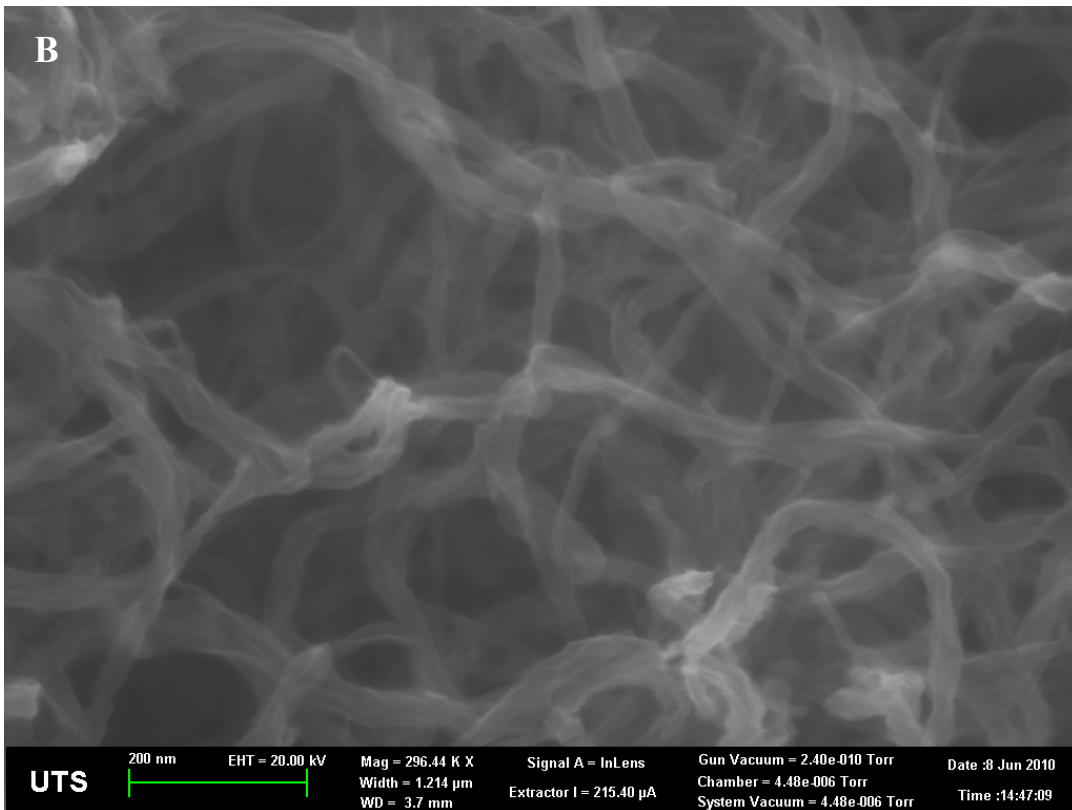
Figure 3

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HTNF
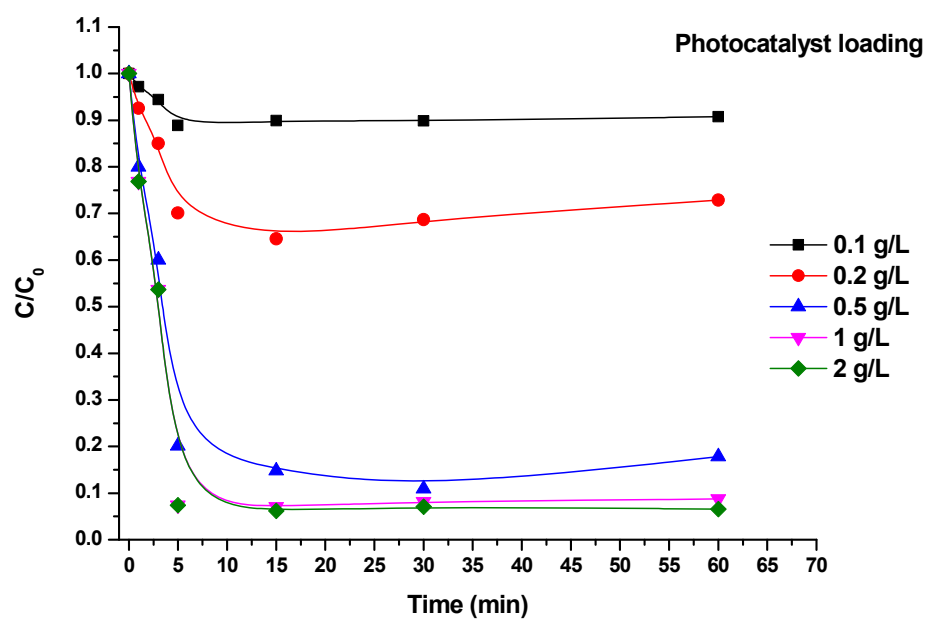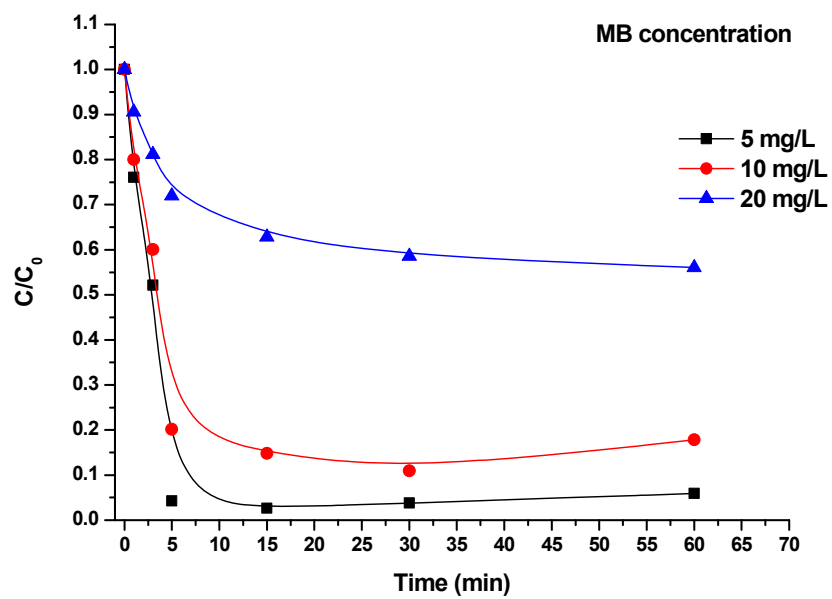
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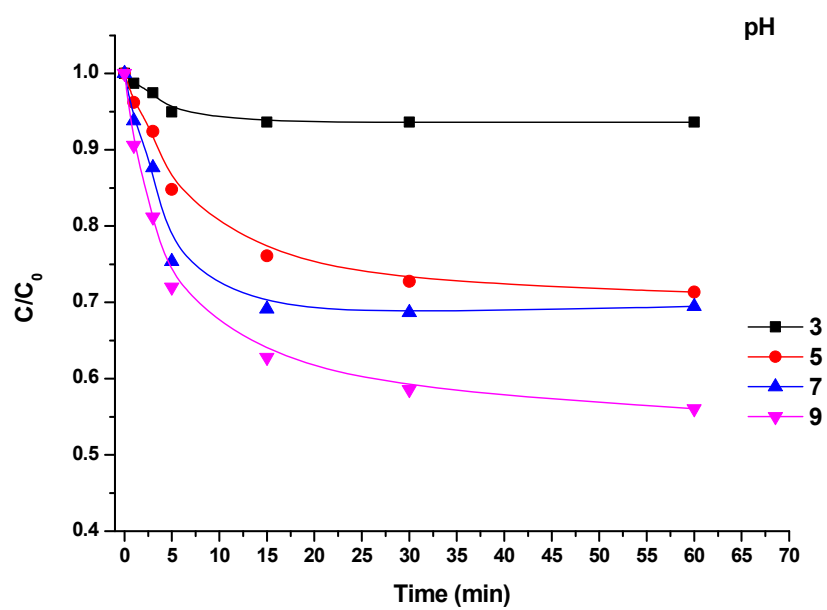
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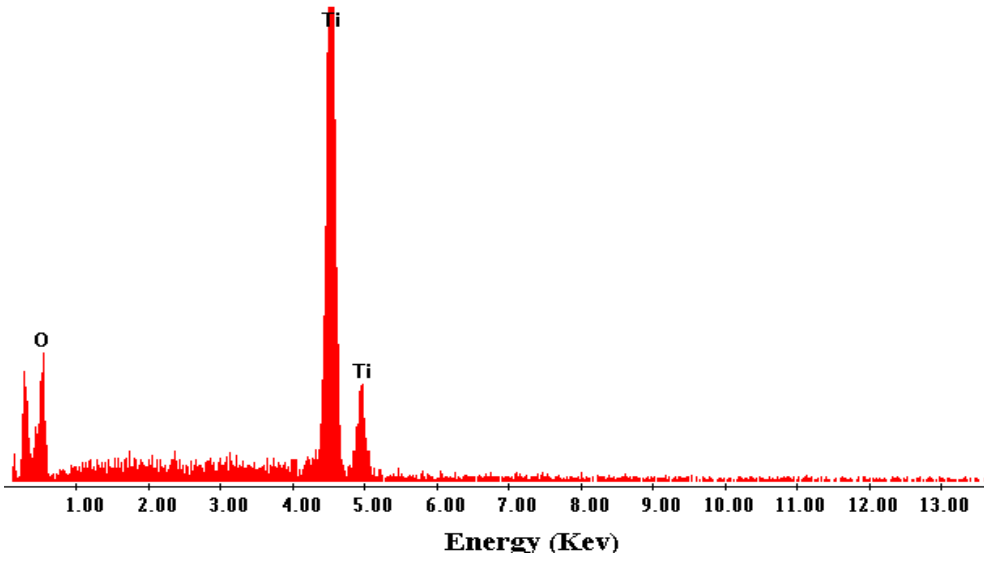
Figure 4

674   **Figure 5**
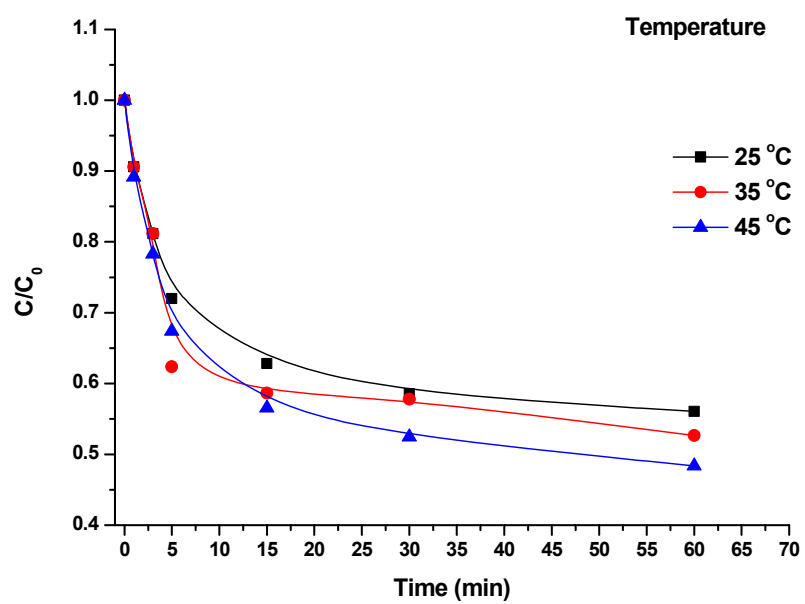
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678   **Figure 6**
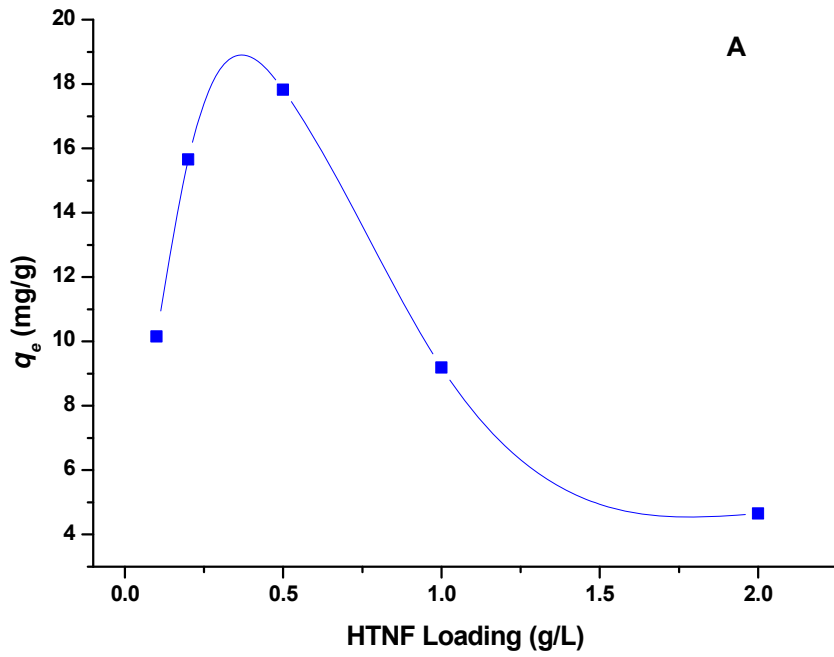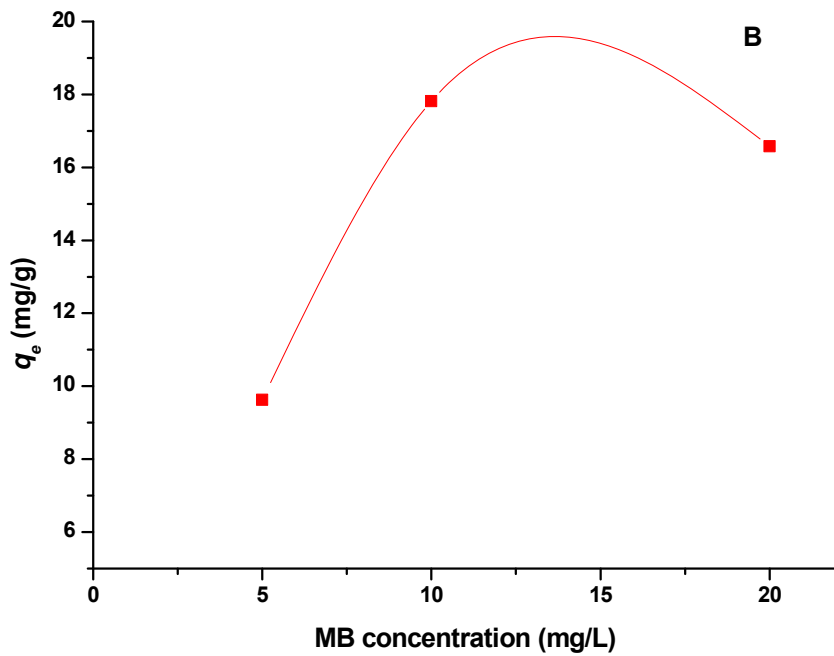
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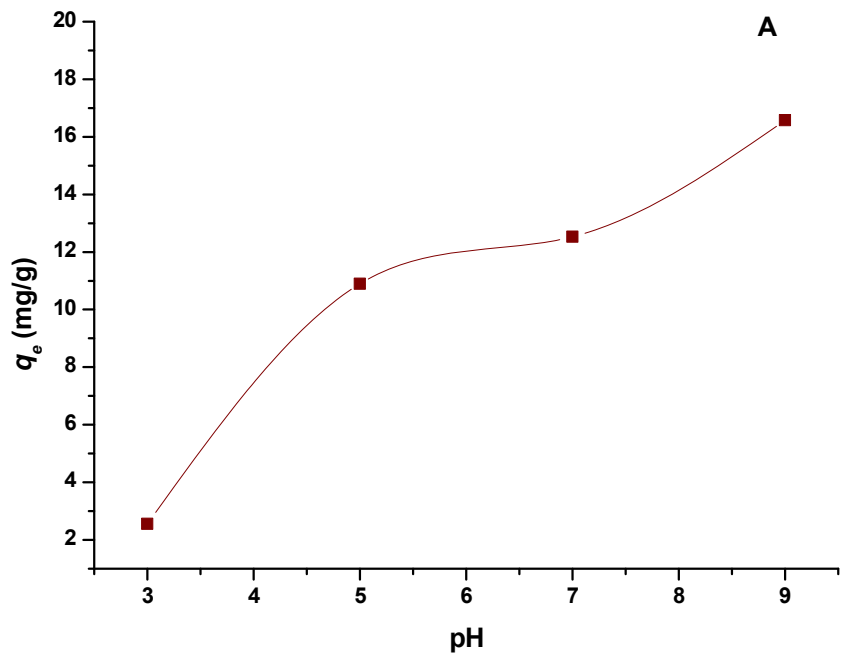682   **Figure 7**

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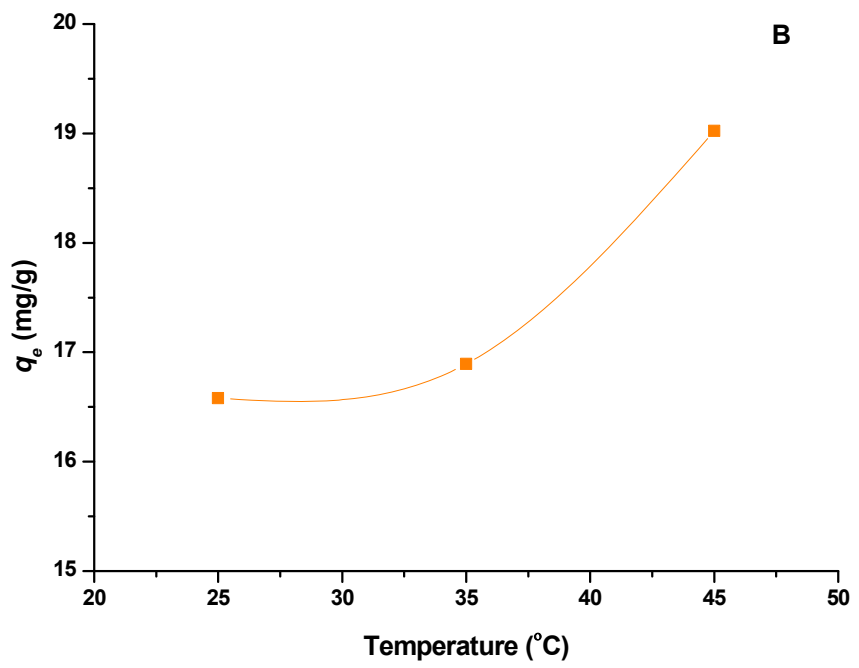684
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686   **Figure 8**

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692   **Figure 9**
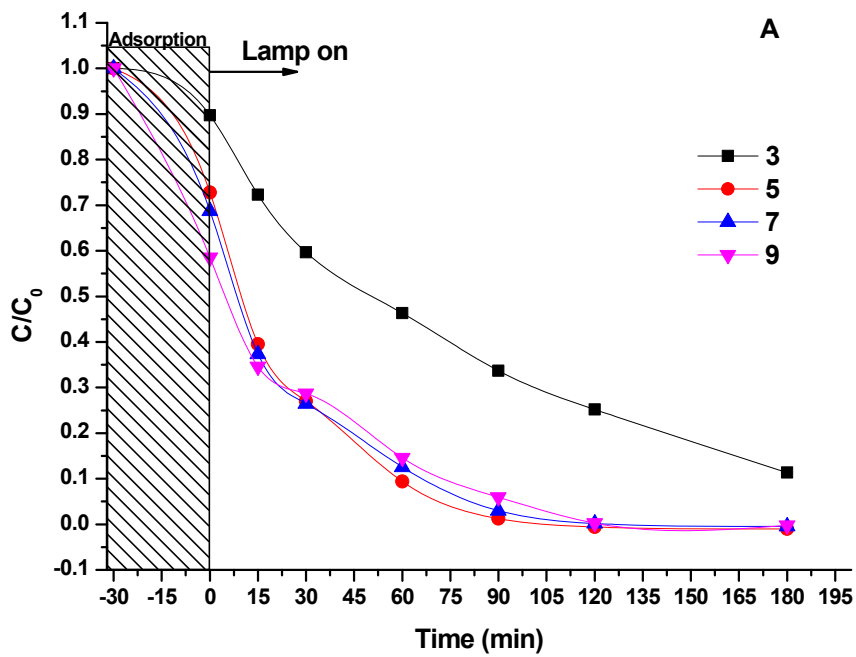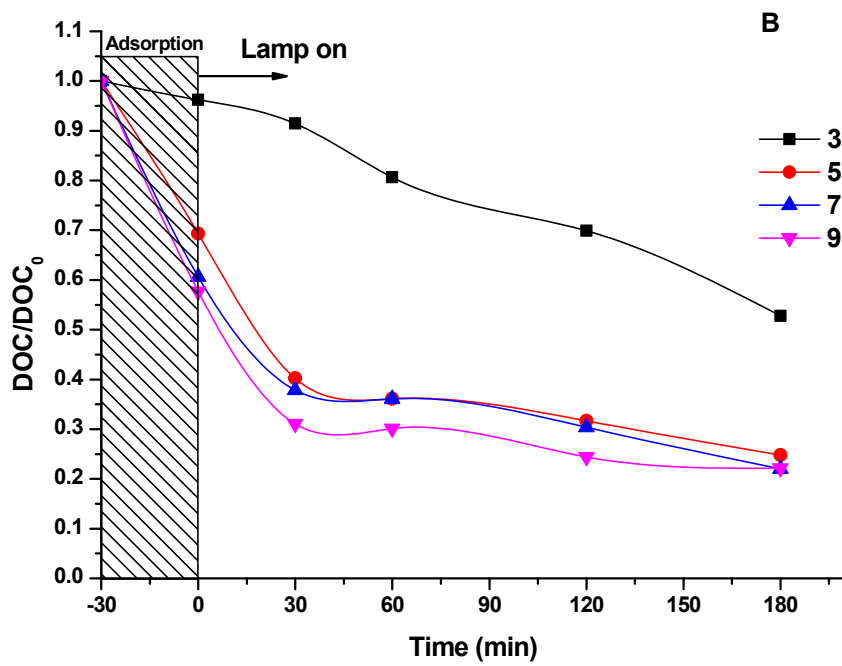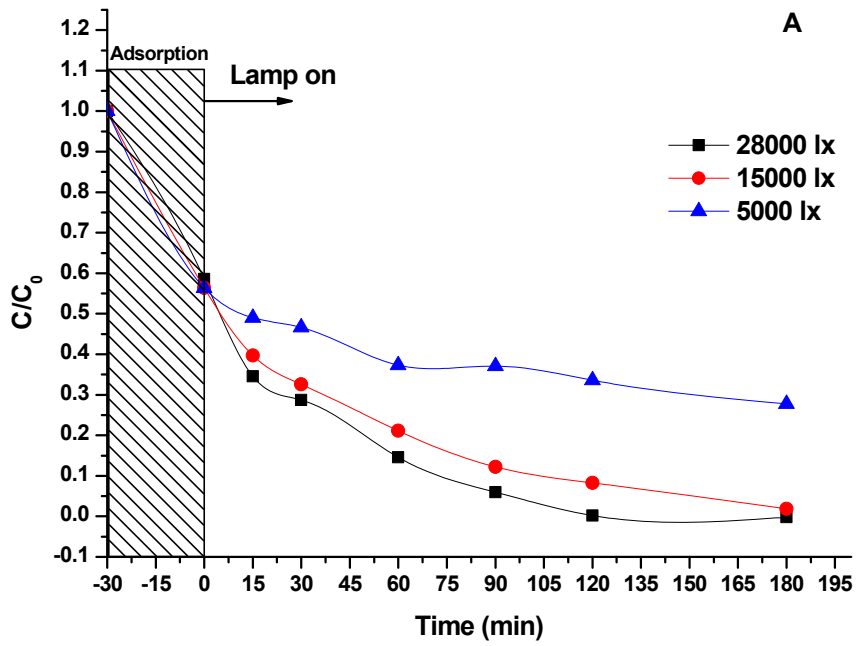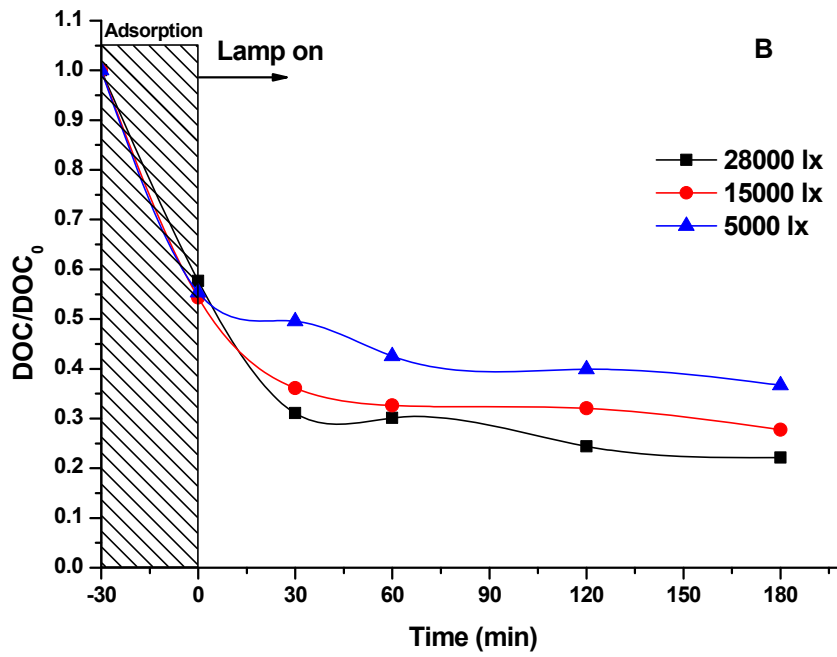
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Figure 10

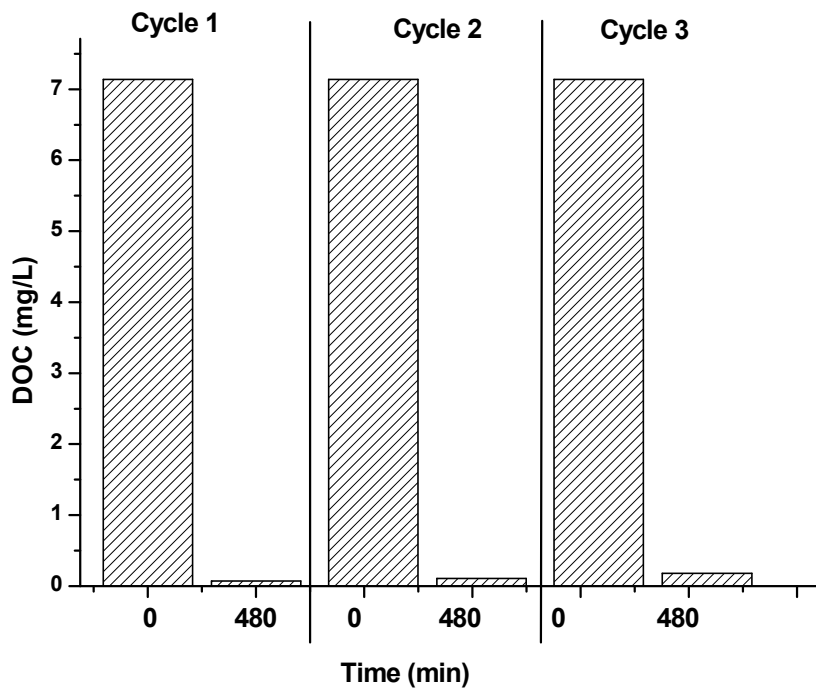703 **Figure 11**

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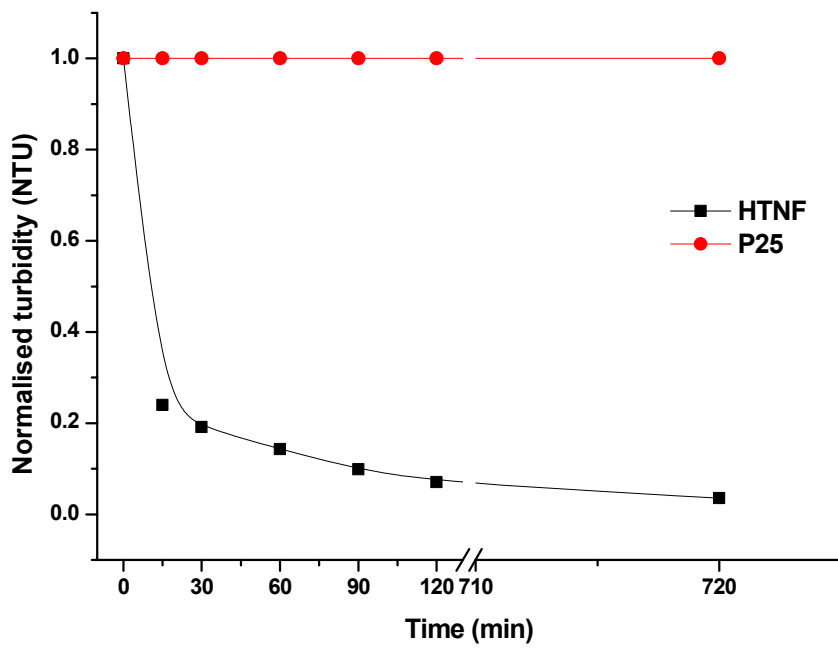705

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708   **Figure 12**

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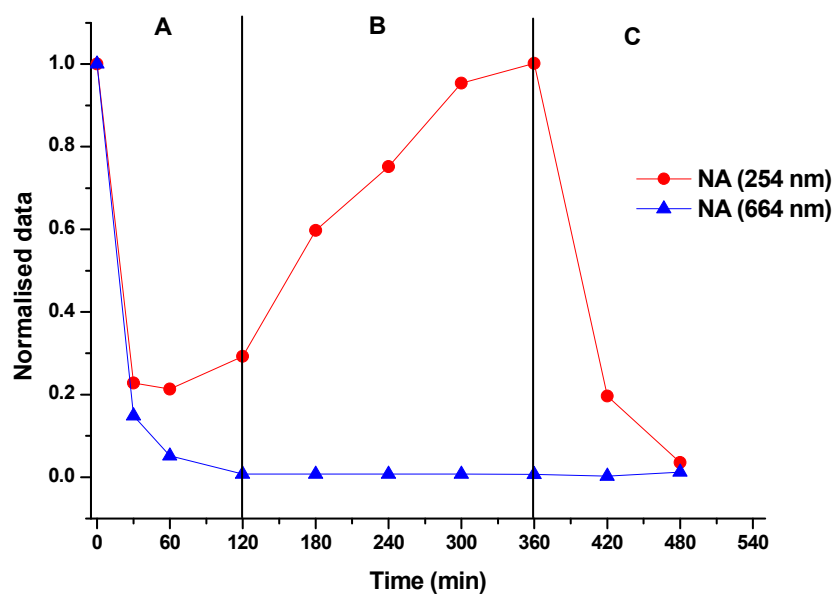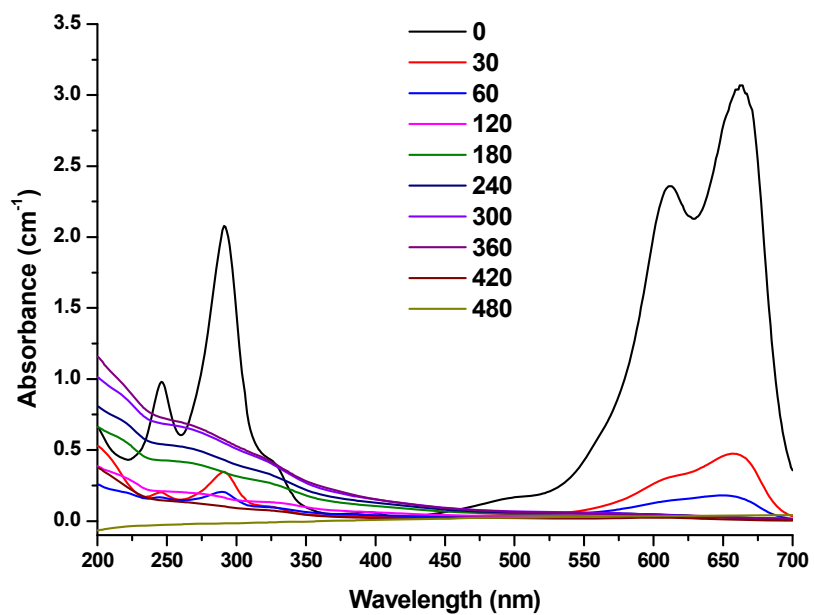
Figure 13

715 **Figure 14**

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718   **Figure 15**

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756 **Table 1**

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Parameters	Operational conditions			
	HTNF Loading	**MB concentration**	**pH**	**Temperature**
q_m(mg/g)	12	16.7	1.1	8.84
k (L/mg)	5.5	30	0.08	0.17
R^2	**0.91**	**0.99**	**0.89**	**0.99**

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760 **Table 2**

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Operational conditions	HTNF loading (g/L)	MB concentration (mg/L)			pH	Temp (°C)
		5	**10**	**20**		
R_L	0.018	0.00002	0.028	0.001	0.37	0.22

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764 **Table 3**

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Parameter	Solution pH			
	3	**7**	**5**	**9**
Linear Regression equation	$y^§ = 0.489x^* + 0.547$	$y^§ = 0.668x^* + 0.272$	$y^§ = 0.677x^* + 0.244$	$y^§ = 0.753x^* + 0.188$
R^2	0.906	0.966	0.942	0.958

766 §y represents normalised DOC

767 *x represents normalised absorbance

768

769 **Table 4**

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Parameter	Operational conditions						
	pH				Light Intensity		
	3	**5**	**7**	**9**	**28000**	**15000**	**5000**
k^1_a(min^{-1})[§]	0.011	0.025	0.037	0.034	same as pH 9	0.018	0.0037
R^2	0.994	0.828	0.915	0.893	same as pH 9	0.986	0.9440
k^2_a(min^{-1})*	0.003	0.004	0.004	0.004	same as pH 9	0.003	0.002
R^2	0.979	0.820	0.888	0.735	same as pH 9	0.708	0.906

771 [§]Constants were calculated from the MB concentration degradation curves.

772 *Constants were calculated from the DOC degradation curves to include the degradation of

773 intermediate compounds.

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