ChemSearch Journal 15(1): 39 – 49, June, 2024
Publication of Chemical Society of Nigeria, Kano Chapter

Received: 28/09/2023 Accepted: 01/03/2024
http://www.ajol.info/index.php/csj

Spectroscopic Profiles and Solubilisation Kinetics of Methylene Blue Dye in Unwholesome Liquid Detergents

[1*]Gyenvwot, I. Y., [1]Itodo, A. U., [1]Ande, S. and [2]Ogah, E.
[1]Department of Chemistry, Joseph Sarwuan Tarka University, Makurdi
[2]Department of Chemistry, Federal University of Health Sciences, Otukpo
***Correspondence Email:** uhinyohe@gmail.com

ABSTRACT

The spectroscopic profiles and solubilisation kinetics of Methylene blue in unwholesome liquid detergents was carried out using mechanical shaker and BK-UV 1900 PC Scanning Spectrophotometer. Sodium dodecyl benzene sulphonate (SDBS) served as control (1), while the registered Potential fabric wash (PFW) served as control (2). Test fabric wash (TFW), test car wash (TCW), test dish water (TDW) and test toilet wash (TTW) were used as unwholesome liquid detergents. Pieces of white cotton fabrics were stained with known concentration of MB and solubilised with known concentrations of the liquid detergents. The effects of dye dosage, detergent dosage, contact time, detergency, solubilisation kinetics and percent weight lost were studied. Data from the research showed that the extent of solubilisation of dyes increased with increasing initial MB and detergents concentrations. The solubilisation kinetics was determined using pseudo first and second order kinetic models. The percent removal of dye from white cotton fabrics using individual detergents at equilibrium times gave the following result in that order: SDBS(99.60) > PFW(67.13) > TFW(62.30) > TDW(45.52) > TTW(37.93) > TCW(21.38). Kinetic studies of the detergents revealed that 2nd order kinetics was relatively more effective for describing the whole detergents solubilisation process. Percent fabric lost showed that all unwholesome liquid detergents have high percent loss ranging between 1.36-2.97 as compared with the registered PFW(0.49) detergent. The present work aims to examine the solubilisation of methylene blue dye in registered and unwholesome liquid detergents concerning detergents concentrations, dye/detergent dosage, contact time, detergency, weight loss and solubilisation kinetics of dye in known concentrations and their (registered and unwholesome liquid detergents) solubilisation efficiencies compared. The results showed that NAFDAC registered (PFW) liquid detergent showed better percent active ingredient, concentration, detergency and washing efficiency than all the unwholesome liquid detergents.

Keywords: Detergent, Kinetics, Methylene blue, Sodiumdodecylbenzenesulphonate, Solubilisation

INTRODUCTION

Unwholesome (substandard) laundry liquid detergents are liquid detergents whose quality are regarded as below the usual or required standard, and are not registered by the National Agency for Food, Drug Administration and Control (NAFDAC) yet are sold and patronized in the market. NAFDAC prevent the dumping of substandard and unwholesome regulated products in Nigeria (NAFDAC, 2004).

Infringing products are no longer limited to falsely branded items such as fashion clothing, luxury watches and designer sunglasses, but now include a growing number of common food and drink, pharmaceutical, chemical, electronic and household products. These products, which are often substandard, can pose significant health and safety risks to consumers (OECD, 2008).The United States Pharmacopoeia defines a substandard product as a 'legally branded or generic product, but one that does not meet international standards for quality, purity, strength or packaging' (Smine, 2002). It therefore became necessary to investigate the quality of some of these liquid detergents used for car wash, kitchen wash, toilet wash and fabrics wash by comparing with the approved standard.

Laundry detergents are complex formulations incorporating a range of functional ingredients that may include surfactants, buffers, chelating agents, enzymes, polymers, fragrances and optical brighteners (Copley, 2017). Laundry detergent has traditionally been a powdered or granular solid, but the use of liquid laundry detergents has gradually increased over the years, and nowadays uses of liquid detergent equals or even exceeds the use of solid detergent (Bajpai and Tyagi, 2007). Surfactants are wetting agents that lower the surface tension of a liquid, allowing easy spreading, and can also lower the interfacial tension between two liquids (Manisha *et al*., 2009). The efficient removal of loosely bound dyes from the substrate via solubilisation and the adsorption and fixation of dyes on a substrate highly depend

on the strength of binding between dyes and the host as well as the extent of dye solubilisation in the surfactant containing solution (Tehrani-Bagha *et al*., 2013). The study of dye/surfactant interaction is the source of useful information to understand several industrial processes, for example, solubilisation processes to remove the organic compounds from aqueous solution and the use of surfactants to assist dying processes in textile industry (Gul *et al*., 2010).

This research work was focused on some commercial unwholesome liquid detergents. They were used to solubilize cationic methylene blue dye and asses their qualities. The dye was used to stain some pieces of cotton fabrics and solubilised in the dilute samples of each detergent. The dye concentration was determined alongside the active ingredient of the liquid detergents before solubilisation.

The aim of this research is to study spectroscopic profiles, and effect of concentration of dye/detergents on solubilisation kinetics of methylene blue dye by some unwholesome liquid detergents.

MATERIALS AND METHODS

Sampling and Sample Treatment

Laboratory grade MB cationic dye and SDBS (control) were purchased at SUNLABI Nigeria Limited chemical store in Jos. The one brand commercial registered liquid detergent Potential Fabric Wash (PFW) made by Unilever UK limited Springfield Drive, Leatherhead, Ireland was purchased at Onigbinde retail shop in Jos. Ingredients of registered PFW on label were: anionic surfactant (5 – 15%), non-ionic surfactant (< 5%), optical brighteners, perfume, phosphate, among others. The four brands of commercial unwholesome liquid detergents, Test Fabric Wash (TFW), Test Car Wash (TCW), Test Dish Wash (TDW) and Test Toilet Wash (TTW) were purchased at Bokkos market, Plateau State, Nigeria. All samples were prepared in desired concentrations for routine laboratory bench work using distilled water and routine laboratory materials. All samples acquired were used without further purification.

Sampling of Fabrics

A piece of white cotton fabric and the dyed textile fabric material used for staining and weight-loss experiment respectively, were purchased at a retail fabric shop in Jos market and used without further pre-treatment.

Preparation and Cutting of Fabrics

The white cotton fabric of equal thickness and dimension was used throughout the experiment. Pieces of the cotton fabric were cut of the dimension 5 cm x 5 cm using measuring tape and scissors for solubilisation, kinetics and thermodynamic experiments. The dyed textile fabric material was cut 12 x 12 cm for weight loss experiment (Ecolabel, 2018).

Preparation of Stock and Standard Solutions

Methylene blue dye stock and standard solutions preparations

The stock solution (1000 mg/L) of the methylene blue dye was prepared by dissolving 1.00 g of the dyes in distilled water and made up to mark in 1000 mL volumetric flasks. All working solutions of the desired concentrations were prepared by diluting the stock solutions with distilled water (Nethaji *et al.*, 2013).

Liquid detergent stock and standard solutions

Stock solution 1000 ppm SDBS was prepared by weighing 1.00 g of SDBS and made up to mark in a 1000 mL volumetric flask for calibration and concentration determination. Standard working solutions of blank, 5, 10, 15, 20, 25 and 30 ppm concentrations were prepared from the stock solution in 100 mL standard flasks. Same procedure was repeated for registered and the four unwholesome liquid detergents in each case. These were used for calibration and initial concentration determination of each detergent.

Stock solution of 200,000 ppm was prepared by weighing 200 g of SDBS and solution made up to mark in a standard 1000 L volumetric flask. The same procedure was carried out using PFW, TFW, TDW, TCW and TTW liquid detergent samples. Dilution of 100 mL each of 1000, 5000, 10000, 15000 and 20000 ppm each of all the detergents were prepared from their individual stock solutions using the laboratory routine methods, and used for solubilisation purposes only.

UV-Visible Spectroscopic Profile of Dye

The method of Khan *et al.* (2014) was employed. Unknown concentration of the dye was determined by finding out the absorbance at the characteristic wavelength using a BK-UV1900PC Scanning UV-Visible spectrophotometer with a matched pair of quartz cuvettes (1 cm in optical path length). Standard calibration charts were prepared by measuring the absorbencies of different detergent concentrations for the unknown concentration of the detergents before solubilisations were carried out (Nethaji *et al.*, 2013).

Determination of maximum wavelength (λ_{max}) for detergents and dyes

From the different working concentrations prepared earlier for SDBS, registered and unwholesome liquid detergents, 20 ppm each of the concentrations was used to determine their various λ_{max} for active ingredient using UV-Visible spectrophotometer. The SDBS concentration was determined by scanning 20 ppm solution using UV–Visible spectrophotometer and maximum

wavelength was obtained at 223 nm (Taffarel and Rubio, 2010). The procedure above was repeated for PFW, TFW, TDW, TCW and TTW liquid detergents. The same method was used for the determination of λ_{max} for the dyes.

UV- Visible Spectroscopic Profile of Liquid Detergents

All absorption spectra of the dye and detergent individual solutions in the UV–Visible region were measured using the UV–visible spectrophotometer (BK-UV1900PC). All measurements were taken at 298 K, with an accuracy of ±0.5 K. A squared shaped measuring cell (cuvette) made up of quartz, with a thickness of 1.0 cm, was used for UV–Visible studies. The absorption "slit width" for the spectrophotometer was kept constant at 1.0 nm throughout the study. To measure the simple absorption spectra of dye or surfactant, first, distilled water was used as the blank and aqueous stock solution of known concentration dye was used to solubilise with corresponding concentration of the detergent solution (Khan *et al*., 2014).

Unknown concentrations of the detergents were determined by finding out the absorbance at the characteristic wavelength using the UV–visible spectrophotometer (BK-UV1900PC). Standard calibration charts were prepared by measuring the absorbance of different detergents concentrations at (λ_{max}) 223 nm for SDBS, PFW, and the other four unwholesome detergents. The unknown concentrations determined before solubilisation were computed from the calibration charts (Nethaji *et al.*, 2013; Singh, 2012).

Staining and Solubilisation Experiment

The amount of dye study on solubilisation was carried out at various initial concentrations of dye for a definite surfactant concentration and at a specific temperature (25°C) (Khandelwal *et al*., 2020)

The cotton fabric was stained with known concentration of the dye and a known concentration of the surfactant solution was added, the mixture was kept under stirring for 2 hours, then the solubilised dye was removed and the absorbance measured. The absorption of the solution was recorded in a UV-Vis spectrophotometer (BK-UV1900PC) and the concentration of solubilised dye was determined from the calibration curve (Tehrani-Bagha *et al*., 2013).

The cut pieces of cotton fabrics of equal diameter were stained with eight drops each of 1000 ppm of the methylene blue dye sample. The stained fabrics were allowed to air-dry for 24 h. From the prepared solutions earlier, 100 mL of blank, 1000, 5000, 10000, 15000 and 20000 ppm of SDBS detergent in 250 mL conical flask and one (8 drops) stained fabric placed in each flask containing different detergent concentrations. The solutions were agitated for 2 h with mechanical shaker at 120 rpm at room temperature of 298K (Mondal *et al.,* 2018). The aliquots were taken for precise measurement for dye at wavelength set at 662 nm. The absorption of the aliquots was measured with UV spectrophotometer. The concentrations of the aliquots were calculated for dye using the calibration curve for dye. The above procedure was repeated for all the detergent samples.

Solubilisation Kinetic Experiment

The kinetics of solubilisation of methylene blue dye by SDBS was carried out by placing 8 dried dye spots fabric in 100 mL of 10000 ppm SDBS. The flasks were shaken in a thermostatic mechanical shaker at 25°C, withdrawn from the shaker and analysed (Mondal *et al*, 2018). The solution was repeatedly agitated, withdrawn and analysed at the time interval of every 5 min for the first 20 min and later at every 10 min at 298K until the consecutive solubilised dye concentrations became closer (Nethaji, 2013). The experiment was repeated using PFW, TFW, TDW, TCW and TTW. The solution was agitated, withdrawn and analysed at different times for a fixed 10000 ppm concentration of each detergent for the effect of contact time and kinetics studies. The kinetic data for the solubilisation of the dye from fabric after solubilising with the liquid detergent using the one initial dye concentrations of 8 dried fabric spots were tested using pseudo first-order model and pseudo second-order model (Nethaji *et al.*, 2013).

RESULTS AND DISCUSSION

UV-Visible Spectroscopic Spectra of Methylene Blue and Sodium Dodecyl Benzene Sulfonate (SDBS)

The spectra determined for MB and SDBS to obtain their individual wavelengths were carried out and their respective maximum wavelengths using UV-Visible spectrophotometer are shown in Figure 1 and Figure 2 respectively. Determination of methylene blue maximum wavelength was measured at 400 – 800 nm. The result showed that photon energy can be absorbed maximally at 662 nm. It means at this wavelength, photon emitted by spectrophotometer was absorbed in the solution maximally. While that of SDBS was measured at 205-240 nm and found to absorbed maximally at 223 nm (Taffarel and Rubio, 2020).

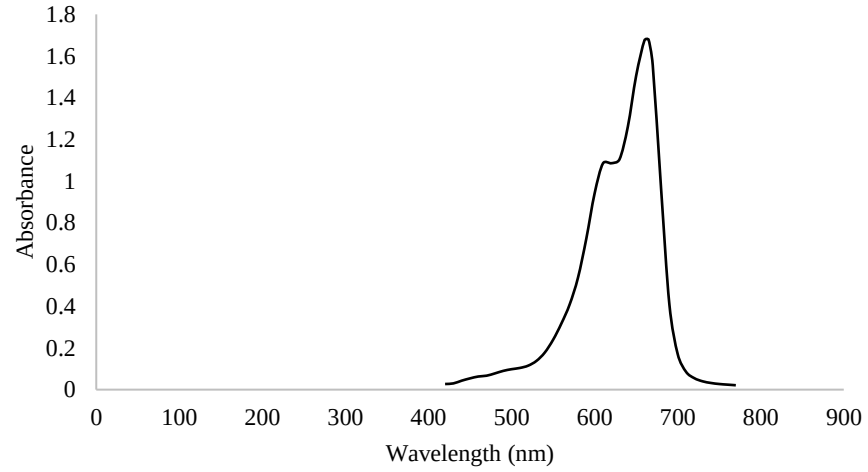

Figure 1: UV-Visible Spectroscopic Spectrum of Methylene Blue (λ_{max} 662 nm)

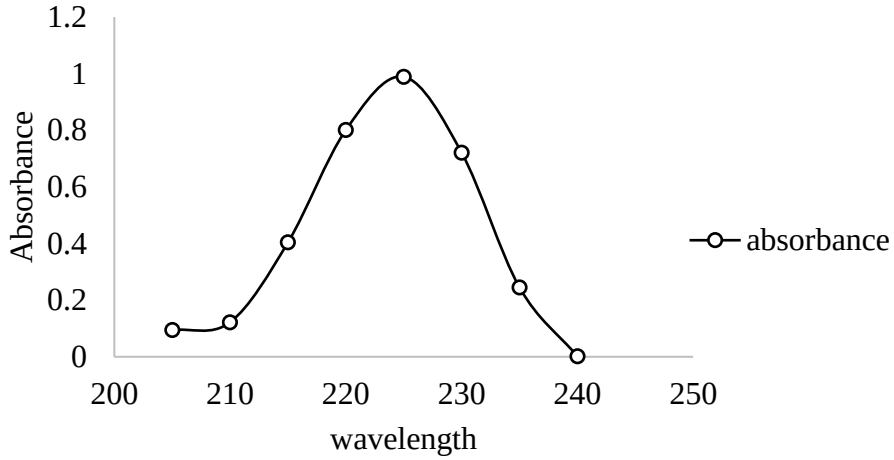

Figure 2: UV-Visible Spectroscopic Spectrum of Detergents (λ_{max} 223 nm)

Effect of Initial Concentrations of all Detergents

The actual initial concentrations (ppm) of individual detergents at 1000 ppm were determined using the dilution factor equation:

$$C_1V_1 = C_2V_2 \quad (1)$$

Table 1 includes the calculated initial concentrations (ppm) of all detergents and percent active ingredient at 1000 ppm. The table showed that SDBS (996 ppm) > PFW(125.5 ppm) > TFW(111.5) > TDW&TTW(6.03) > TCW(5.90). The percent active ingredient was similarly determined to be SDBS(99.6%) > PFW(12.55%) > TFW(11.15%) > TDW and TTW(6.03%) > TCW(5.89%). The percent active ingredient in PTW and TFW is agreement with standard proposed by Millera *et al*. (1993) to be at a range of 10-40%, but PFW showed better active ingredient.

Table 1: **Effect of Initial Concentrations (1000 ppm) and Percent Active Composition of all Detergents Using SDBS Calibration Curve**

Concentration (ppm)	SDBS	PFW	TFW	TCW	TDW	TTW
1000	996	125.5	111.5	58.95	60.25	60.25
%Anionic Surfactant	99.60	12.55	11.15	5.90	6.03	6.03

Table 2 Effect of Initial Concentrations (ppm) on Absorbance Readings and Regressions of all Detergents

Concentration (ppm)	Abs SDBS	Abs PFW	Abs TFW	Abs TDW	Abs TCW	Abs TTW
blank	0.00	0.00	0.00	0.00	0.00	0.00
5	0.182	0.028	0.024	0.012	0.014	0.013
10	0.410	0.051	0.045	0.024	0.025	0.025
15	0.607	0.073	0.064	0.035	0.035	0.036
20	0.777	0.098	0.087	0.047	0.046	0.047
25	0.985	0.120	0.110	0.056	0.057	0.059
30	1.184	0.145	0.134	0.070	0.069	0.070
R^2	0.999	0.999	0.9992	0.9994	0.9987	0.9984

Effects of Dye Dosage

Absorbance readings of solubilised fabric spots of MB by all detergents for the effect of dye dosage at 25ºC are shown in Table 3. The dye spots on the fabric were increased from 1 to 10. The result showed the increase in absorbance in each detergent as the dye spots increases.

The listed data in Table 3 showed the solubilisation of stained fabric spots of MB by 10,000 ppm of the SDBS detergent, absorbance increased from 0.052 to 0.526 as the initial dye concentration increased from fabric stained spot of 1 to 10 at 25 ºC. Results obtained for PFW higher than the unwholesome detergents. They showed similar absorbance and similar solubilisation efficiencies. The solubilisation extent of dyes was increased with an increase in the initial MB concentration due available active sites under concentration condition of detergent. The results show that among the five detergents, PFW solubilised better than the unwholesome detergents due to their high concentration.

Table 3 : **Effect of Dye Dosage on Absorbance Readings of Solubilised Fabric Spots of MB by all Detergents**

Abs Spots	SDBS	PFW	TFW	TCW	TDW	TTW
Blank	0.00	0.00	0.00	0.00	0.00	0.00
1	0.05	0.035	0.031	0.011	0.024	0.020
2	0,105	0.071	0.062	0.021	0.047	0.039
4	0.208	0.140	0.125	0.045	0.096	0.081
6	0.316	0.212	0.187	0.067	0.145	0.120
8	0.427	0.279	0.272	0.089	0.194	0.160
10	0.526	0.350	0.312	0.121	0.241	0.210

Effect of Detergent Dosage

The experiment data is given in Table 4. As the concentration of detergents increased, the solubilisation rate of MB gradually increased due to the increase of the number of active sites on detergents. At high detergent dosages, the available number of MB dye molecules in solution was enough to completely combine with all effective active sites on the detergent, resulting in a surface equilibrium state and a reduction in the solubilisation capacity per unit concentration of solubilisation.

The results showed that absorbance of dye solubilised by PFW showed high than the unwholesome detergents. At 10000 ppm detergent dosage, the solubilisation is as follow: SDBS(0.428) > PFW(0.265) > TFW(0.176) > TDW(0.174) >TCW(0.143) >TTW(0.133). The results showed that PFW solubilised better than the unwholesome detergents.

Table 4: Effect of Detergent Dosage on Absorbance readings of solubilised MB dyed fabric using various detergent concentrations

Concentration (ppm)	Blank	SDBS	PFW	TFW	TCW	TDW	TTW
1000	0.00	0.385	0.043	0.034	0.021	0.022	0.027
5000	0.00	0.418	0.127	0.106	0.064	0.056	0.052
10000	0.00	0.428	0.265	0.176	0.143	0.174	0.133
15000	0.00	0.427	0.349	0.265	0.228	0.245	0.241
20000	0.00	0.429	0.428	0.333	0.267	0.314	0.354

Effect of Contact Time

Table 5 showed the relationship between the solubilisation of MB by all detergents as a function of time at fixed initial detergents concentrations of 10,000 ppm each. It can be seen that the solubilisation of MB by detergents was increased with an increase in time and then reached a maximum value. The process was divided into two phases. The first step took 5–40 min to reach the relative solubilisation equilibrium state called

fast solubilisation in all detergents except in TTW which took 5-20 min. The difference could be due to stain removal that could have been introduced in toilet wash detergents. This performance was due to the binding process between MB dye and the detergent active sites, and functional groups on the detergents were fully and efficiently completed. The solubilisation rate of the dye was controlled by the rate of the dye transported from the dyed fabric to the surface of the detergent particles in the solution.

The second step is called slow solubilisation process. After 40 min of contact time, the relative increase in the removal extent of MB was not significant, and with the increase over time, the solubilisation rate decreased and gradually stabilised. This performance was due to the binding process between MB dye and the solubilisation active sites, and functional groups on the detergents were gradually saturated. The solubilisation rate of the dye was controlled by the rate of the dye transported from the exterior to the interior pore sites of the detergent particles. Moreover, the lower the dye initial concentration, the shorter the time to achieve the solubilisation equilibrium state. The contact time was observed to be 80 min for SDBS and 110 min for the remaining detergents except for TTW which was found to be 50 min. Among the five sample detergents, solubilisation decreased from SDBS to PFW > TFW > TTW. Thus, PFW solubilised better.

The amount of MB solubilised at time t (mg/g), q_t, by detergents were calculated by a mass balance relationship, adopted by Mondal *et al*. (2018) as shown by equation (2).

$$q_t = \frac{(Co - Ct)V}{m} \quad (2)$$

At equilibrium time, the amount of MB absorbed, q_e (mg/g), was calculated using equation (3),

$$q_e = \frac{(Co - Ct)V}{m} \quad (3)$$

where, C_o is the initial dye concentration in the solution (mg/L); C_t is the residual dye concentration in the solution at any time t (mg/L); C_e is the residual dye concentration in the solution at equilibrium time (mg/L); V is the solution volume (L), and m is the mass of detergent (g). Concentrations (mg/L) of solubilised dyed fabric by individual detergent concentrations at equilibrium times (Co-Ce) are shown in Table 5. The result showed the trend of concentration at contact time as follow: SDBS (746.35) > PFW (503.45) > TFW (467.24) > TDW (341.38) > TTW (284.48) > TCW (160.34).

Table 5: Effect of contact time on the concentration of solubilised MB dyed fabric using fixed detergent concentration

Time (min)	**SDBS**	**PFW**	**TFW**	**TCW**	**TDW**	**TTW**
0	0.00	0.00	0.00	0.00	0.00	0.00
5	401.71	334.48	110.34	29.31	74.14	224.14
10	577.59	381.03	196.55	60.34	146.55	248.28
15	617.24	403.45	275.86	77.59	167.24	256.90
20	634.48	417.24	312.07	87.93	194.83	265.52
30	670.69	429.31	353.45	101.72	224.14	272.41
40	696.55	439.66	394.83	115.52	253.45	279.31
50	722.41	451.72	415.52	118.97	263.79	284.48
60	734.48	460.34	425.86	134.48	287.93	284.48
70	744.83	468.97	446.55	139.66	303.45	282.76
80	746.55	475.86	456.90	146.55	315.52	282.76
90	746.55	484.48	463.79	153.45	318.97	284.48
100	746.28	491.38	465.52	156.90	322.41	281.03
110	748.83	503.45	467.24	160.34	341.38	282.76
120	748.28	505.17	465.52	158.62	343.10	281.03
130	748.28	503.45	467.24	160.34	341.38	284.48

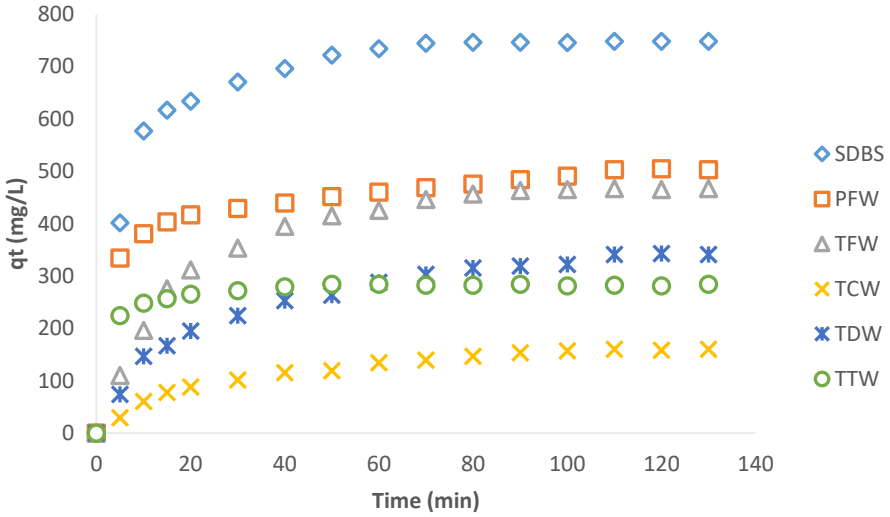

Figure: Plot of Concentrations (ppm) at Equilibrium Times as a Function of Time

Detergency (Percent Removal) of Dye

The percentage removal of the dye was calculated using equation (5) adopted by Mondal *et al*. (2018):

$$\text{Dye removal (\%)} \frac{(Co-Ce)\ x\ 100}{Co} \qquad (5)$$

where, C_0 is the initial dye concentration in the solution (mg/L); C_t is the residual dye concentration in the solution at any time t (mg/L); C_e is the residual dye concentration in the solution at equilibrium time (mg/L).

The percent removal of dye (detergency) by individual detergents at equilibrium times are shown in Table 6. The percent removal followed the trend: SDBS (99.60) > PFW (67.13) > TFW (62.30) > TDW (45.52) > TTW (37.93) > TCW (21.38). The remaining three unwholesome detergents are the least. Thus, PFW meet the minimum percent quality detergent. The detergency result is agreement with the findings of (Hemalatha *et al*., 2018) of 65% as grade 1 detergent.

Table 6: Percent Removal of Dye (Detergency) by all Detergents at Different Equilibrium Times

Time (min)	%SDBS	%PFW	%TFW	%TCW	%TCW	%TTW
0	0.00	0.00	0.00	0.00	0.00	0.00
5	53.56	44.60	14.71	3.91	9.89	29.89
10	77.01	50.80	26.21	8.05	19.54	33.10
15	82.30	53.79	36.78	10.34	22.30	34.25
20	84.60	55.63	41.61	11.72	25.98	35.40
30	89.43	57.24	47.13	13.56	29.89	36.32
40	92.87	58.62	52.64	15.40	33.79	37.24
50	96.32	60.23	55.40	15.86	35.17	37.93
60	97.93	61.38	56.78	17.93	38.39	37.93
70	99.31	62.53	59.54	18.62	40.46	37.70
80	99.54	63.45	60.92	19.54	42.07	37.70
90	99.54	64.60	61.84	20.46	42.53	37.93
100	99.54	65.52	62.07	20.92	42.99	37.47
110	99.54	67.13	62.30	21.38	45.52	37.70
120	99.54	67.36	62.07	21.15	45.75	37.47
130	99.53	67.13	62.30	21.38	45.52	37.93

Solubilisation Kinetics and Rate Constants Comparison

The kinetic data for the solubilisation of MB by five different detergents initial concentrations of 1000, 5000, 10000, 15000 and 20000 ppm were tested with the well-known kinetic models namely pseudo first order model and pseudo second-order model. The list data calculated for pseudo first-order is shown in Table 7. While the plot of Figure 3 shows the pseudo first-order kinetics of solubilisation for all detergents. The result showed that the pseudo first – order of all detergents are non-linear. The results of R^2 determined were in the range of 0.9561–0.9919, slightly far from 1. While the pseudo second-order are linear with determined correlation coefficients (R^2) closer to 1 (0.9963 – 0.9998). The linearity of the plots shows the pseudo second -

order kinetics of solubilisation and the values of rate constant determined from the slope values are reported in Table 7. Figures 4 and 5 showed the plot of values for the second-order of SDBS and the remaining detergents respectively. The values of rate constant of pseudo first-order are determined from the slope values, reported and compared with pseudo second – order rate.

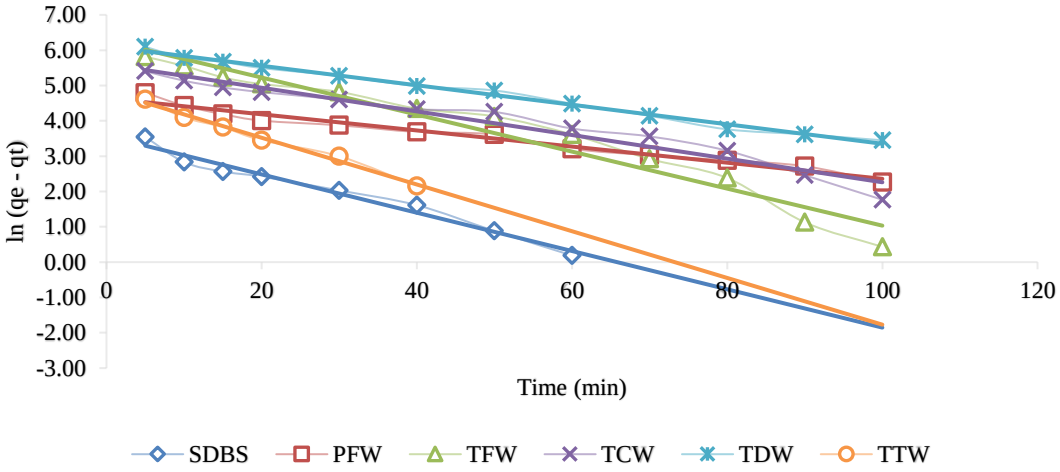

Figure 3: Plot of Pseudo First-Order Model (ln (q_e-q_t) of Solubilised MB Stained Fabric by all Detergents as a Function of Time

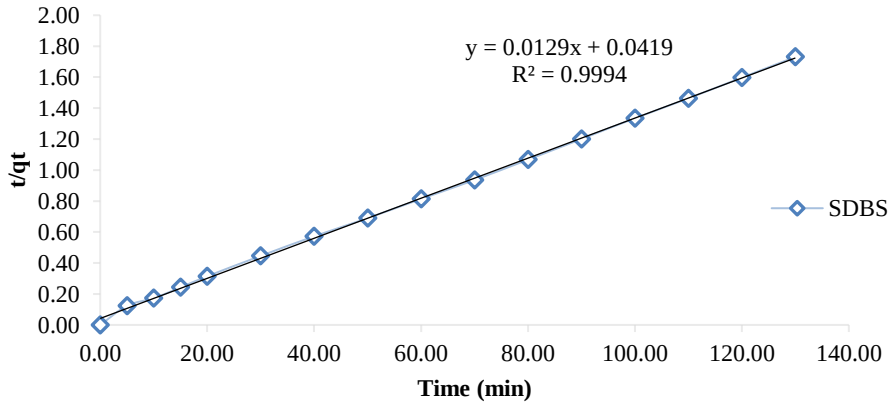

Figure 4: Plot of Pseudo Second-Order Model (t/q_t) of Solubilised Fabric spots of MB by SDBS Surfactant as a Function of Time

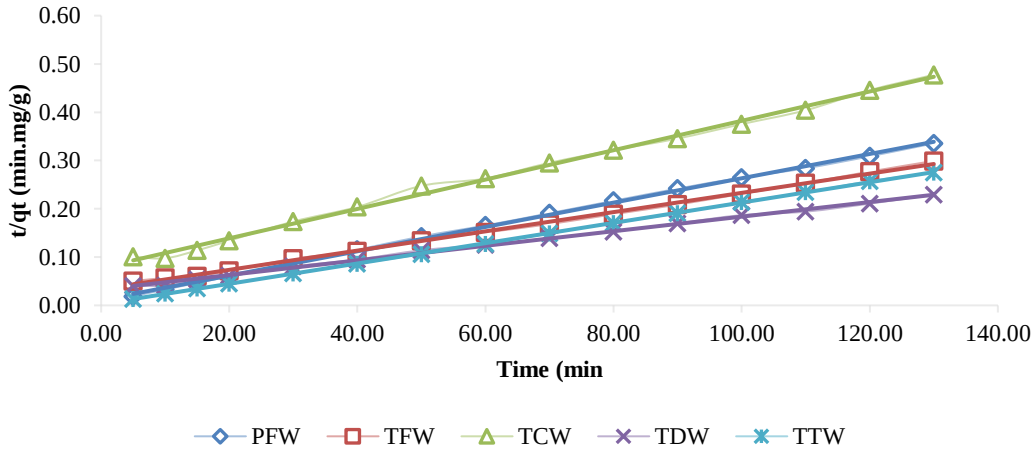

Figure 5: Plot of Pseudo Second-Order Model t/q_t (min. mg/g) of Solubilised Fabric Spots of MB by PFW, TFW, TCW, TDW and TTW Detergents as a Function of Time

Pseudo first-order model

The principle of the pseudo-first-order kinetic model is that the reaction rate is proportional to the number of ions remaining in the solution, assuming that adsorption is controlled by diffusion steps. It is assumed that the adsorption rate is proportional to the difference between the saturated concentration and the adsorption amount of dye with time. The integral equation is shown below in Equation:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

where k_1 is the rate constant of adsorption (min^{-1}), q_e is the quantity of dye adsorbed (solubilised) at equilibrium (mg/g), and q_t is the equilibrium concentration at various times t (in mg/L). The rate constant in this model was determined by the slope of the plot of ln (q_e- q_t) over time (t) (Nethaji *et al*., 2013, Kuang *et al*., 2020).

The plot of Figure 3 shows the pseudo first order kinetics of solubilisation. The values of rate constant calculated from the slope values are reported and compared with pseudo second – order in Figure 5. The result showed that the pseudo first – order is non-linear. The results of R^2 determined were in the range of 0.9561–0.9919, slightly far from 1. In addition, the lower value of R^2 indicated that the pseudo-first order model was not an effective model to explain the solubilisation process.

Pseudo second-order model

The solubilisation kinetics can also be described by pseudo second-order model. The linear form of pseudo second-order equation is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

Where k_2 (g/mg min) is the equilibrium rate constant of pseudo second-order solubilisation. Equation (7) does not have the problem of assigning an effective q_e. Application of the pseudo second-order kinetic equation, the plot of t/q_t against t should give a linear relationship, from which q_e and k_2 can be determined from the slope and intercept of the plot (Bulut and Ozacar, 2008; Nethaji *et al*., 2013; Kuang *et al.*, 2020).

Figure 5 showed the correlation coefficients (R^2) of all detergents were found to be much closer to 1 (0.9963 and 0.9998 respectively). s This showed that the micelles of all detergents are spontaneously formed with the addition of more surfactant leading to increasing the micellar concentration or the micellar growth in the bulk of the surfactant solution and thereby enhancing the rate of solubilisation by accommodating more dye molecules. This behaviour indicated that the pseudo-second order model was the best model to explain the solubilisation process of MB by all detergents.

Table 7: Report procedure under Constants (k) and q_e Values for Different MB Concentrations by all Detergents

		Pseudo First Order			Pseudo Second Order		
Det.	**Co(mg/L)**	**q_e,(mg/g)**	**R^2 1**	**k_1 (1/min)**	**q_e**	**R^2 2**	**k_2 (mg/L/min)**
SDBS	750	3.57	0.9746	-0.054	0.004	0.999	0.999
PFW	750	4.64	0.9725	-0.023	0.011	0.998	0.003
TFW	750	6.27	0.9579	-0.052	0.034	0.998	0.002
TCW	750	5.61	0.9561	-0.033	0.078	0.996	0.003
TDW	750	6.11	0.9919	-0.028	0.032	0.997	0.002
TTW	750	4.84	0.9884	-0.066	0.003	0.999	0.002

Effect of Fabric Weight Lost

Table 8 showed the result of percent weight lost experiment. SDBS, which is an analytical grade sulphonic acid, have the highest percent loss of 7.40, the blank test being the least of about 0.165. The result showed that all unwholesome liquid detergents have high percent lost, ranging from TCW (2.97) to TTW (1.36), while PFW registered product has very low percent lost. Thus, unwholesome detergents have high bleaching effect, though in agreement with findings Uddin, (2018) (3-6%) than PFW (0.49) registered product

Table 8: Percent Fabric Weight Lost

Weight (g)	**BLANK**	**SDBS**	**PFW**	**TFW**	**TCW**	**TDW**	**TTW**
Initial Weight (g)	0.605	0.608	0.609	0.699	0.640	0.636	0.589
Final Weight (g)	0.604	0.563	0.606	0.679	0.621	0.625	0.581
Difference (g)	0.001	0.045	0.003	0.020	0.019	0.011	0.008
%Weight Lost	0.165	7.40	0.49	2.86	2.97	1.73	1.36

Bleaching is a destructive process where the colour producing molecules are destroyed by oxidation. It also destroys oil and dirt residues left form the scouring process. The textile fibre can also be attacked by the bleaching process resulting in fibre damage. This fibre damage can be severe if the process is not well controlled (Cotton Incorporated, 2012).

Comparative Study

Comparative study of solubilisation profiles of MB dye by all detergents is shown in Table 9. The table showed better results in SDBS followed by PFW, TTW, TDW&TTW and lastly TCW.

Table 9: Comparative Study (Summary)

Parameters	SDBS	PFW	TFW	TCW	TDW	TTW
Concentration (ppm)	9600	125.5	111.5	58.95	60.25	60.25
%Active Surfactant	96.00	12.55	11.15	5.90	6.03	6.05
Detergency	99.54	67.13	62.30	21.38	45.52	37.9
Effect of Det. Initial Conc.	Very Good	Good	Fair	Poor	Fair	Fair
Effect of Dye Dosage	Very Good	Good	Fair	Poor	Fair	Fair
Effect of Det. Dosage	High	Good	Fair	Poor	Fair	Fair
Effect of Contact Time (min)	80	110	110	110	110	50
1st Order Kinetics	Non-effective for the whole detergents					
2nd Order Kinetics	Effective for the whole detergents					
% Fabric Weight Loss	7.4	0.49	2.86	2.97	1.73	1.36

CONCLUSION

The solubilisation rate of Methylene blue at different concentrations by all detergents tested was achieved by uv-visible spectroscopic tests. The present study in Bokkos, Plateau State, Nigeria, was carried out by comparative analysis of five (PFW, TFW, TCW, TDW and TTW) brand of liquid detergents in terms of their quality/concentration, detergency, cleaning action and weight loss/bleaching effects. The parameters tested were: solubilisation profiles, effect of dye dosage, effect of detergent dosage, kinetic models, effect of temperature and weight loss experiment. The concentration/percent active ingredients determined the quality of a detergent. Among the five liquid detergents investigated in solubilising the MB dye, it showed that NAFDAC PFW (12.55%) detergent show the highest percent active ingredient than the unwholesome detergents. UV-Vis spectroscopic investigation on effect of contact time, detergent (concentration) dosages enhances solubilisation detergency in all the detergents with PFW (67.13%) showing better detergency. This show that time is a very important factor in cleaning efficiency by detergents. Also increase in detergent concentration influences detergency. Thus the low detergency is shown in unwholesome detergents. Kinetic model investigation revealed that solubilisation of dye by all the detergents follow pseudo second-order kinetics. The constant rate values obtained with the increase of surfactant concentration clearly explains the role of surfactant concentration on the solubilisation of the dye. The constant values of rate constant with different amounts of dye shows the second-order dependence of solubilisation rate with respect to amount of dye. The rate of solubilisation of dye was higher in PFW than the unwholesome detergents because of lower active ingredient in the unwholesome liquid detergents. Though all the detergents except for SDBS control (7.40) were found to have percent weight loss within acceptable range of 3-6%, thus exhibiting acceptable bleaching effect. However, PFW showed better bleaching properties. It could be concluded that NAFDAC registered liquid detergent is better than unwholesome detergents which were found to show lower percent active ingredient, lower, concentration, lower detergency and poor solubilisation efficiencies. The study in the present detergent market could serve as an initiative to make the consumer more aware, so as to demand eco-friendly liquid detergents with good cleaning action, stain removing and less bleaching effect. This would pressurize the government/NAFDAC to place more stringent regulations and the manufacturers to sell detergents which are less bleaching, eco-friendlier, and have solubilisation efficiency with good cleaning performance. Informed public opinion would bring about stricter norms and regulations as in the western countries and bring better products in the market.

REFERENCES

Bajpai, D. and Tyagi, V. K. (2007). Laundry Detergents: An Overview Copyright by Japan Oil Chemists' Society *Journal of Oleo Science. 56(7):327-340.*

Bulut, E. and Ozacar, M. (2008). Adsorption of malachite green onto bentonite: equilibrium and kinetic study and process design**.** *Journal of Microporous and Mesoporous Materials*. 115 (3): 234-246

Cotton Incorporated (2012). Texile Dyeing. Http://www.cottoninc.com.World Headquarters 6399 Weston Parkway Cary, North Carolina 27513. Pp 13.

Copley, T. (2017) Testing Detergents: Establishing Efficient Methods for Formulation, 6QC and Comparative Assessment, *sofwjournal 143pp*

Ecolabel, (2018). Revised EU Ecolabel Protocol for Testing Laundry Detergents. Version 1.1/26.03.2018 pp 10.

Gul, F; Khan, A.M; Shah, S. S; and Nazar, M. F; (2010). Spectroscopic Study of Alizarin Red Binding with Cetyltrimethylammoniumbromide at Low Concentrations, *Coloration Technology, 126 (2): 109–113.*

Hemalatha, M; Hemasruthi, P; Gokila P. S; Gayathri, N; Kavinilavu, K. S. (2018). Formulation of Ecofriendly Detergent Powder Using Paddy Husk Ash *Asian Journal of Applied Science and Technology (AJAST) 2(4):70-78,*

Khan, A. Asim, M. Usman, M. Farooqi, Z. H. Zaman, K. Rauf, A. and Zada, A. (2014). The Interactions of Co-Solvent, Co-Solute and Amphiphilic Anionic Dye with Aqueous Solutions of Sodium Dodecyl Sulphate. *Walailak Journal of Science & Technology 12(12): 1107-1119.*

Khandelwal. M, Ampily. J.S and Sarasan, G. (2020).A Kinetic study on solubilisation of Sudan I dye by Sodium dodecyl sulphate Department of Chemistry, Holkar Science College, Indore (India) Department of Chemistry, R. Sankar Memorial SNDP Yogam Arts and Science College, Koyilandy, Calicut, Kerala (India).*Journal of Engineering Science, 11 (5): 26-33.*

Kuang, Y., Zhang, X. and Zhou, S. (2020). Adsorption of Methylene Blue in Water onto Activated Carbon by Surfactant Modification. *Water*, 12: 587;

Manisha, M., Muthuprasanna, P., K. Surya, P. P. Sobhita, R. P. Satishbabu, A. Sarath, C. I. Arunachalam, G. and Shalini, S. (2009). Basics and Potential Applications of Surfactants: A Review. *International Journal of Pharmaceutical Technological Research CODEN (USA): IJPRIF 1 (4): 1354-1365*

Millera, C. A., Kirk H. Raneyb, K. H. (1993). Solubilisation-emulsification mechanisms of detergency. Review. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 74, 169-215*

Mondal, A. K., Rabeya, T., Asad, M. A., (2018). Removal of methylene blue from wastewater using Fe_2O_3 as an adsorbent. *Indian Journal of Advances in Chemical Science 6(4): 200-204; 2320-0928*

NAFDAC (National Agency for Food and Drug Administration and Control) (2004) Laws of the Federation of Nigeria (LFN) Email nafdac@nafdac.gov.ng.

Nethaji, S; Sivasamy, A. and Mandal, A. B. (2013) Adsorption Isotherms, Kinetics and Mechanism for the Adsorption of Cationic and Anionic Dyes onto Carbonaceous Particles prepared from *Juglansregia* Shells Biomass. *International Journal Environmental Science Technology, 10:231-242.*

OECD (Organisation for Economic Co-Operation and Development) (2008).The Economic Impact of Counterfeiting and Piracy (www.oecd.org/publishing/corrigenda).

Singh, R. (2012) Solubilisation of Organic Dyes in Surfactant Micelles. Department of Chemical and Biological Engineering. Chalmers University of Technology. SE-412 96 Göteborg, Sweden.

Smine, A. (2002). Malaria Sentinel Surveillance Site Assessment. Mekong Region. United States Pharmacopoeia, Rockville, MD.

Taffarel, S. R; Rubio, J. (2010) Adsorption of sodium dodecyl benzene sulfonate from aqueous solution using a modified natural zeolite with CTAB. *Journal of Minerals Engineering, 23 (2010): 771–779.*

Tehrani-Bagha, A.R.; Singh, R.G.; Holmberg, K. (2013) Solubilisation of two organic water-insoluble dyes by anionic, cationic and non-ionic surfactants. *Colloid Surface Journal, 417: 133–139*.

Uddin, M. G. (2010). Determination of Weight Loss of Knit Fabrics in Combined Scouring-Bleaching and Enzymatic Treatment. *Journal of Innovation and Development Strategy, 4(1):18-21*.