

**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 TiO₂ powder as the adsorbent, and several variables such as initial concentration of the dye, contact time and TiO₂ 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 TiO₂ powder needed to remove CuPc dye from solution was also studied and it was observed that 19.86 mg g⁻¹ of CuPc was adsorbed.

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, 7×10^5 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 [3], catalyst supports, filters, coatings, photoconductors, photocatalyst [4] 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 [5], by comparison TiO₂ is cheap and can be reused, several dyes like methylene blue, Remazol blue R and Orange G have been reported to degrade in TiO₂ [6]. In a recent research by Holliman et al [7], the sorption kinetics of Direct Red 23 dye, were studied using TiO₂ 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 was used 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 were supplied by Sigma-Aldrich UK except where 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 TiO₂ 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⁻¹ 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 and 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.

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2.4 Sorption equilibrium

0.02 g of TiO₂ powder in each case was transferred into six different vials, after which 20ml of six different initial concentrations of the dye [20 mg L⁻¹, 30 mg L⁻¹, 40 mg L⁻¹, 50 mg L⁻¹, 60 mg L⁻¹ and 70 mg L⁻¹] were added to each vial containing the TiO₂ powder. The resulting solution were placed on a shaker and allowed to shake for 120 minutes at a speed of 400 rpm in order to attain equilibrium. The resulting dye solution was transferred into a 1cm cuvette with a micropipette and the final absorbance was measured using a Lambda 35 UV/VIS spectrometer machine manufactured by Perkin Elmer.

2.5 Kinetics studies

The kinetics study was carried out using 20 ml volume of the CuPc with a concentration of 30 mg L⁻¹, 50 mg L⁻¹ or 70 mg L⁻¹. These were transferred into a vial containing 0.02 g each of TiO₂ powder. The resulting TiO₂/dye solutions were placed on shaker at a speed of 400 rpm and at room temperature [25°C ±3]. Each solution of the different dye concentrations were withdrawn after 5, 20, 30, 40, 50, 60 and 120 minutes, the samples were then centrifuged for 10 minutes at a speed of 1,200 rpm and the solution were measured using a UV- UNICAM spectrometer.

3.0 Results and Discussion

3.1 Effect of adsorbent concentration

The relationship of varying the mass of TiO₂ with a given concentration of CuPc dye (70 mg L⁻¹) was correlated. Table 1 shows the entire dye uptake. The percentage of dye removal and amount of dye adsorbed were calculated as using Equation 1.0 as shown below.

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

- q_e = Amount of dye adsorbed
- C_i = initial concentration of the dye
- C_f = final concentration of the dye
- v = volume of the dye in liters (L)
- m = mass of adsorbent (TiO₂) in g

Table 1: Showing effect of adsorbent mass at an initial dye concentration of 70 mg L⁻¹ and a volume of 20 ml

Mass of TiO ₂ (g)	Average Absorbance	Standard error	Final concentration of dye (mg L ⁻¹)	% of dye removal	Standard error (%)	amount absorbed (qe) (mg g ⁻¹)
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

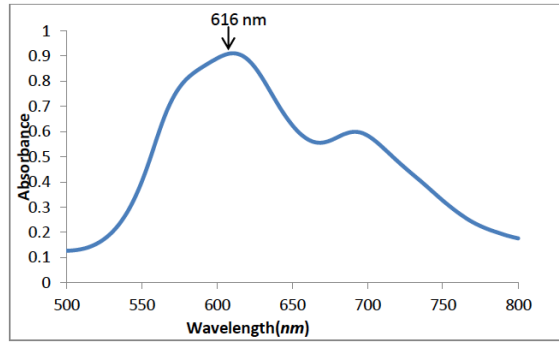


Figure 1: The UV spectrum of CuPc dye showing maximum absorption at 616nm.

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

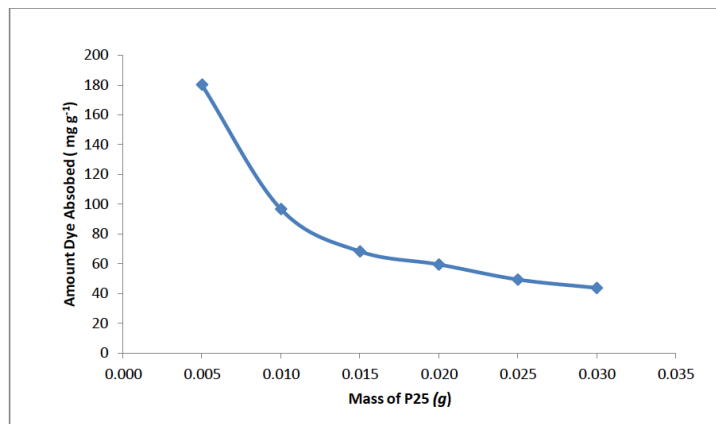


Figure 2: The Effect on the mass of adsorbent used on the amount of dye absorbed CuPc

A close observation of the figure indicates that the amount of the dye adsorbed 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⁻¹ to 43.62 mg g⁻¹. At a high ratio of TiO₂ powder to dye concentration, there is larger amount of CuPc dye adsorbed onto the TiO₂ powder surface, which makes the concentration of the dye lower in the solution, than when a higher amount of the TiO₂ powder is used. This is due to the fact that a given amount of TiO₂ can adsorb a fixed amount of dyes due to increase in active sites. It also explains why the amount of dye adsorbs 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 adsorbed in mg g⁻¹ with an increasing amount of TiO₂ 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 TiO₂ 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⁻¹ dye concentration after equilibrium time [8].

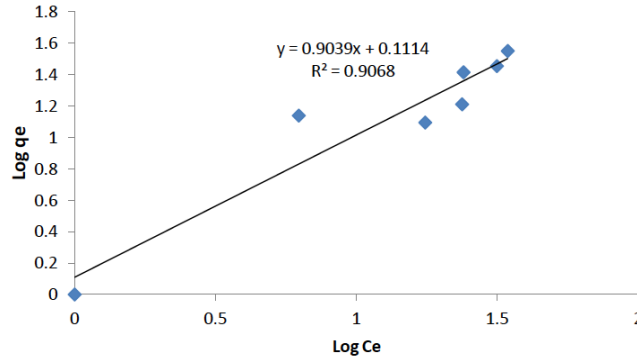
3.2 Sorption Equilibrium

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

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

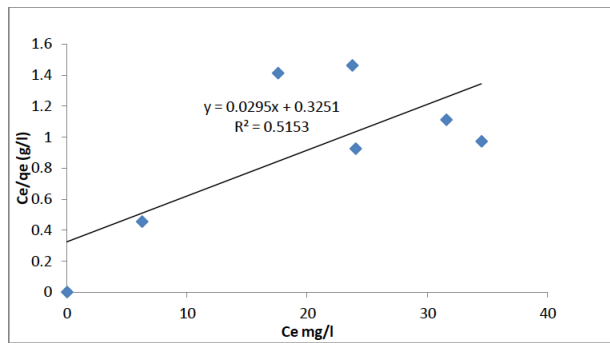
$$\log q_e = \log K_f + \frac{1}{n} (\log C_e) \quad (\text{Freundlich equation}) \quad (3)$$

127 Where C_e = Concentration of the dye at equilibrium in mg L^{-1}
 128 q_e = Amount of dye adsorbed onto the adsorbent 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 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 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 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 was adsorbed onto CuPc is 34 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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Table 2: Equilibrium constants for CuPc sorption onto TiO_2 powder at a temperature of $25^\circ \pm 2$

Freundlich Isotherm				Langmuir Isotherm		
K_f [$\text{mg g}^{-1} \text{L g}^{-1}$]	$1/n$	n	R^2	Q [mg g^{-1}]	b	R^2
1.29	0.90	1.10	0.91	34.00	0.09	0.52

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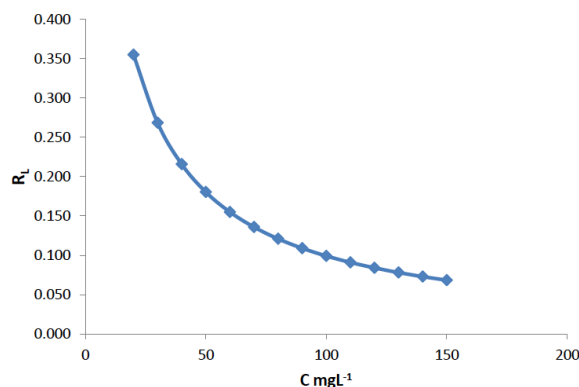
$$R_L = \frac{1}{(1+bc)} \quad (4)$$

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Where b is the Langmuir constant and C is the highest initial CuPc concentration in 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 ($R_L = 0$).

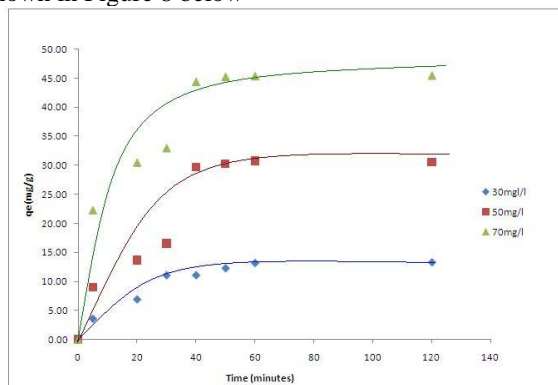
159 The calculated values of R_L at various initial CuPc concentrations are shown in Figure 5. This suggests
160 that the adsorption of the dye onto TiO_2 powder is favourable with increase in concentration; the value of
161 R_L in all the concentrations range calculated indicates a favourable uptake 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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166 Figure 5: The separation factor of CuPc dye onto TiO_2 powder at $25^\circ C \pm 2$
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168 3.3 Kinetics Studies

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 mg L^{-1} , 50 mg L^{-1} and 70 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 mg L^{-1} , 50
180 mg L^{-1} and 70 mg L^{-1} as shown in Figure 8 below



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182 Figure 6: Graph to show dye uptake versus time for CuPc dye on TiO_2 powder (initial dye concentration
183 are 30 , 50 or 70 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 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 adsorb more solute in the solution hence a
188 decrease in the adsorption rate is observed. This could be illustrated in with an example of car park. Early
189 in the morning, the car park is empty and so more car space is available for parking and so it take less time

190 to park a car. However when the car park gets nearly full the more time it takes to park in same car park.
 191 The pseudo-first order and pseudo- second order kinetics were further used to analyse the rate of reaction
 192 of the dye in TiO₂ 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 TiO₂ powder were analysed using the pseudo-first order
 197 equation as shown below:

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 199 Natarajan and Khalaf equation [9]

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

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202 Where C_i = Initial concentration of the dye (mg L⁻¹) C_t = concentration of the at time t (mg L⁻¹)
 203 t = time in minutes

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 205 k= rate constant (min⁻¹)
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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.

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 210 Table 4: *Pseudo*-first order kinetics for the sorption of CuPc dye, calculated using Natarajan and Khalaf
 211 equation [9].
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C _i (mg L ⁻¹)	k (min ⁻¹) × 10 ⁻³	r ²
30	4.606	0.622
50	7.830	0.597
70	8.291	0.633

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215 The result indicates that the rate constant increases with increase in initial concentration. But the linear
 216 correlation as shown in the table 4 above is not close to unity, this shows that the sorption studies of CuPc
 217 dye on TiO₂ cannot be explained by pseudo first order kinetics. Hence the data's were further analysed by
 218 pseudo- second order kinetics.

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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226 Where k₂ is the pseudo second order constant in gm⁻¹min⁻¹, q_e and q are the amount of dye absorbed in
 227 mg g⁻¹ at equilibrium while t is the time in minutes. Table 5 shows pseudo second order plot for the
 228 adsorption of CuPc dye for initial dye concentration of 30, 50 and 70mgL⁻¹ respectively. It was observed
 229 that the regression value obtained for pseudo- second order reaction has a higher value and it all falls in the
 230 range of 0.9133 to 0.9724 which is close to unity. This indicates that the sorption of CuPc dye obeys the
 231 second order reaction which indicates that an ester was formed with the TiO₂ powder in the process
 232 (chemisorption) This shows a similar result obtained for the sorption of methylene blue onto risk husk by
 233 V. Vadivelan and K. Vasanth Kumar [10] Ho [11] also reported a similar result for the sorption kinetics of
 234 copper ion using fern as an adsorbent, in both case the sorption kinetics obeys a *pseudo*- second order as
 235 obtained in this work. The values of k₂, regression and maximum dye absorption are shown in the table
 236 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 TiO₂ required remove CuPc from a solution

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There is a need to know the amount of TiO₂ 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 TiO₂ powder surface with time i.e. 12.00 mg g⁻¹ to 19.86 mg g⁻¹, these also support the fact that the adsorption capacity of the titanium dioxide is affected by operating condition of the research [12]. Therefore as the colour is removed from the solution it gets soaked onto the TiO₂ 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 ⁻¹]	Error (mg L ⁻¹)	% of dye Absorbed	qt [mg g ⁻¹]
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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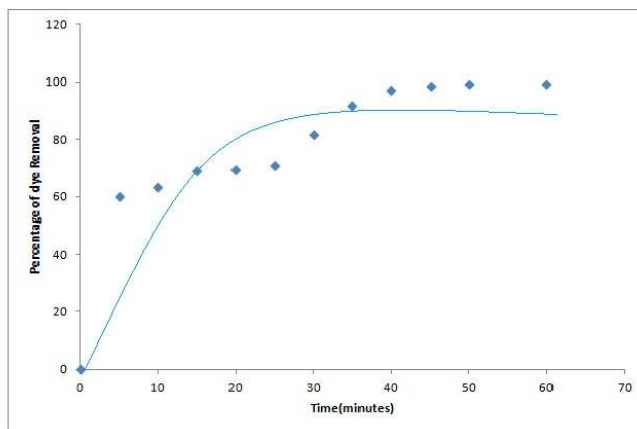


Figure 7: graph of percentage of dye absorbed against time for CuPc

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

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This studies shows that TiO_2 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_2 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_2 involves the formation of multi-layer and a maximum absorption capacity of 19.86 mg g^{-1} . 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 0.579 mg g^{-1} in less than one hour. This shows that TiO_2 powder may be effectively used for the clean-up of CuPc dye from effluents.

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