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Kinetic study of adsorption and photo-decolorization of Reactive Red 198 on TiO₂
surface

3 S. Dutta^{1*}, S. A.Parsons², C. Bhattacharjee¹, P. Jarvis², S. Datta¹, S. Bandyopadhyay³

4 ¹Chemical Engineering Department, Jadavpur University, Kolkata – 700032, India

5 ²Centre for Water Science, Cranfield University, Cranfield, Bedfordshire MK43 0AL, UK

6 ³ *Central Glass and Ceramic Research Institute, Kolkata – 700032, India*

8 Abstract

Recycling and reuse of wastewater after purification will reduce the environmental pollution as well as fulfill the increasing demand of water. Adsorption-based water treatment process is very popular for dye-house wastewater treatment. The present study deals with treatment of wastewater contaminated by reactive dye. TiO_2 is used as adsorbent and the spent adsorbent has been regenerated by Advanced Oxidation Process (AOP), without using any other chemicals. TiO_2 adsorbs dye molecules and then those dye molecules have been oxidized via a photocatalytic reaction in presence of UV irradiation. Kinetics of dye adsorption and photocatalytic oxidation reaction has been developed in this study. Photocatalyst adsorbent (TiO_2) has been reused several times after regeneration. The activity of catalyst decreases after each cycle; due to poisoning cause by intermediate by-products. Kinetic of this catalyst deactivation has been incorporated with L-H model to develop the photocatalytic reaction kinetic model.

21

22 **Keywords:** Adsorption, Advanced Oxidation Process, Catalyst regeneration, Reactive
23 Red 198, TiO₂-Photocatalysis, Catalyst activity

*Corresponding author Tel.: +91 9433678055; Fax: +91 33 2414 6203

E-mail: ss.dutta@hotmail.com (Suman Dutta)

1. Introduction

Demand of water is increasing day by day, accordingly recycling and reuse of water from various sources are being given due priority in recent times. Wastewater from industries, domestic wastewater, and municipal wastewater can be recycled after proper purification. Recycling of textile effluent is very essential because, dyeing 1 kg of cotton with reactive dyes requires an average of 70 – 150 litre water [1]. Various research works have been carried out on dye-house wastewater purification by Advanced Oxidation Process employing TiO_2 catalyst under UV irradiation. The advantages of UV/ TiO_2 process are manifold; it produces less residual pollutants compared to other conventional processes and reduces the disposal cost, consequently water treatment cost [2]. Some authors investigated decolorization of textile effluent using ozone, which was found to be highly effective [3] AOP (UV/ TiO_2) produces hydroxyl radical, which is able to oxidize a range of organic compounds significantly faster than ozone [4].

Decolorization of wastewater contaminated with RR198 was studied by Robert et. al [5] in which TiO_2 powder was used in colloidal form. Result of this investigation showed that use of TiO_2 powder in colloidal form was much more effective than the immobilized system because of higher available surface area. Various authors have investigated adsorption of reactive dyes on different adsorbent like activated carbon [6], fly ash [7], and chitosan/oil palm ash composite beads [8] etc. Different synthesized and commercial acyclic ester resins were also used for dye adsorption efficiently [9]. All these studies confirm that the dye removal is possible by adsorption.

Beside these, other processes like electrochemical process [10], coagulation/flocculation process [11], and microbial decolorization [12] were studied by researchers. But the disposal of these spent adsorbents and final waste cause additional environmental pollution. Hence, regeneration of spent adsorbent is the way to solve this disposal problem. Activated carbon adsorbent can be regenerated using some chemicals (NaOH and HCl) [13].

With reference to the previous investigations, we have emphasized the regeneration of TiO_2 catalyst without using any chemicals. Only UV irradiation has been employed to decompose adsorbed dye molecules by photocatalytic oxidation reaction. We also studied the possibility of recycling and reuse of TiO_2 catalyst after regeneration. TiO_2 catalyst has been reused in five successive cycles and the result shows that TiO_2 catalyst can be recycled after regeneration. A kinetic model equation of photocatalytic reaction has been developed considering deactivation of catalyst due to effect of intermediate product and some inorganic ions [14] on the catalyst surface. Kinetic of catalyst deactivation also has been studied in this present work.

2. Materials and methods

Chemicals used for this study are, Reactive Red 198 (MW: 923 g.mol^{-1}), which is a diazo dye (Fig.1). This dye was supplied from a dye-house near Kolkata, West Bengal, India. TiO_2 powder Hombikat UV – 100 was used as catalyst. This catalyst was supplied by Sachtleben Chemie GmbH. The catalyst contains 99 % of anatase with a specific surface area (BET) $>250 \text{ m}^2.\text{g}^{-1}$ and primary crystal size $< 10 \text{ nm}$ dia. Water used for all these experiments is deionized water.

2.1 Experimental setup

A Jar Tester manufactured by Phipps and Bird, Virginia, USA was used for experimental purpose. The Jar Tester comprising six jars with six stirrers (uniform speed). The volume of each jar is 1 litre. A UV illuminating bulb was placed on the top of these jars. Stirrers of this Jar Tester consist of 2 flat bladed rectangular paddles with an area $1.9 \times 10^{-3} \text{ m}^2$. A uniform speed of 150 rpm has been maintained by using a control panel with digital display. The schematic diagram of the jar tester has been shown in Fig.

2.

2.2 Experimental procedure

Firstly adsorption of dye was studied to ensure the decolorization by photocatalytic reaction on TiO_2 surface, because the substances that are adsorbed strongly degrade faster [15]. A series of experiment were conducted to find the optimum pH and TiO_2 dose for adsorption. Dark adsorption test of dye on TiO_2 surface was carried out in the Jar Tester. All of these experiments were conducted in presence of infrared light to prevent any decolorization of dyes by photocatalytic reaction. This test was performed with six different TiO_2 doses in between 1 g.L^{-1} and 5 g.L^{-1} . This test was conducted at three different pH (pH: 3, 5.5, and 7) with an initial dye concentration 350 mg.L^{-1} . The pH of the test solution (mixture of dye solution and TiO_2 adsorbent) was controlled using 10 M HCl and 10 M NaOH solution. After starting the experimental run, samples were collected from the Jar Tester with time to time. Then the collected samples were filtered using $0.45 \text{ }\mu\text{m}$ polyethersulfone microfiltration membranes (Pall, Gelman Laboratory, Michigan) to separate the TiO_2 particles. After filtration, the concentration of dye was

1 measured using a spectrophotometer (Jenway 6505 UV/Vis spectrophotometer;
2 Dunmow, Essex, UK) at a wavelength $\lambda_{\max}$ =516 nm.

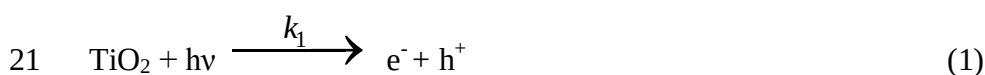
3 After completing adsorption test, decolorization test of dyes was carried out in
4 presence of UV ray illumination. A UV light illuminating bulb (100 watt) was used for
5 this purpose. Samples were collected and filtered as earlier and concentrations of dyes
6 were measured using an UV- Vis spectrophotometer. The dye decolorization test was
7 also conducted without TiO₂ and only in presence of UV irradiation to verify if it is
8 catalytic reaction. Viability of TiO₂ recycling was tested after both adsorption and
9 decolorization test. A five cycles experiment was performed with TiO₂ catalyst and
10 RR198; the initial concentration of dye and catalyst was 350 m g.L⁻¹ and 5 g.L⁻¹
11 respectively. TiO₂ was filtered by 0.45 μ m microfiltration membrane after each cycle and
12 reused to the next cycle.

13

14 **3. Kinetics of photo-decolorization of RR198 on TiO₂ surface**

15 In presence of UV illumination and TiO₂ in aqueous solution, the azo bond (-
16 N=N-) of RR198 breaks down and produces some colorless intermediate product. Those
17 colorless intermediates goes further oxidation to produce non-toxic final product.

18 We consider the following reactions take place during photo-decolorization of reactive
19 dye. In presence of UV irradiation TiO₂ in aqueous solution produces electrons (e⁻) and
20 holes (h⁺) as:



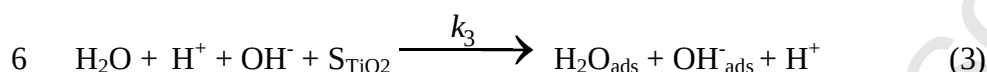
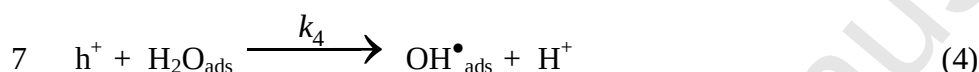
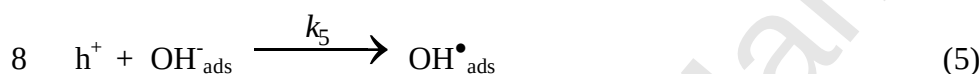
22 Where h is Plank's constant and v is frequency of UV irradiation.

23 Again some electrons and holes combine and produce heat



2 The intensity of UV irradiation was same through out the study, so the kinetic of Eq. (1)
3 and Eq. (2) depends only on the concentration of catalyst.

4 In aqueous medium, at low pH (below pH_{pzc}) positively charged active sites of TiO_2
5 surface adsorb water molecules and negatively charged hydroxyl ions

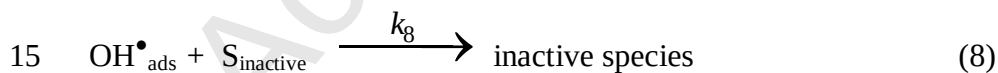


9 As the RR198 molecules contain negatively charged sulfonate groups (as shown by
10 dotted circle in Fig. 1), it will be adsorbed on positively charged TiO_2 surface.



13 Eq (7) represents the reactions for breaking the azo bonds by photocatalytic reaction.

14 Inactive sites on TiO_2 surface interfere to the process by adsorbing hydroxyl radicals



16

17 Kinetic model equations of this photocatalytic reaction have been developed
18 based on the above mentioned reactions.

19 The concentration of photon-induced holes (h^{+}) can be obtained at steady state

$$\frac{d[h^+]}{dt} = k_1 I [TiO_2]^n - k_2 [h^+][e^-] - k_4 [h^+][H_2O]_{ads} - k_5 [h^+][OH^-]_{ads} = 0 \quad (9)$$

$$\frac{d[h^+]}{dt} = k_1 I [TiO_2]^n - k_2 [h^+][e^-] - k_9 [h^+] = 0 \quad (10)$$

$$k_9 = k_4 [H_2O]_{ads} + k_5 [OH^-]_{ads} \quad (11)$$

When h^+ trapping competes effectively with electron-hole recombination [16]

$$k_9 [h^+] \gg k_2 [h^+][e^-] \quad (12)$$

Combining Eq. (10) and Eq. (12)

$$[h^+] = \frac{k_1 I [TiO_2]^n}{k_9} \quad (13)$$

The rate of change of hydroxyl radical ($OH^\bullet_{ads}$) is according to the equation:

$$\frac{d[OH^\bullet]_{ads}}{dt} = k_4 [h^+][H_2O]_{ads} + k_5 [h^+][OH^-]_{ads} - k_7 [OH^\bullet]_{ads} [Dye]_{ads} - k_8 [OH^\bullet]_{ads} [S]_{inactive} = 0 \quad (14)$$

Considering deactivation of $OH^\bullet$ with inactive surface is higher than other process [17]

$$[OH^\bullet]_{ads} = \frac{k_9}{k_8 [S]_{inactive}} [h^+] \quad (15)$$

The rate of decolorization reaction according to the Eq. (7) is

$$r_{decol} = k_7 [OH^\bullet]_{ads} [Dye]_{ads} \quad (16)$$

Combining Eqs. (13), (15) and (16) we obtain

$$r_{decol} = \frac{k_7 k_1 I}{k_8 [S]_{inactive}} [TiO_2]^n [Dye]_{ads} \quad (17)$$

In presence of constant light intensity Eq. (17) becomes

$$r_{decol} = k [TiO_2]^n [Dye]_{ads} \quad (18)$$

1 Now we consider the deactivation of catalyst

$$2 \quad r_{decol} = ka[TiO_2]^n [Dye]_{ads} \quad (19)$$

3 Eq. (18) is similar to an empirical relation given by Galindo et al. [18] and at constant
4 TiO_2 concentration

$$5 \quad r_{decol} = k'a[Dye]_{ads} \quad (20)$$

6 It is observed from the isotherm data that the Langmuir isotherm fits better than the
7 Freundlich one, and hence we get

$$8 \quad r_{decol} = a \frac{k'K_L [Dye]}{1 + b[Dye]} \quad (21)$$

9 Eq. (21) represents the Langmuir – Hinshelwood (L-H) model equation combined with
10 catalyst activity (a). When dye concentration reaches almost zero ($[Dye] \rightarrow 0$) then we
11 assume $1 \gg b[Dye]$ and Eq. (21) becomes

$$12 \quad r_{decol} = -\frac{d[Dye]}{dt} = ak'K_L [Dye] \quad (22)$$

13 Integrating Eq. (22) with respect to time (t) we get

$$14 \quad \ln \frac{[Dye]}{[Dye]_0} = -ak'K_L t \quad (23)$$

15 Eq. (23) is a modified form of L-H model equation, which describes kinetic of dye
16 decolorization by photocatalytic oxidation reaction.

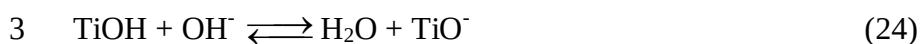
17

18 **4. Results and Discussions**

19 *4.1 Dark Adsorption of RR198 on TiO_2 surface*

20 Results of this study show that adsorption capacity of RR198 on TiO_2 catalyst
21 surface is very high at acidic condition. The point of zero charge of TiO_2 (pH_{pzc}) is close

1 to pH 6.8. At pH higher than 6.8 TiO_2 surface becomes negatively charged according to
 2 the electrochemical equilibrium:



4 And at pH lower than 6.8 TiO_2 surface becomes positively charged



6 RR198 (Fig.1) contains negatively charged sulfonate groups thus at acidic condition
 7 interaction between positively charged catalyst surface and negatively charged dyes favor
 8 the adsorption. At any pH (pH 7) higher than pH_{pzc} , the adsorption capacity is relatively
 9 low whereas adsorption capacity is high at pH (pH 3 and 5.5) lower than pH_{pzc} ; as shown
 10 in Fig. 3.

11 Fig. 4 shows adsorption quantity vs time plot. This figure shows that most of
 12 adsorption takes place within 20 minutes from the starting and equilibrium reaches after 1
 13 hr.

14 Fig. 5 represents the Langmuir and Freundlich adsorption isotherms; values of
 15 constants are given in Table 1. It is clear from Table 1 that Langmuir isotherm fits
 16 experimental data better than the Freundlich isotherm. The value of dimensionless
 17 separation factor (R_L) indicates that the Langmuir isotherm is of favorable type.

18 According to Freundlich Isotherm model equation

$$19 \quad Q = k_F C_e^{\frac{1}{n_F}} \quad (26)$$

20 The linear form of Freundlich Isotherm is

$$21 \quad \ln Q = \ln k_F + \frac{1}{n_F} \ln C_e \quad (27)$$

1 According to Langmuir isotherm

$$2 \quad \frac{1}{Q_{eq}} = \frac{1}{k_L Q_m} \frac{1}{C_{eq}} + \frac{1}{Q_m} \quad (28)$$

3 And dimensionless separation factor

$$4 \quad R_L = \frac{1}{1 + k_L C_0} \quad (29)$$

5 As the value of R_L is much lower than 1, adsorption is favorable type

6

7 4.2 Photo-decolorization of RR198 on TiO_2 catalyst

8 Eq. (20) shows that rate of photo-decolorization depends on the adsorbed quantity
9 of dye on catalyst surface ($[Dye]_{ads}$). Eq. (21) has been developed considering Langmuir
10 adsorption isotherm. Experimental data of photo-decolorization reaction have been fitted
11 to the Eq. (23) as shown in Fig. 6. Initially the activity of catalyst is 1, as we use fresh
12 catalyst. Fitting the experimental data for pH 3 ($R^2 = 0.991$) the Eq. (23) becomes

$$13 \quad \ln \frac{[Dye]}{[Dye]_0} = -0.35t \quad (30)$$

14 Eq. (30) confirms that decolorization reaction follows L-H model at lower pH. The value
15 of $k'K_L$ from the above equation is 0.35 min^{-1} or 20.98 hr^{-1} . The value of the constant K_L
16 ($= k_L Q_m$) is 106.304 L.g^{-1} so the calculated value of k' is $0.197 \text{ g.L}^{-1}\text{hr}^{-1}$

17

18 4.3 Recycling of TiO_2 catalyst

19 Fig. 7 describes the dye concentration ratio vs. time (hr) plot during catalyst
20 recycling experiment. The subsequent cycles are taking longer time than the preceding
21 one, because the activity of catalyst decreases due to poisoning. RR198 contains sulfonate

1 group so there must be inorganic sulfate ion in final solution; this sulfate ions even at low
 2 concentration reduce the oxidation rate [14].

3

4 *4.4 Calculation of catalyst activity for successive cycles*

5 Experimental results show that recycling of catalyst is possible after regeneration.
 6 Incomplete oxidation of dye causes catalyst poisoning due to presence of intermediate
 7 product. The calculated value of initial rate of reaction (r_{0i}) and catalyst activity (a) for
 8 each cycle have given in Table 2.

9 We consider 1st order decay of catalyst activity, and we have the equation

$$10 \quad a = a_0 e^{-k_{cd} t} \quad (31)$$

11 Where k_{cd} is catalyst deactivation co-efficient. Fitting the value of catalyst activity
 12 against starting time of each cycle ($R^2 = 0.975$) from Table 2 we get

$$13 \quad a = 1.02 e^{-0.1034 t} \quad (32)$$

14 The activity of catalyst at any time can be calculated from Eq. (32). The value of catalyst
 15 deactivation co-efficient (k_{cd}) is 0.1034 hr^{-1}

5. Conclusion

The present study shows that TiO₂ adsorbs RR198 effectively at acidic condition (pH 3) and adsorption follows Langmuir isotherm ($R^2 = 0.99$) better than Freundlich isotherm ($R^2 = 0.96$). Regeneration of spent adsorbent is possible by oxidizing the dye molecules via a photo-decolorization reaction using UV illumination. Photo-decolorization reaction follows the L-H kinetics ($R^2 = 0.99$). This study shows that recycling of catalyst is also possible after regeneration. The activity of catalyst decreases due to poisoning and deactivation which follows first order kinetics.

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Nomenclature

a	Activity of catalyst (-)
a_0	Initial activity of catalyst (-)
b	Langmuir isotherm constant (L.mg ⁻¹)
$C_0, [Dye]_0$	Initial concentration of dye (mg.L ⁻¹)
$[Dye]_{ads}$	Concentration of adsorbed dye molecule on TiO ₂ surface (mg.g ⁻¹)
H_2O_{ads}	Adsorbed water molecule on TiO ₂ surface (-)

1	I	Intensity of light (candela, cd)
2	$k = \frac{k_7 k_1 I}{k_8 [S]_{inactive}}$	Overall reaction rate constant with fixed light intensity ($L^{n-1} \cdot hr^{-1} \cdot g^{n-1}$)
3	$k_1 - k_9$	Reaction rate constants (-)
4	k_{cd}	Rate constant of catalyst deactivation reaction (hr^{-1})
5	k_F	Freundlich isotherm constant ($mg \cdot g^{-1}$)
6	K_L	Langmuir isotherm constant ($= k_L Q_m$ as in Eq.(28)) ($L \cdot g^{-1}$)
7	k_L	Langmuir isotherm constant ($L \cdot mg^{-1}$)
8	$k' = k [TiO_2]^n$	Reaction rate constant with fixed TiO_2 concentration ($g \cdot L^{-1} \cdot hr^{-1}$)
9	n	Constant (-)
10	n_F	Freundlich isotherm constant (-)
11	$OH^{\bullet}_{ads}$	Adsorbed hydroxyl radical on TiO_2 surface (-)
12	OH^-_{ads}	Adsorbed hydroxyl ion on TiO_2 surface (-)
13	Q_m	Maximum dye adsorption for monolayer formation ($mg \cdot g^{-1}$)
14	r_{decol}	Rate of dye decolorization reaction ($Mol \cdot hr^{-1} \cdot g \text{ cat}^{-1}$)
15	r_{0i}	Initial rate of decolorization reaction for i^{th} cycle ($Mol \cdot hr^{-1} \cdot g \text{ cat}^{-1}$)
16	R_L	Dimensionless separation factor (-)
17	$S_{inactive}$	Inactive adsorption sites on TiO_2 surface (-)
18	S_{TiO_2}	Active adsorption sites on TiO_2 surface (-)
19	$[TiO_2]$	Concentration of TiO_2 in the solution ($g \cdot L^{-1}$)

1

2 **Abbreviation**

3	AOP	Advanced Oxidation Process
4	RR198	Reactive Red 198
5	UV	Ultraviolet
6	L-H model	Langmuir-Hinshelwood model

7

8 **Reference**

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9

10 **Figure captions:**

11 Fig. 1: Molecular structure of Reactive Red 198

12 Fig. 2: Schematic diagram of Jar Tester

13 Fig. 3: Percentage removal of dye with different TiO₂ concentration at different pH

14 (points denote experimental data and lines indicate model equations)

15 Fig. 4: Adsorption quantity vs. time plot at different pH (points denote experimental data

16 and lines indicate model equations)

17 Fig. 5: Langmuir and Freundlich isotherm at pH 3 (points denote experimental data and

18 lines indicate model equations)

19 Fig. 6: Dye concentration ratio vs. time plot for photo-decolorization reaction (points

20 denote experimental data and lines indicate model equations)

21 Fig. 7: Dye concentration ratio vs. time plot for successive cycles (pH 3) (points denote

22 experimental data and lines indicate model equations)

23

1 **Table captions:**

2 Table 1: Values of Langmuir and Freundlich isotherm constants

3 Table 2: Values of starting time, initial rate constant and catalyst activity for successive
4 cycles

5

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12 **Appendix: I**

13 ***Calculation of initial rate of reaction and activity of catalyst***

14 The initial rate of reaction has been calculated by the method as described below.

15 We have calculated the initial rate of reaction using the equation

16
$$r_{0i} = \frac{1}{W} \frac{dc}{dt} \Big|_{t=0} \quad (A1)$$

17 Where r_{0i} is initial rate of reaction, W is the weight of catalyst, c is the concentration of

18 dye. The slope of the concentration vs. time graph at time $t = 0$, $\frac{dc}{dt} \Big|_{t=0}$ has been

19 calculated from the figure, as shown below. The slope of the red line in figure represents

20 the initial rate of change of dye concentration. Weight of catalyst W is known, so we

21 can calculate the value of r_{0i} .

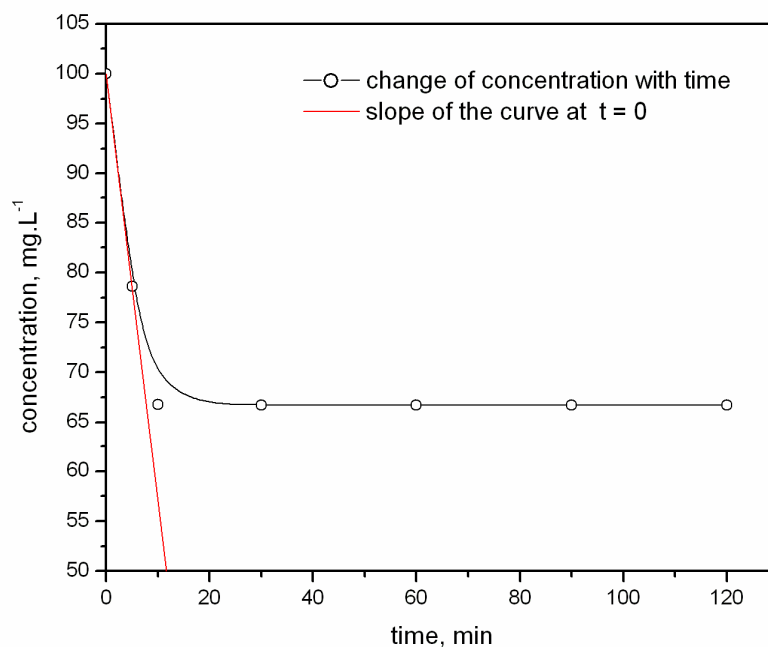


Fig. A1: Dye concentration vs. time plot with slope at time $t = 0$

Activity of catalyst has been calculated using the relation as:

$$a = \frac{r_{0i}}{r_0} \quad (A2)$$

Where a is catalyst activity, r_{0i} is the initial rate of reaction for i^{th} cycle and r_0 is the initial rate of reaction for 1st cycle (with fresh catalyst).

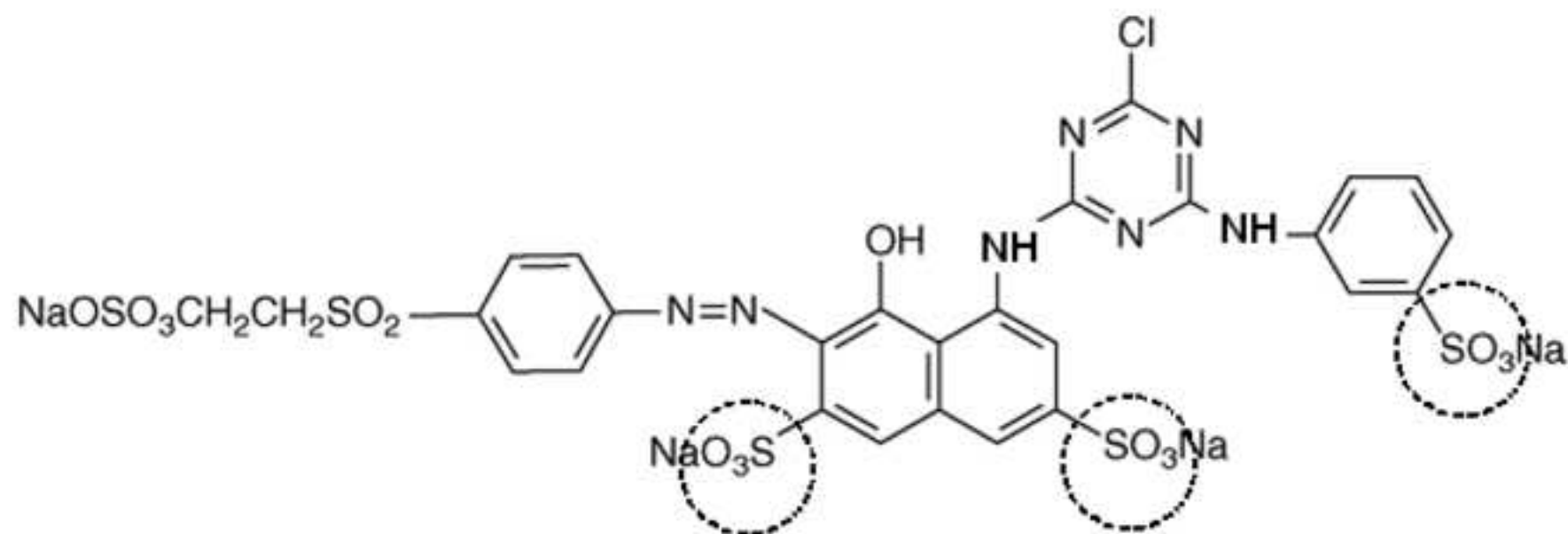
Table 1: Values of Langmuir and Freundlich isotherm constants

Freundlich isotherm constants		Langmuir isotherm constants	
k_F	93.029 mg.g ⁻¹	k_L	0.489 L.mg ⁻¹
n_F	4.948	Q_m	217.391 mg.g ⁻¹
R^2	0.957	R^2	0.988
		R_L	0.006

Table 2: Values of starting time, initial rate constant and catalyst activity for successive cycles

No. of cycle	Starting time of each cycle (cumulative) (hr)	Initial rate of photo-decolorization (r_{0i}) (Mol.hr⁻¹g cat⁻¹)	Catalyst activity (a)
1 st cycle	0.0	7.24×10^{-7}	1.000
2 nd cycle	1.0	6.65×10^{-7}	0.919
3 rd cycle	2.0	6.06×10^{-7}	0.837
4 th cycle	3.0	5.69×10^{-7}	0.786
5 th cycle	4.5	4.30×10^{-7}	0.594

Figure 1



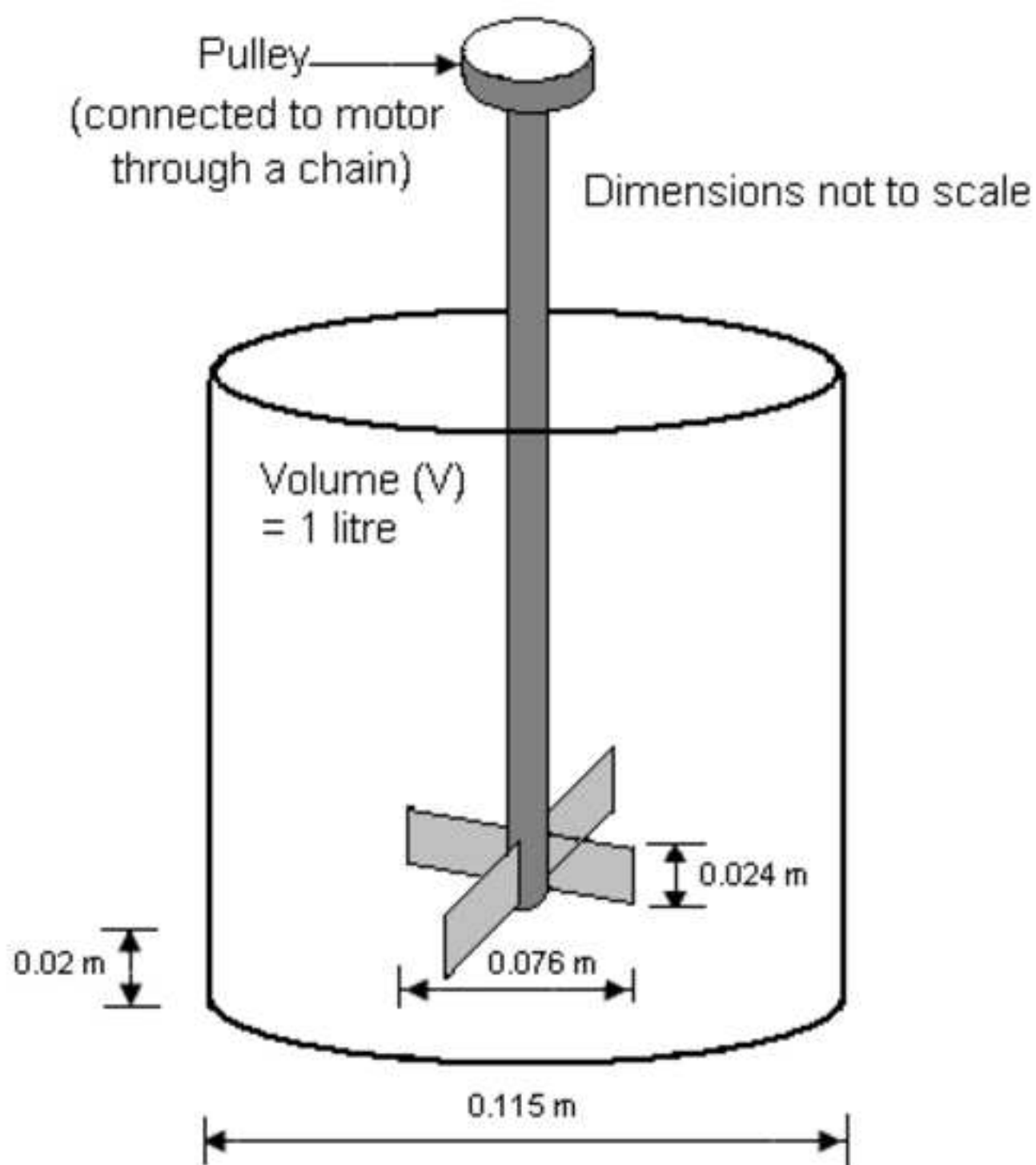


Figure 3

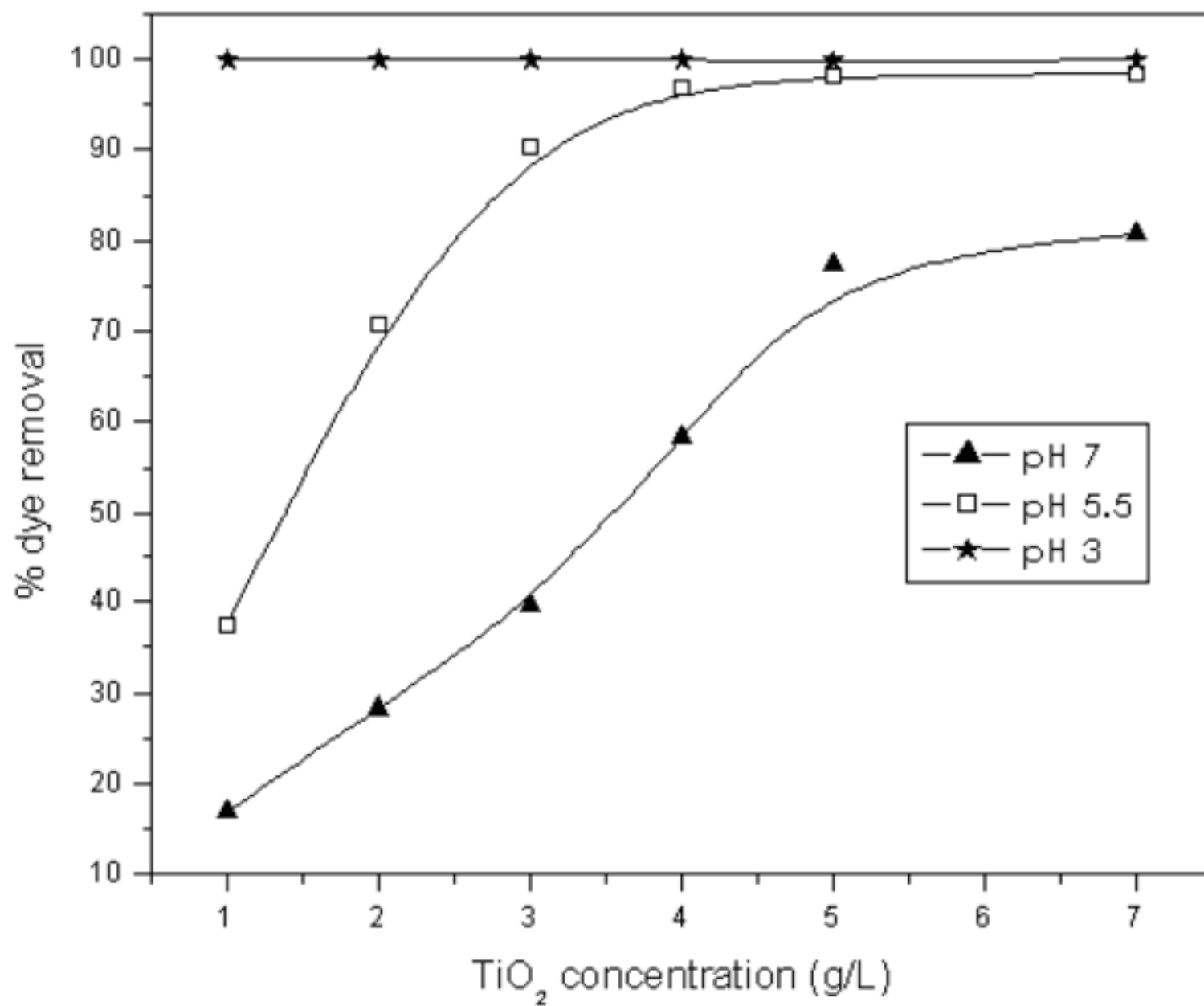


Figure 4

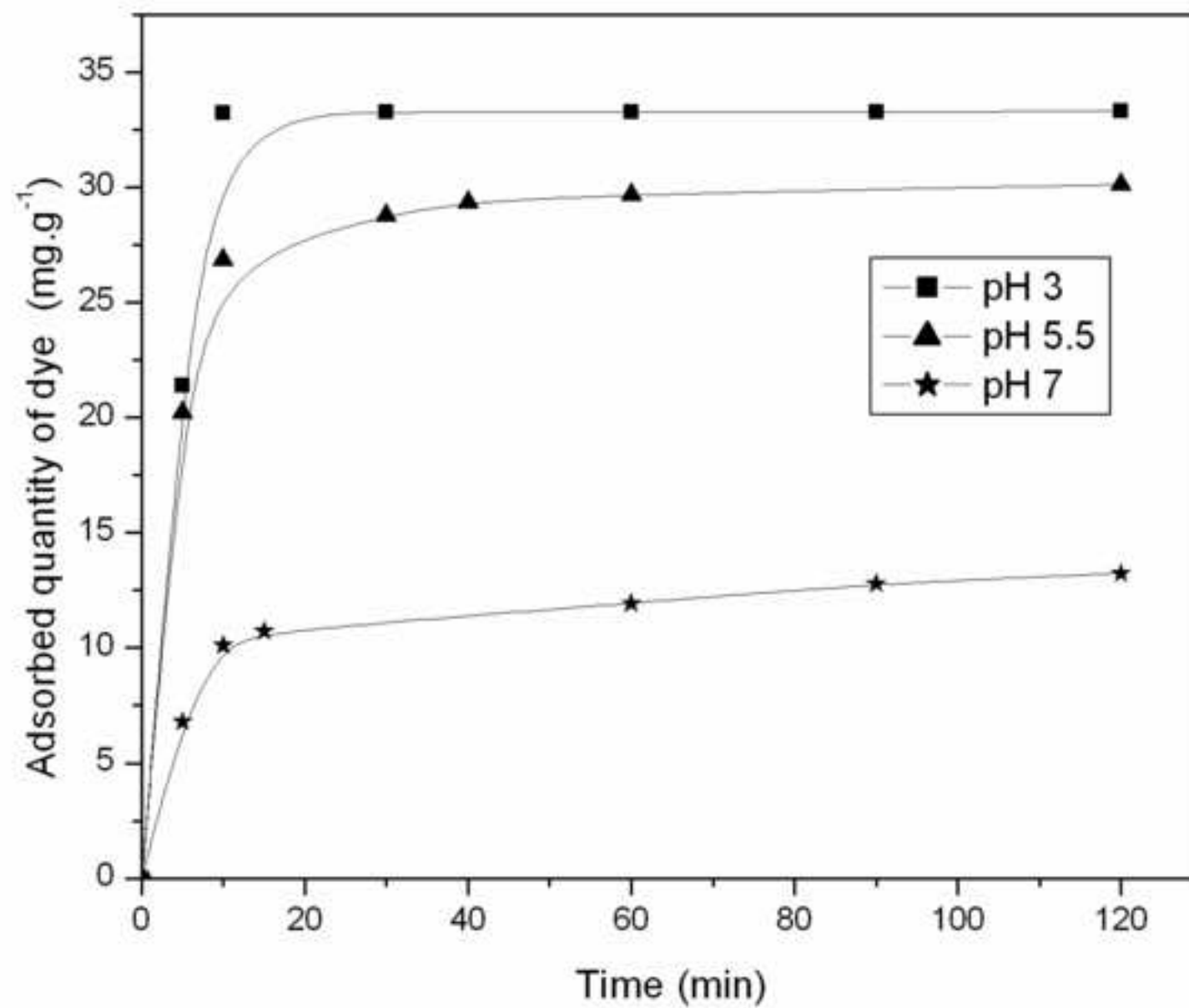


Figure 5

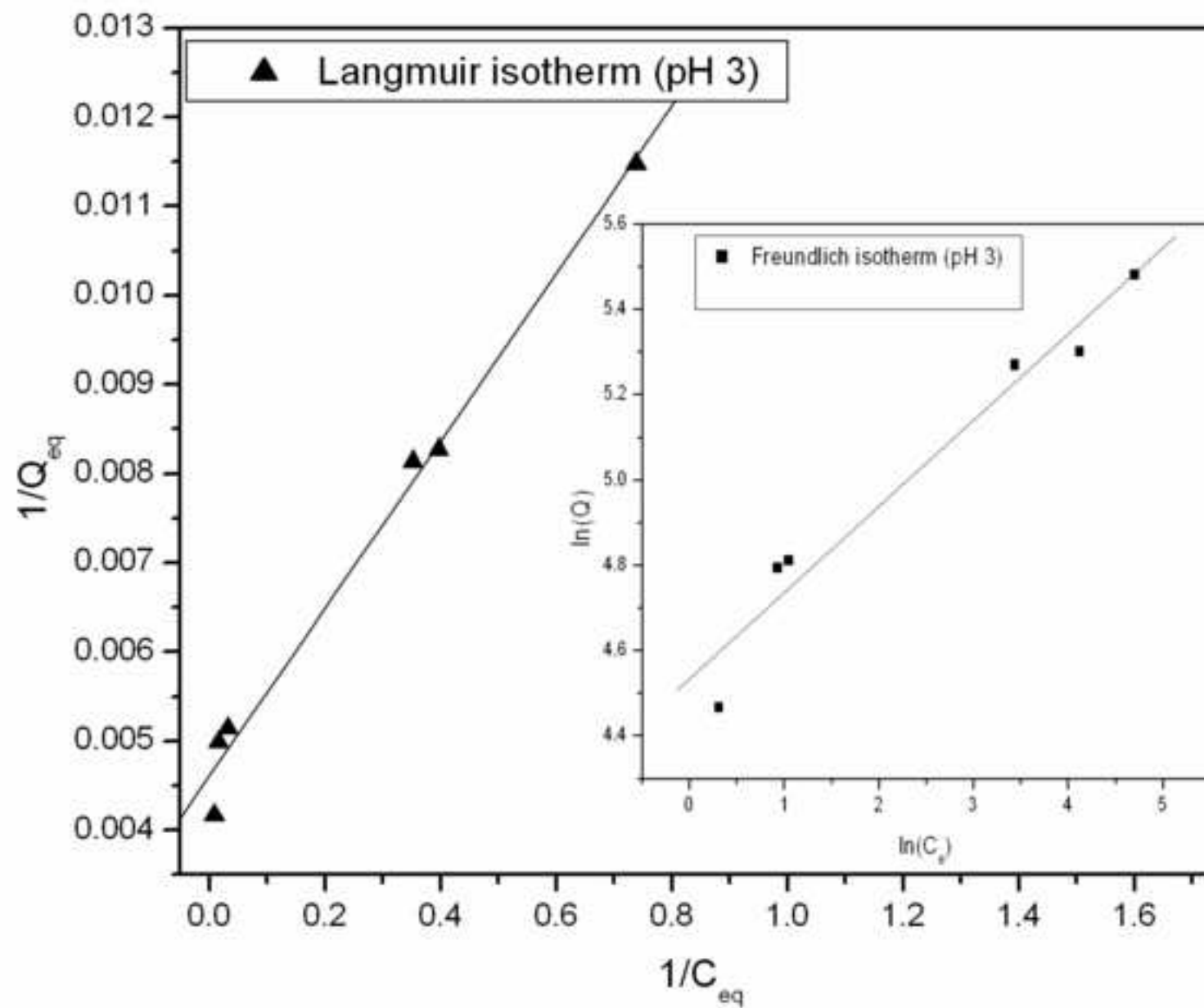


Figure 6

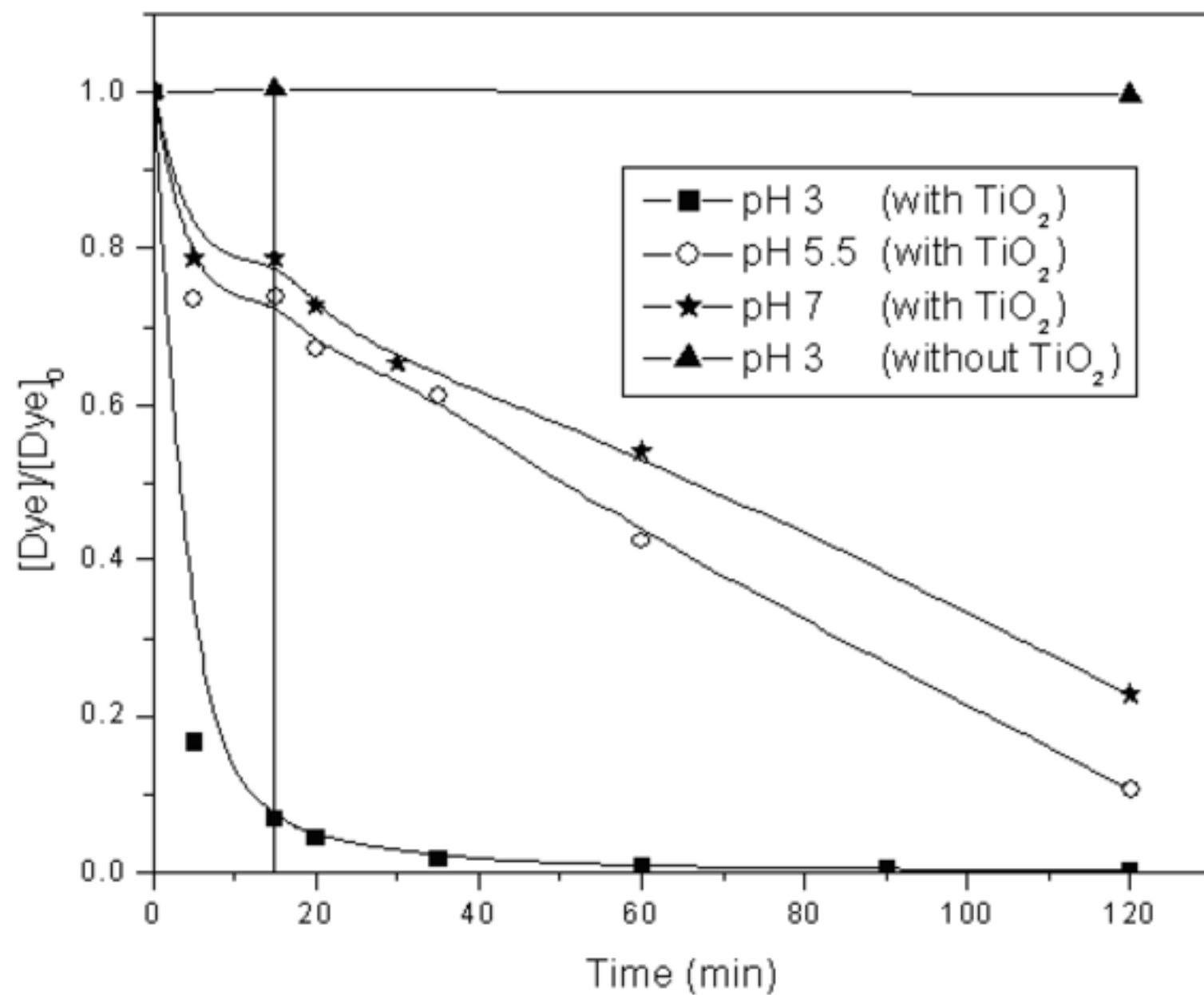
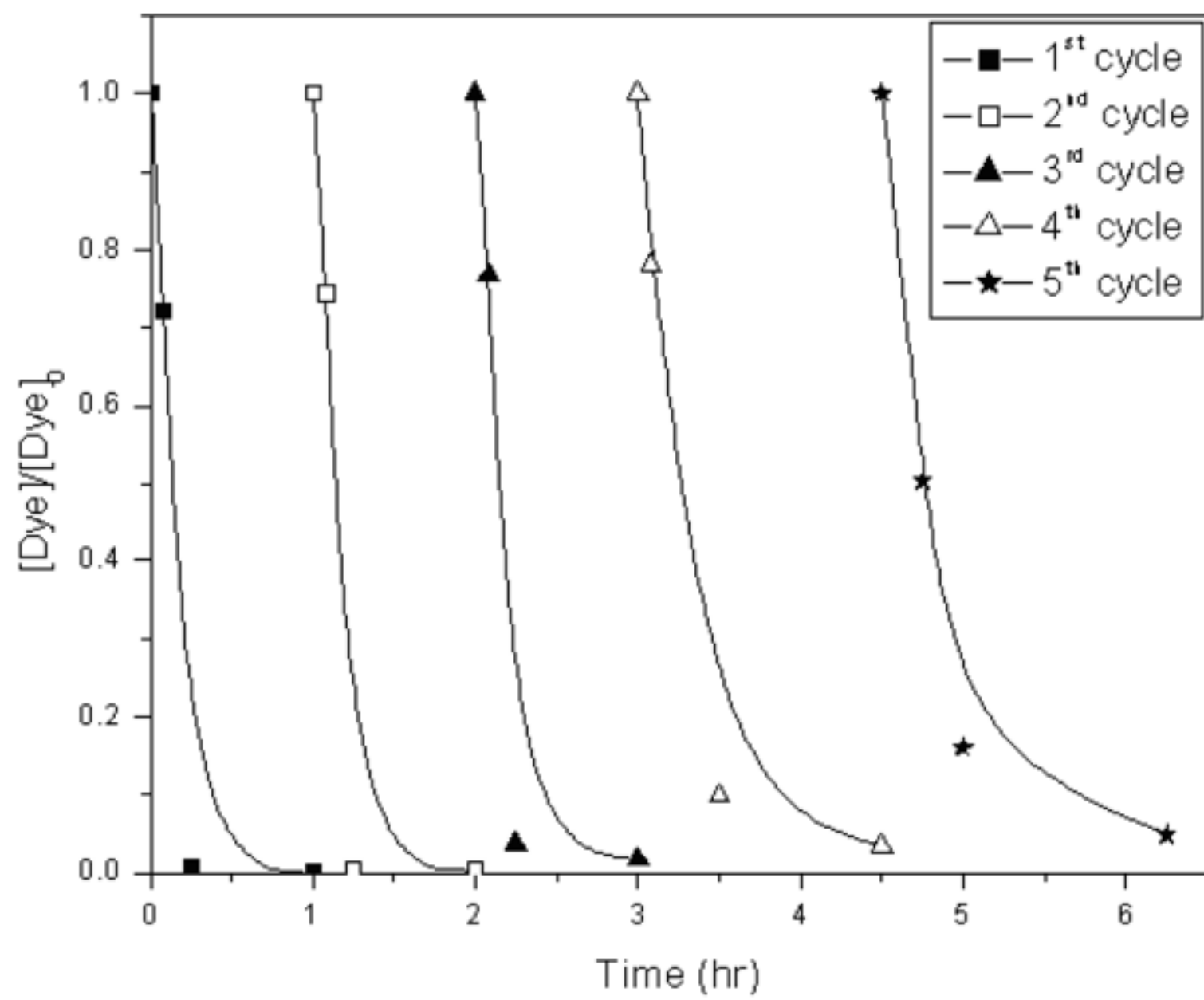


Figure 7





DSpace

<https://dspace.org/>

Kinetic study of adsorption and photo-decolorization of Reactive Red 198 on TiO₂ surface

Dutta, S.; Parsons, Simon A.; Bhattacharjee, C.; Jarvis, Peter; Datta, S. ...

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