

**Kinetics of the Sorption Of Copper (II) Phthalocyanine  
Tetrasulfonic Sodium Acid (CuPc) Dye Onto Titanium Dioxide**

**Abstract:** Sorption studies of copper (II) phthalocyanine tetrasulfonic sodium acid (CuPc) was done using a batch method with TiO<sub>2</sub> powder as the adsorbent, and several variables such as initial concentration of the dye, contact time and TiO<sub>2</sub> loading was determined. The sorption data were analysed using first order and second order kinetics, and the sorption studies were found to be second order kinetics. The data were also fitted to Langmuir and Freundlich isotherms and the equilibrium data fitted very well to Freundlich isotherm. The amount of TiO<sub>2</sub> powder needed to remove CuPc dye from solution was also studied and it was observed that 19.86 mg g<sup>-1</sup> of CuPc is absorbed.

**KEYWORD:** Kinetics, CuPc, Dye, Titanium Dioxide, sorption, Dye.

**1. Introduction**

The protection of the environment against deforestation, global warming and pollution has become of great concern over the past decades. Annually,  $7 \times 10^5$  tons of dyestuffs are produced from over 100,000 types of dye. These are used by many industries including textile, cosmetics, paper, leather, drugs and food industries [1]. The removal of dye from the environment is of concern because this is a source of water pollution and some dyes can be harmful. The treatment of water polluted with dyes is difficult due to the complexity of the methods used, which include biological treatment, coagulation, floatation, adsorption, oxidation and hyper filtration [2]. Among the methods mentioned above, sorption shows promise for the removal of colour from industrial waste.

However, this method is not always cost effective because of the chemicals required to activate the adsorbent. Hence the search for cheaper ways of removing colour effluent from the environment is ongoing. Phthalocyanines have an interesting characteristic because of their bright colours and chemical stability.

Titanium dioxide is nontoxic and stable and can have a high surface area. Hence it can be used as adsorbents, catalyst supports, filters, coatings, photoconductors, Photocatalyst [3] and dielectric materials. It also has the potential to be used for environmental purification, decomposition of toxic gases and in the generation of hydrogen gas [4], by comparison TiO<sub>2</sub> is cheap and can be reused, several dyes like methylene blue, Remazol blue R and Orange G have been reported to degrade inTiO<sub>2</sub> [5]. In a recent research by Holliman et al [6], the sorption kinetics of Direct Red 23 dye, were studied using TiO<sub>2</sub> powders. However sulfonated copper phthalocyanine is water soluble and is a very stable compound. Hence the absorption of the dye is of great concern.

In this study, titanium dioxide will be studied for the uptake and adsorption kinetics of copper (II) phthalocyanine tetrasulfonic sodium acid (CuPc). This is pertinent because a better understanding of sorption of dyes using metal oxides can also be used to increase the efficiency of dye sensitized solar cells which is a clean source of energy

**2. Materials and methods****2.1 Reagents**

All the reagents used for the experiment are of analytical grade and are supplied by Sigma-Aldrich UK except were stated. Deionised water was supplied by the School of Chemistry Bangor University.

**2.3 Effect of adsorbent concentration**

0.005 g, 0.010 g, 0.015 g, 0.020 g and 0.025 g of TiO<sub>2</sub> P25 powder were measured using an analytical weighing balance and they were transferred into a vial, after which 20 ml of the dye solution with an initial concentration of 70 mg L<sup>-1</sup> of the CuPc dye were added to each vial and sealed. The solutions were placed on shaker and the speed of the shaker was adjusted to 400 rpm allowed for 120 minutes in order to attain equilibrium. The experiment was done at room temperature (25 °C). After equilibration each sample were transferred into a 2 ml centrifuge tube (Fisher) and centrifuged for 10 minutes. The absorbance of the supernatant dye solution was analysed with a UV-UNICAM machine.

56 **2.4 Sorption equilibrium**

57 0.02 g of TiO<sub>2</sub> powder in each case was transferred into six different vials, after which 20ml of six  
 58 different initial concentrations of the dye [20 mg L<sup>-1</sup>, 30 mg L<sup>-1</sup>, 40 mg L<sup>-1</sup>, 50 mg L<sup>-1</sup>, 60 mg L<sup>-1</sup> and 70  
 59 mg L<sup>-1</sup>] were added to each vial containing the TiO<sub>2</sub> powder. The resulting solution were placed on a  
 60 shaker and allowed to shake for 120minutes at a speed of 400 rpm in order to attain equilibrium. The  
 61 resulting dye solution was transferred into a 1cm cuvette with a micropipette and the final absorbance was  
 62 measured using a Lambda 35 UV/VIS spectrometer machine manufactured by Perkin Elmer.

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 64 **2.5 Kinetics studies**

65 The kinetics study was carried out using 20 ml volume of the CuPc with a concentration of 30 mg L<sup>-1</sup>, 50  
 66 mg L<sup>-1</sup> or 70 mg L<sup>-1</sup>. These were transferred into a vial containing 0.02 g each of TiO<sub>2</sub> powder. The  
 67 resulting TiO<sub>2</sub>/dye solutions were placed on shaker at a speed of 400 rpm and at room temperature [25°C  
 68 ±3]. Each solution of the different dye concentrations were withdrawn after 5, 20, 30, 40, 50, 60 and 120  
 69 minutes, the samples were then centrifuged for 10 minutes at a speed of 1,200 rpm and the solution were  
 70 measured using a UV- UNICAM spectrometer.

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 72 **3.0 Results and Discussion**

73 **3.1 Effect of adsorbent concentration**

74 The relationship of varying the mass of TiO<sub>2</sub> with a given concentration of CuPc dye (70 mg L<sup>-1</sup>) was  
 75 correlated. Table 1 shows the entire dye uptake. The percentage of dye removal and amount of dye  
 76 absorbed were calculated as using Equation 1.0 as shown below.

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$$q_e = \left( \frac{C_i - C_f}{m} \right) \times v$$
 Equation 1.0

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 81  $q_e$  = Amount of dye absorbed  
 82  $C_i$  = initial concentration of the dye  
 83  $C_f$  = final concentration of the dye  
 84  $v$  = volume of the dye in liters (L)  
 85  $m$  = mass of adsorbent (TiO<sub>2</sub>) in g

86  
 87 **Table 1:** Showing effect of adsorbent mass at an initial dye concentration of 70 mg L<sup>-1</sup> and a volume of 20  
 88 ml

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Mass of TiO <sub>2</sub> (g)	Average Absorbance	Standard error	Final concentrati on of dye (mg L <sup>-1</sup> )	% of dye removal	Standard error (%)	amount absorbed (qe) (mg g <sup>-1</sup> )
0.005	0.5243	±0.00042	24.964	64.34	±0.020	180.14
0.010	0.4551	±0.00019	21.673	69.04	±0.009	96.65
0.015	0.3962	±0.00040	18.866	73.05	±0.019	68.18
0.020	0.2233	±0.00007	10.633	84.81	±0.003	59.37
0.025	0.1768	±0.00014	8.418	87.97	±0.007	49.27
0.030	0.0959	±0.00002	4.565	93.48	±0.001	43.62

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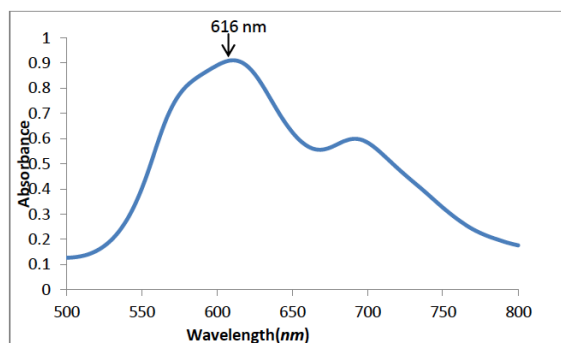


Figure 1: The UV spectrum of CuPc dye showing maximum absorption at 616nm.

The UV spectrum in Figure 1 shows that the absorption peak of CuPc in UV spectrum is 616nm

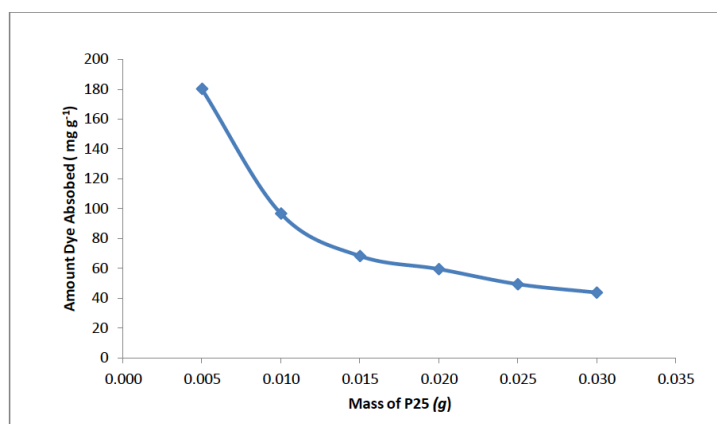


Figure 2: The Effect on the mass of adsorbent used on the amount of dye absorbed CuPc

A close observation of the figure indicates that the amount of the dye absorbed depends on the amount of the adsorbent used. When the mass of the adsorbent was changed from, 0.005 g to 0.030 g, the percentage of dye removal increases from 63.34 % to 93.48 %, while Figure 2 shows the amount of the dye adsorbed decreases from 180.14 mg g<sup>-1</sup> to 43.62 mg g<sup>-1</sup>. At a high ratio of TiO<sub>2</sub> powder to dye concentration, there is larger amount of CuPc dye adsorbed onto the TiO<sub>2</sub> powder surface, which makes the concentration of the dye lower in the solution, than when a higher amount of the TiO<sub>2</sub> powder is used. This is due to the fact that a given amount of TiO<sub>2</sub> can adsorb a fixed amount of dyes due to increase in active sites. It also explains why the amount of dye absorbs increases as the amount of adsorbent increases. This trend continues until the maximum amount of adsorbent required is used. The decrease in the amount of CuPc dye absorbed in mg g<sup>-1</sup> with an increasing amount of TiO<sub>2</sub> powder is explained as a result of concentration difference between the dye concentration in the solution and the dye concentration on the surface of the TiO<sub>2</sub> powder. Therefore with an increase in the amount of adsorbent used proportion of surface sites decreases. V.K Garg *et al* reported a similar result of 59.6% to 99.8% increase in percentage of malachite green dye adsorbed on saw dust activated with sulphuric acid when the adsorbent was increased from 0.2 to 1.0 g /100 ml with 250 mg L<sup>-1</sup> dye concentration after equilibrium time [7].

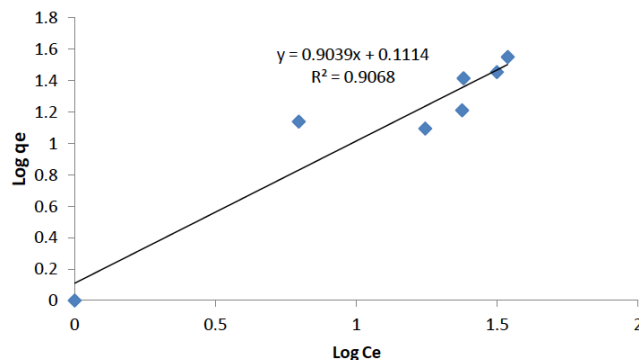
### 3.2 Sorption Equilibrium

The adsorption equilibrium was analysed using Langmuir and Freundlich isotherm equations. The equations for the two isotherms are shown in the equation below

$$\frac{c_e}{q_e} = \frac{1}{Qb} + \frac{c_e}{Q} \quad \text{(Langmuir equation)} \quad (2)$$

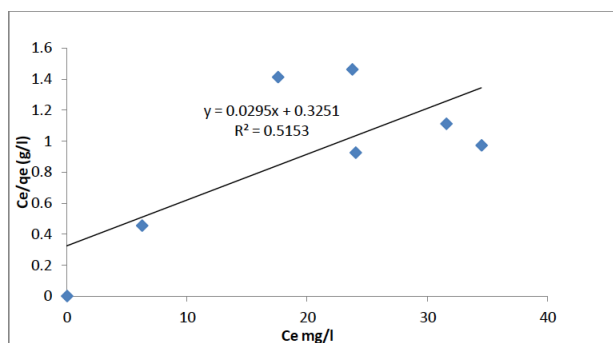
$$\log q_e = \log K_f + \frac{1}{n} (\log C_e) \quad \text{(Freundlich equation)} \quad (3)$$

127 Where  $C_e$  = Concentration of the dye at equilibrium in  $\text{mg L}^{-1}$   
 128  $q_e$  = Amount of dye absorbed onto the adsorbent  $\text{mg g}^{-1}$   
 129  $Q$  and  $b$  = Langmuir constants,  $K_f$  and  $1/n$  = Freundlich constant and a measure of adsorption capacity  
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Figure 3: Freundlich curve of  $\text{TiO}_2$  sorption of CuPc dye at a constant solution temperature of  $25^\circ \pm 2$



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Figure 4: Langmuir curve onto  $\text{TiO}_2$  sorption at a constant solution temperature of  $25^\circ \pm 2$

141 The equilibrium data are better represented by the Freundlich isotherm equation when compared to the  
 142 Langmuir isotherm as shown in Figure 3 and 4. The sorption equilibrium data gives a correlation  
 143 coefficient of 0.91 and 0.52 for Freundlich and Langmuir isotherm respectively. The value of  $n$  [1.10] from  
 144 Table 2 it shows that there is less interaction between the CuPc molecule and the  $\text{TiO}_2$  this could be  
 145 attributed to the large structure of the dye used in the sorption studies.  
 146 However using Langmuir equation the maximum amount of dye that is absorbed onto CuPc is  $34 \text{ mg g}^{-1}$   
 147 can be deduced from the value of  $Q$  as shown in Table 2. The essential characteristics of Langmuir  
 148 isotherm can be expressed by a dimensionless constant known as equilibrium parameter:  
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150 Table 2: Equilibrium constants for CuPc sorption onto  $\text{TiO}_2$  powder at a temperature of  $25^\circ \pm 2$   
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Freundlich Isotherm				Langmuir Isotherm		
$K_f$ [ $\text{mg g}^{-1} \text{L g}^{-1}$ ]	$1/n$	$n$	$R^2$	$Q$ [ $\text{mg g}^{-1}$ ]	$b$	$R^2$
1.29	0.90	1.10	0.91	34.00	0.09	0.52

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$$R_L = \frac{1}{(1+bc)} \quad (4)$$

Where  $b$  is the Langmuir constant and  $C$  is the highest initial CuPc concentration in  $\text{mg L}^{-1}$

157 The value of  $R_L$  shows the type of the isotherm to be unfavourable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favourable ( $0$   
 158  $< R_L < 1$ ) or irreversible ( $R_L = 0$ ).  
 159 The calculated values of  $R_L$  at various initial CuPc concentrations are shown in Figure 5. This suggests  
 160 that the adsorption of the dye onto  $TiO_2$  powder is favourable with increase in concentration; the value of  
 161  $R_L$  in all the concentrations range calculated indicates a favourable uptake of the dye [ $0 < R_L < 1$ ]. The  
 162 high value of  $R_L$  at low concentration indicates the adsorption is much favourable with a decrease in initial  
 163 concentration.  
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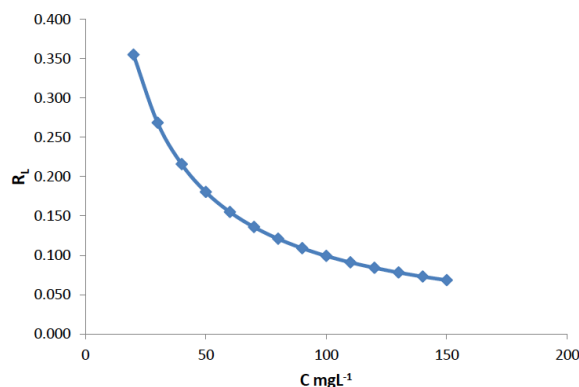


Figure 5: The separation factor of CuPc dye onto  $TiO_2$  powder at  $25^{\circ}C \pm 2$

### 3.3 Kinetics Studies

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 169 The understanding of sorption kinetics of dyes is pertinent for designing industrial processes for water  
 170 purification. The sorption of dyes depends on the physicochemical properties of the adsorbent and it  
 171 also depends on the reaction conditions. There are several studies done by previous researchers on the  
 172 kinetics of dye uptake and they used several methods which include: first order, second order, the  
 173 Elovich kinetic equation and the parabolic diffusion model. These methods were used in order to  
 174 determine the mechanism of the reaction involved in the process. In this study, the kinetics was  
 175 investigated using first order and second order models to study the adsorption of CuPc onto  $TiO_2$  powder.  
 176 Figure 6 shows the amount of dye absorbed against time for various concentrations of CuPc dye and  
 177 contact times, it indicates an increase in the amount of dye uptake with time for all the initial dye  
 178 concentrations used [ $30 \text{ mg L}^{-1}$ ,  $50 \text{ mg L}^{-1}$  and  $70 \text{ mg L}^{-1}$ ]. The sorption rate for the first 5 minutes was  
 179 found to be  $0.722$ ,  $1.804$  and  $4.453 \text{ mg g}^{-1} \text{ min}^{-1}$  respectively for initial dye concentration of  $30 \text{ mg L}^{-1}$ ,  $50$   
 180  $\text{mg L}^{-1}$  and  $70 \text{ mg L}^{-1}$  as shown in Figure 8 below

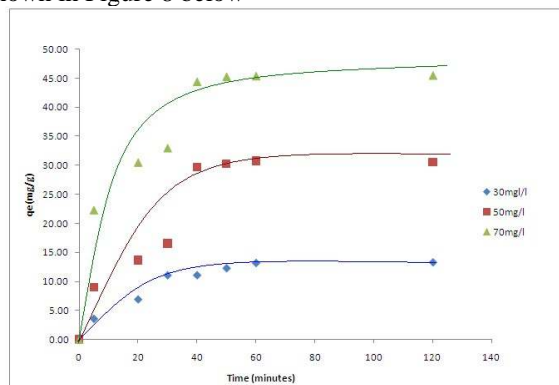


Figure 6: Graph to show dye uptake versus time for CuPc dye on  $TiO_2$  powder (initial dye concentration are 30, 50 or  $70 \text{ mg L}^{-1}$ )

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 185 After 50 minutes the sorption rate decreased to  $0.247$ ,  $0.606$  and  $0.904 \text{ mg g}^{-1} \text{ min}^{-1}$  respectively for initial  
 186 dye concentrations of  $30$ ,  $50$  and  $70 \text{ mg L}^{-1}$ . The low sorption rates observed after 50 minutes might be due  
 187 decrease in the amount of available space in the  $TiO_2$  powder to absorbed more solute in the solution hence  
 188 a decrease in the absorption rate is observed. This could be illustrated in with an example of car park.  
 189 Early in the morning , the car park is empty and so more car space is available for parking and so it take

190 less time to park a car. However when the car park gets nearly full the more time it takes to park in same  
 191 car park. The pseudo-first order and pseudo- second order kinetics were further used to analyse the rate of  
 192 reaction of the dye in TiO<sub>2</sub> powder.  
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194 **3.3.1 Pseudo-first order kinetics**

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 196 The kinetics for the sorption of CuPc dye onto TiO<sub>2</sub> powder were analysed using the pseudo-first order  
 197 equation as shown below:  
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199 Natarajan and Khalaf equation [8]

$$\log_{10} \frac{C_i}{C_t} = \frac{k}{2.303t}$$

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 202 Where C<sub>i</sub> = Initial concentration of the dye (mg L<sup>-1</sup>) C<sub>t</sub> = concentration of the at time t (mg L<sup>-1</sup>)  
 203 t = time in minutes  
 204

205 k= rate constant (min<sup>-1</sup>)  
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207 The first order rate constants (k) for each of the initial dye concentration was calculated from the graph  
 208 shown on Table 4.  
 209

210 Table 4: *Pseudo*-first order kinetics for the sorption of CuPc dye, calculated using Natarajan and Khalaf  
 211 equation [8].  
 212

C <sub>i</sub> (mg L <sup>-1</sup> )	k (min <sup>-1</sup> ) × 10 <sup>-3</sup>	r <sup>2</sup>
30	4.606	0.622
50	7.830	0.597
70	8.291	0.633

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 214 The result indicates that the rate constant increases with increase in initial concentration. But the linear  
 215 correlation as shown in the table 4 above is not close to unity, this shows that the sorption studies of CuPc  
 216 dye on TiO<sub>2</sub> cannot be explained by pseudo first order kinetics. Hence the data's were further analysed by  
 217 pseudo- second order kinetics.  
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219 **3.3.2 Pseudo second order kinetics**

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 221 The Ho pseudo- second order kinetics equation was used to further analysed kinetics of reaction for the  
 222 CuPc dye. The equation is shown below  
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$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

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 225 Where k<sub>2</sub> is the pseudo second order constant in gm<sup>-1</sup>min<sup>-1</sup>, q<sub>e</sub> and q are the amount of dye absorbed in  
 226 mg g<sup>-1</sup> at equilibrium while t is the time in minutes. Table 5 shows pseudo second order plot for the  
 227 adsorption of CuPc dye for initial dye concentration of 30, 50 and 70mgL<sup>-1</sup> respectively. It was observed  
 228 that the regression value obtained for pseudo- second order reaction has a higher value and it all falls in the  
 229 range of 0.9133 to 0.9724 which is close to unity. This indicates that the sorption of CuPc dye obeys the  
 230 second order reaction which indicates that an ester was formed with the TiO<sub>2</sub> powder in the process  
 231 (chemisorption) This shows a similar result obtained for the sorption of methylene blue onto risk husk by  
 232 V. Vadivelan and K. Vasanth Kumar [9] Ho [10] also reported a similar result for the sorption kinetics of  
 233 copper ion using fern as an adsorbent, in both case the sorption kinetics obeys a *pseudo*- second order as  
 234 obtained in this work. The values of k<sub>2</sub>, regression and maximum dye absorption are shown in the table  
 235 below.  
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Table 5: Pseudo-second order kinetics for the sorption of CuPc dye

$C_i(\text{mgL}^{-1})$	$k_2 (\text{gmg}^{-1}\text{min}^{-1}) \times 10^{-3}$	$r^2$	$q_e (\text{magg-1})$
30	6.398	0.9724	14.598
50	3.628	0.9858	47.846
70	2.013	0.9133	34.602

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**3.4 Maximum amount of TiO<sub>2</sub> required remove CuPc from a solution**

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There is a need to know the amount of TiO<sub>2</sub> required in soaking a given amount of CuPc dye in a solution, this can be applied in industries for the clean-up dyes in water bodies and effluents. Table 6 shows a variation of the amount absorbed CuPc against time with the percentage error calculated in each case. A close observation of the result shows that the percentage of dye absorbed increased from 59.98 % in five minutes to 97.04 % after 40 minutes. This indicates that more dye is absorbed on to the TiO<sub>2</sub> powder surface with time i.e. 12.00 mg g<sup>-1</sup> to 19.86 mg g<sup>-1</sup>. Therefore as the colour is removed from the solution it gets soaked onto the TiO<sub>2</sub> powder. As shown in Figures 7 and 8, after 35 minutes there is no significant change in the amount of CuPc absorbed. This could be as a result of the adsorbent being saturated with the maximum amount of dye required per unit area.

Table 6: Table showing the amount of CuPc absorbed with time

Time(minutes)	Ct [mg L <sup>-1</sup> ]	Error (mg L <sup>-1</sup> )	% of dye Absorbed	qt [mg g <sup>-1</sup> ]
5	80.04	±0.0005	59.98	12.00
10	73.81	±1.7153	63.10	12.62
15	61.92	±1.7283	69.04	13.81
20	61.32	±1.0377	69.34	13.87
25	57.99	±0.9867	71.00	14.20
30	36.83	±0.7586	81.58	16.32
35	16.34	±0.4461	91.83	18.37
40	5.91	±0.2057	97.04	19.41
45	2.53	±0.6294	98.73	19.75
50	1.58	±0.1806	99.21	19.84
60	1.42	±0.5822	99.29	19.86

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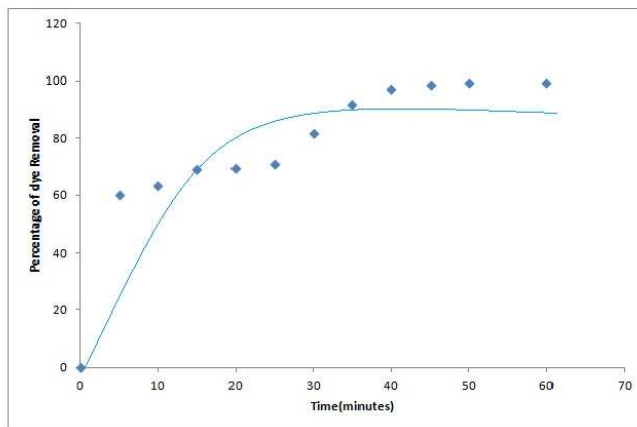


Figure 7: graph of percentage of dye absorbed against time for CuPc

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Figure 8: picture of showing the colours of CuPc dye absorbed for 0 to 60 minutes

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**Conclusions**

This studies shows that TiO<sub>2</sub> powder can be used as an alternative to activated carbon for the clean-up of CuPc from effluents. The results indicate that the amount of dye adsorbed increased with time in each case, and about 90% of the dyes were adsorbed in less than one hour. The amount of dye uptake of CuPc dye was found to increase with initial dye concentration and time but decreased with an increase in the amount of TiO<sub>2</sub> used.

The sorption kinetics of CuPc was found to obey the pseudo-second order kinetics and the equilibrium data fitted well to Freundlich isotherm, indicating that the sorption of CuPc dye onto TiO<sub>2</sub> involves the formation of multi- layer and a maximum absorption capacity of 19.86 mg g<sup>-1</sup>. The molar extinction coefficient of CuPc dye obtained [ $1.25 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ ] with a maximum absorption capacity of 0.579mg g<sup>-1</sup> in less than one hour. This shows that TiO<sub>2</sub> powder may be effectively used for the clean-up of CuPc dye from effluents.

**References**

[1] C.I. Pearce, J.R. Lloyd, J.T. Guthrie, *Dyes and Pigments*, 2003, **58**, 179–196.  
 [2] V.K. Gupta and Suhas, *Journal of Environmental Management*, 2009, **90**, 2313- 2342.  
 [3] M.T Yilleng, C.E Gimba, I.G Ndukwe And I.M Bugaje (2015) Assessing the Photo Catalytic Activity of Rutile Ore from the Middle Belt Region of Nigeria on the Degradation of Phenol in Water. IOSR Journal of Applied Chemistry (IOSR-JAC). Volume 8, Issue 7 Ver. I, PP 36-43. DOI: 10.9790/5736-08713643  
 [4] Zhang, Q., L. Gao and J. Guo. *J. Eur. Ceram. Soc.*, 2000, 20, 2153-2158.  
 [5] K. Nagaveni , G. Sivalingam , M.S. Hegde and Giridhar Madras, *Catalysis B: Environmental*, 2004, 48, 83–93.  
 [6] P. J. Holliman, B. V. Velasco, I. Butler, M. Wijdekop, and D. A.Worsley, *International Journal of Photoenergy*, 2008, **827605**, 1-7.  
 [7] V.K. Garg, R. Gupta, A. B. Yadav and R. Kumar, *Bioresource Technology*, 2003,89 121–124.  
 [8] N. Kannan, and G. Rengasamy, *Water, Air, and Soil Pollution*, 2005, 163, 185– 201.  
 [9] V. Vadivelan and K. V. Kumar, *Journal of Colloid and Interface Science*, 2005, 286, 90–100.  
 [10] Y.S. Ho. *Water Res.*, 2003, 37, 2323.