

Decolourisation of Methylene Blue in Aqueous Solution using Locally Sourced Photocatalysts via UV Irradiation Photocatalytic Degradation

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Abstract

Locally sourced periwinkle shell ash (PSA) and snail shell ash (SSA) were investigated as potential photocatalysts for the photocatalytic decolourisation of methylene blue in aqueous solution. Preliminary studies showed that PSA performed better than SSA hence it was adopted for further investigations. The effects of process variables such as irradiation time, initial dye concentration and catalyst dosage on the decolourisation process were evaluated. The optimum values of the process variables were: irradiation time, 50 minutes; initial dye concentration, 7 mg/L and PSA dosage, 2 g/L. The adsorption equilibrium was well described by the Langmuir isotherm equation ($R^2=0.999$) indicating mono layer type adsorption while the kinetics of the process was well described by the pseudo first order and Langmuir-Hinshelwood kinetic models with high R^2 values (>0.90).

Keywords: *Periwinkle shell ash, Snail shell ash, Photocatalysis, Kinetics, Adsorption Equilibrium*

1. Introduction

A lot of industries use colouring matter to colour their products to make them attractive [1]. These industries include textile, paper, food and beverage, cosmetics etc. They produce large volumes of wastewater due to the high consumption of water in the operations typically encountered in these industries [2]. The wastewater usually contains residual dye and coloured matter [3]. It has been reported that about 10 to 15% of the total world production of dyes is lost as liquid effluent during the dyeing process [4,5]. The discharge of these wastewaters to the environment in their untreated form poses a serious threat to the environment through aesthetic pollution, eutrophication and the release of toxic and potentially carcinogenic substances; hence the need for proper and efficient treatment methods [6-8].

A variety of physical, chemical and biological methods, such as adsorption, coagulation, membrane process, oxidation, ozonation, chlorination, biodegradation etc have been applied for the treatment of coloured wastewater [9-11]. These methods cannot sufficiently treat the wastewater to the level of purity that will enable its reuse and moreover, they are mere phase transfer methods in that the

pollutants are merely transferred from the aqueous phase to another phase thus introducing the need for further treatment [12,13].

Heterogeneous photocatalysis has been identified as a treatment option with a great potential for the abatement of most organic pollutants as well as dyes in aqueous media [14-17]. Its operation is based on the principle of surface activation of semiconductors notably zinc oxide (ZnO) and titanium dioxide (TiO₂) by ultraviolet (UV) radiation. It has several advantages over conventional treatment processes which include complete mineralisation of pollutants into stable and non toxic forms, use of near UV or light from the sun which favours the economics of the process. Furthermore, there is no need for the use of additional chemicals which results in the generation of more waste as in the case of other chemical treatment methods and the catalyst can easily be regenerated and reused [8,18,19].

ZnO and TiO₂ are the most commonly used photocatalysts as a result of their high efficiency and quantum yield. They are also inexpensive, stable to photocorrosion and safe to handle [8,20]. Nevertheless, these catalysts have certain important deficiencies as their response and capacity to utilise radiation is limited in the UV region, thus they require a high power UV excitation source [21]. Furthermore, the recovery potential of the catalysts is limited. It is therefore imperative to source for alternative photocatalysts with better recovery potential and light absorption capacity, with important focus on locally sourced catalysts.

This study is aimed at investigating the potential use of locally sourced periwinkle and snail shell ash for the photocatalytic decolourisation of methylene blue dye in aqueous solution. The effects of factors such as irradiation time, initial dye concentration and catalyst dosage on the decolourisation process were investigated. The photocatalytic decolourisation of methylene blue was further evaluated by carrying out kinetic studies using the pseudo-first-order, pseudo-second-order and Langmuir-Hinshelwood kinetic models. Isotherm studies were carried out using the Langmuir and Freundlich isotherms.

2. Materials and methods

2.1. Preparation and characterisation of photocatalysts

Periwinkle and snail shells were sourced locally from Benin City in Edo State of Southern Nigeria. The shells were washed and dried to constant mass in an oven at 110°C. The dried shells were crushed, calcined at 600°C in a muffle furnace and then sieved to obtain fine particles (< 350µm) of periwinkle and snail shell ash (PSA) and (SSA). The PSA and SSA were characterised by determining the composition of oxides and elements using X-Ray Fluorescence (XRF) and X-ray diffraction (XRD) analysis respectively [22]. The surface structure and other properties were evaluated by nitrogen adsorption method at -196°C using an adsorption equipment (BET 624, Micro-meritics, Germany). The surface area was determined using the standard BET equation.

2.2. Preparation of dye solution

Methylene blue, an azo dye with molecular formula C₁₆H₁₈N₃SCl and molecular weight 319.85 g/mol was obtained from Stanvac Laboratories in Benin City, Edo State, Nigeria. The chemical structure of the dye is shown in Figure 1. The commercially obtained sample of the dye was used without further purification. A stock solution of methylene blue was prepared by dissolving an appropriate amount of

the dye in 1000 mL of deionised water. Working solutions with different concentrations of dye were prepared by appropriate dilutions of the stock solution with deionised water before each experimental run.

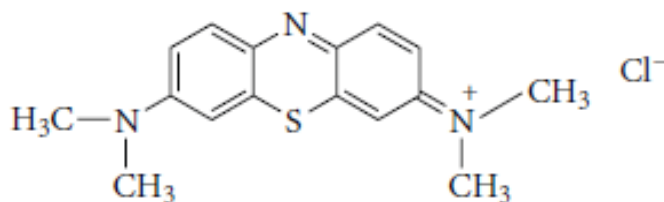


Figure 1. Chemical structure of methylene blue

2.3. Experimental set up and photocatalytic degradation Studies

All the photocatalytic degradation experimental runs were carried out in a photoreactor. The photoreactor was designed in the form of a 1.2 m quartz tube with an internal diameter of 25 mm. Radiation was provided by four UV lamps (40W, TUV G6T5, $\lambda_{\max} = 254$ nm, manufactured by Philips, Holland) which surrounded the reactor so as to ensure a homogenous radiation field inside the reactor. The lamp arrangement was covered by a sheet of reflective aluminium to shield against external UV radiation and to concentrate the UV radiation from the lamps onto the reactor. The light intensity at the centre of the photoreactor was measured by Lux-UV-IR meter (Leybold Co.). Heat effect from the lamps was eliminated by blowing cooled air between the lamps and the quartz reactor such that the temperature of the reaction medium was maintained constant at 25 °C. The mixture of the photocatalyst and dye solution was held in a 10 L substrate holding tank which was stirred at 600 rpm to ensure a complete suspension of catalyst particles. Silicone tubing was connected to both ends of the reactor with one end connected to an easy load Masterflex peristaltic pump which served to convey the photocatalyst-dye mixture to the reactor. The progress of the photocatalytic degradation reaction was followed by monitoring the disappearance of methylene blue at a wavelength of 663 nm using a UV–Visible spectrophotometer (Shimadzu UV 2101 PC). This was done by taking samples at regular intervals, centrifuging at 8000 rpm for 10 min to remove suspended catalyst particles and analysing for undegraded dye. The decolourisation efficiency was measured in terms of the disappearance of the dye and was calculated as follows.

$$\text{Decolourisation efficiency} = \frac{C_o - C_t}{C_o} \times 100 \quad (1)$$

C_o and C_t are the initial and the instantaneous concentration of dye respectively.

3. Results and Discussions

3.1. Characterisation of photocatalysts

The results of the chemical composition analysis of the PSA and SSA carried out using X-Ray Fluorescence (XRF) and X-ray diffraction (XRD) as well as other properties such as the surface area, bulk density and porosity of the photocatalysts have been reported previously by Aisien et al. [2]. It was reported that the major constituents of the PSA were calcium oxide (CaO), silica (SiO₂) and aluminium oxide (Al₂O₃) which accounted for 41.3, 33.2 and 9.2% of the weight of PSA respectively. The SSA was composed mainly of iron oxide (Fe₂O₃), silica and aluminium oxide which accounted

respectively for 36.4, 21.3 and 11.2% of the weight of SSA. The major elements in PSA were iron (19.2%) and zinc (16.5%) while those in SSA were zinc (19.68%) and iron (16.44%). These elements and oxides have been reported to possess photocatalytic properties.

3.2. Preliminary studies

Figure 2 shows the results of preliminary studies to determine the choice of photocatalyst between PSA and SSA. The results show that PSA performed better than SSA during a photocatalytic decolourisation study carried out for 40 minutes. PSA was therefore chosen for further investigations.

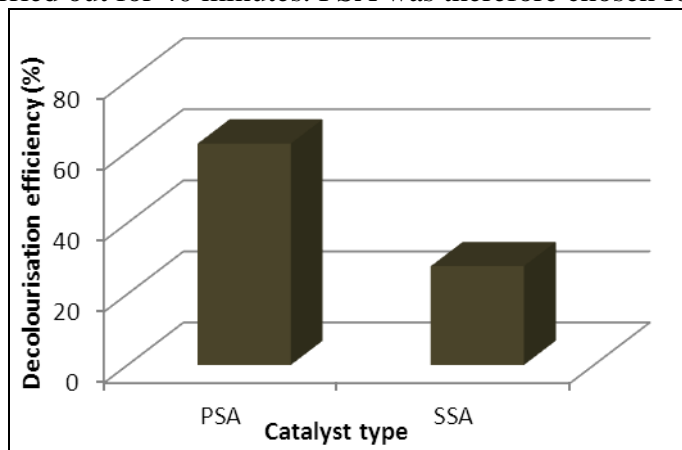


Figure 2. Results of preliminary studies carried out to determine the choice of catalyst

3.3. Effect of irradiation time

Figure 3 shows the effect of irradiation time on the photocatalytic decolourisation of methylene blue. The decolourisation efficiency increased with increase in irradiation time up to about 50 minutes. No significant increase in the decolourisation efficiency was observed beyond 50 minutes. At the initial stages of the decolourisation process, there is an abundance of active sites on the photocatalyst surface. Hence, it should be expected that the photocatalytic reaction will be fast during these early stages. Similar observations have been reported by other researchers [18,23].

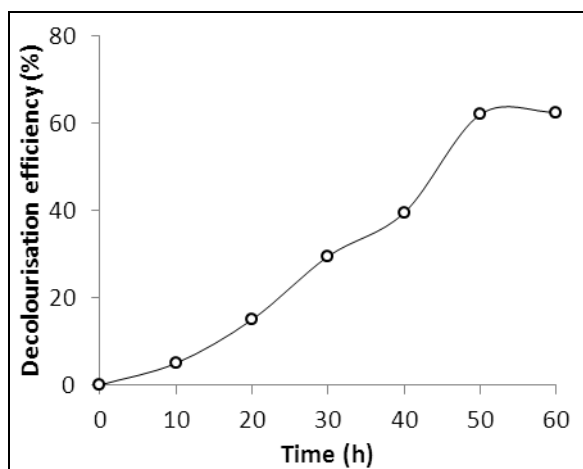


Figure 3. Effect of irradiation time on photocatalytic decolourisation (pH 4; PSA dose, 2 g/L; initial concentration, 7 mg/L; temperature, 25°C)

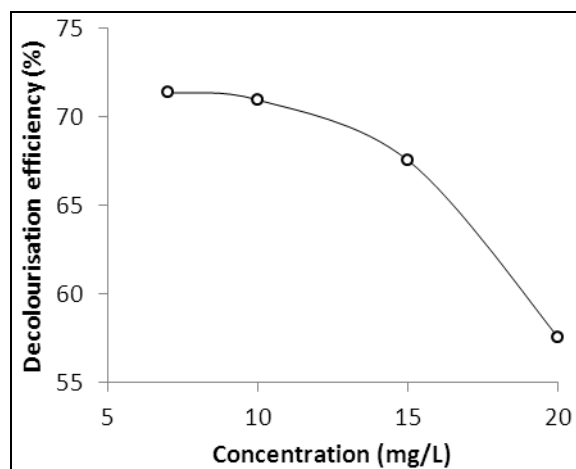


Figure 4. Effect of initial concentration on photocatalytic decolourisation (pH 4; PSA dose, 2 g/L; temperature, 25°C)

The decline in the rate of decolourisation reaction observed beyond 50 minutes could indicate that the system had attained a state of equilibrium. This means that the active sites on the photocatalyst surface have become occupied by layers of dye molecules thus resulting in the insignificant change in the decolourisation efficiency observed beyond 50 minutes

3.4 Effect of initial dye concentration

The initial dye concentration influenced the decolourisation process as shown in Figure 4. The decolourisation efficiency showed a steady and progressive decrease with increase in the initial dye concentration. At low concentrations of the dye, there will be unoccupied active sites on the catalyst surface which facilitates the decolourisation process. However, since the number of active sites on the catalyst surface is constant, an increase in the initial concentration of the dye results in a corresponding increase in the relative ratio of the concentration of dye to available active sites and further increase in concentration results in the saturation of the active sites on the catalyst surface [24]. The trend reported here agrees with the observations of Ahmed et al. [20] who explained that as the concentration of the dye is increased, more of the dye molecules get adsorbed on the surface of the photocatalyst. Hence, the relative proportions of the reactive species (hydroxyl ($\bullet\text{OH}$) and oxygen free radicals ($\text{O}_2\bullet$)) needed for the degradation of the dye will decrease. However, the generation of the free radicals on the surface of the photocatalyst remains constant for a given UV radiation intensity, catalyst dosage and irradiation time.

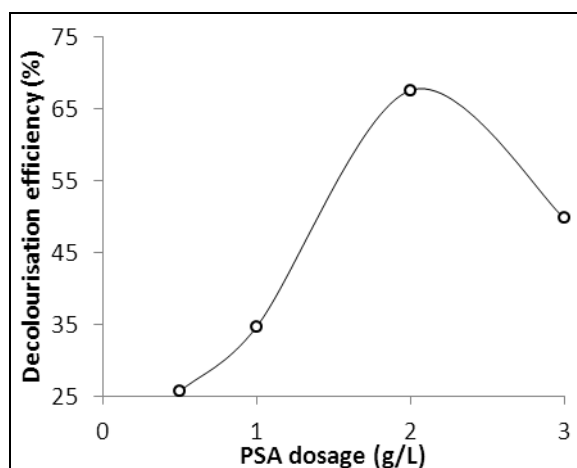


Figure 5. Effect of PSA loading on photocatalytic decolourisation (pH 4; initial concentration, 7 mg/L; temperature, 25°C)

Therefore the relative ratio of the available free radicals to the concentration of dye decreases. Hence the available radicals become inadequate for the degradation of the dye. Consequently the decolourisation efficiency decreases. Furthermore, Akyol et al. [6] reported that the implication of the Beer–Lambert law becomes apparent under conditions of high dye concentration. According to them, increasing the initial dye concentration reduces the path length of photons entering the solution which results in a lower penetration of radiation to the catalyst particles and consequently lowers the photocatalytic reaction rate.

3.5 Effect of photocatalyst loading

The decolourisation efficiency increased from about 25% to a maximum of about 68% when the PSA loading was increased from 0.5 to 2 g/L as shown in Figure 5. Increasing the PSA loading beyond 2 g/L resulted in a decrease in the decolourisation efficiency. The catalyst loading has been reported to be an important variable in photocatalysis as it determines the capacity of the catalyst for a given initial concentration of dye [23]. The initial increase in decolourisation efficiency observed might be due to the increase in the number of active sites on the photocatalyst surface [25,26]. The decrease in decolourisation efficiency observed beyond a catalyst loading of 2 g/L could be attributed to a number of factors. Firstly, increase in catalyst loading leads to an increase in the turbidity of the solution. The increased turbidity results in increased opacity of the aqueous medium which consequently increases the light reflectance, interception and scattering as a result of the excess of catalyst particles [27]. According to Sun et al. [28], the interception of light by the photocatalyst/dye suspension results in a decrease in the generation of hydroxyl radicals which are the primary oxidants in the photocatalytic reaction system. Akyol et al. [6] reported that the catalyst surface and absorption of light by the catalyst surface are the limiting factors at low catalyst dosage. Hence, an increase in catalyst loading will enhance the efficiency of the decolourisation process. However, at higher catalyst loading, the irradiation field inside the photoreactor is diminished as a result of light scattering by the catalyst particles. So et al. [29] observed some level of agglomeration and sedimentation of the catalyst particles at high catalyst loading. Konstantinou and Albanis, [30] then suggested that under such conditions of high catalyst loading, a fraction of the catalyst surface could become inaccessible for radiation absorption thus resulting in a decrease in the decolourisation efficiency.

3.6 Photocatalytic degradation kinetics

For the present study, three kinetic models were applied in order to explain the mechanism of adsorption of the dye onto the adsorbent. The models are the pseudo first-order, pseudo second order and the Langmuir-Hinshelwood kinetic models.

3.6.1 Pseudo first order model

The pseudo first-order equation is expressed as follows:

$$r = -\frac{dC}{dt} = kC \quad (2)$$

The pseudo first order reaction rate constant, k was obtained from the integrated linear form of Equation (2) as follows:

$$k = \frac{\ln C_o / C_t}{t} \quad (3)$$

The plot of $\ln C_o / C_t$ versus t as shown in Figure 6 resulted in a linear relationship from which the value of k was determined. The pseudo first order rate constants calculated from the plot at different initial dye concentrations are given in Table 1. The straight line plots as well as the high R^2 values obtained for the range of concentration investigated show that the pseudo first order equation was able to describe the kinetics of the process.

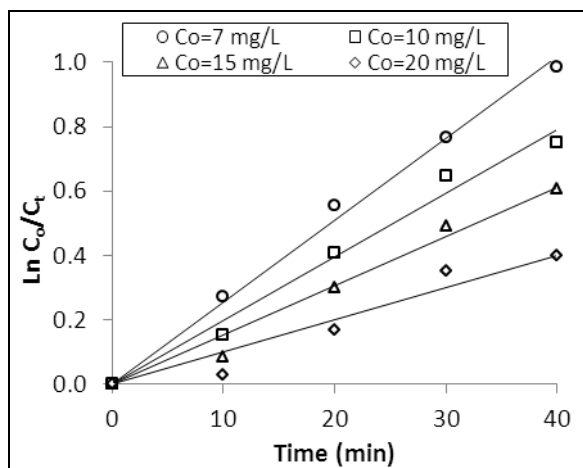


Figure 6. Pseudo first order kinetic model results

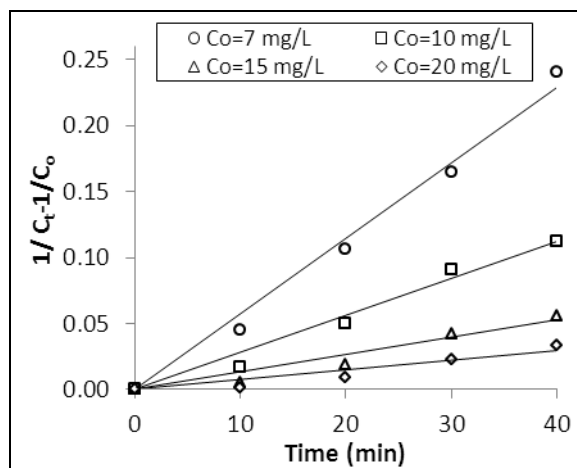


Figure 7. Pseudo second order kinetic model results

3.6.2 Pseudo second order model

The linearised form of the pseudo second order rate equation is expressed as follows:

$$\frac{1}{C_t} - \frac{1}{C_o} = kt \quad (4)$$

Figure 7 shows a plot of $1/C_t - 1/C_o$ versus time at different initial dye concentrations. The results of regression analysis are shown in Table 1. High R^2 values (>0.90) are indicative of significant fit between the experimental data and the pseudo second order model

3.6.3 Langmuir-Hinshelwood model

The Langmuir-Hinshelwood kinetic equation is expressed as follows:

$$r_o = -\frac{dc}{dt} = \frac{k_r K C_{eq}}{1 + K C_{eq}} \quad (5)$$

r_o is the initial rate of reaction in mg/L.min, k_r is the rate constant for photocatalysis in mg/L min, K is the rate constant for adsorption in L/mg, C_{eq} is the equilibrium dye concentration and c is the instantaneous dye concentration. The linearised form of Equation (5) is given as follows:

$$\frac{1}{r_o} = \frac{1}{k_r K} \frac{1}{C_{eq}} + \frac{1}{k_r} \quad (6)$$

The plot of $1/r_o$ versus $1/C_{eq}$ resulted in a straight line as shown in Figure 8. The values of the kinetic parameters calculated from the plot are given in Table 1. The high R^2 value obtained shows that the model was able to describe the kinetics of the process.

Summarily, all three kinetic models showed significant fit with the experimental data. However, the highest R^2 values were recorded for the case of the pseudo first order kinetic equation suggesting that the equation best describes the kinetics of the photocatalytic decolourisation process.

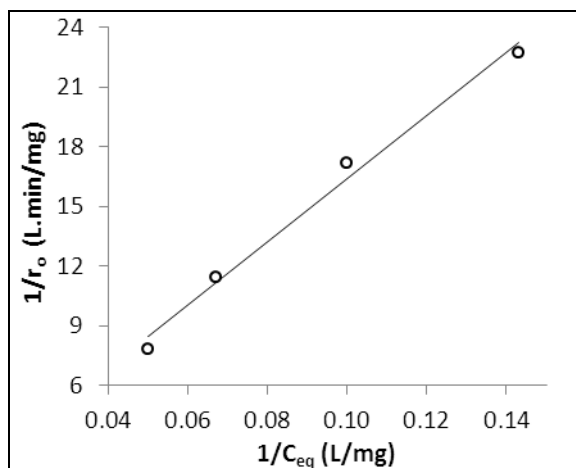


Figure 8. Langmuir-Hinshelwood kinetic model results

Table 1: Kinetic constant parameter values for the photocatalytic decolourisation of methylene blue

C_o (mg/L)	Pseudo first order		Pseudo second order		Langmuir-Hinshelwood		
	k	R^2	k	R^2	k_r	K	R^2
10	0.0255	0.994	0.0057	0.989	1.994	0.00316	0.990
20	0.0197	0.983	0.0028	0.976			
30	0.0153	0.978	0.0013	0.947			
40	0.0100	0.935	0.0007	0.900			

3.7 Isotherm studies

For the present study, two isotherm equations namely Langmuir and Freundlich isotherm were used to analyse the distribution of dye molecules between the solid and the liquid phase.

3.7.1 Langmuir isotherm

The Langmuir adsorption isotherm is based on the assumption that adsorption occurs at specific homogenous sites within the adsorbent and once an adsorbate molecule occupies a site, no further adsorption can take place. The linear form of the Langmuir equation is expressed as:

$$\frac{C_e}{q_e} = \frac{1}{q_o} C_e + \frac{1}{K_L q_o} \quad (7)$$

q_o is the maximum sorption capacity (mg/g) of the adsorbent while K_L is the sorption constant (L/mg). A linear plot of C_e/q_e against C_e as shown in Figure 9 was employed to obtain the values of q_o and K_L from the slope and intercept of the plot respectively. The values of the Langmuir isotherm parameters as well as the correlation coefficient (R^2) of the Langmuir equation are given in Table 2.

Table 2: Kinetic parameters for Langmuir and Freundlich isotherms

Langmuir isotherm			Freundlich isotherm		
q_o (mg/g)	K_L (L/mg)	R^2	K_f (mg/g)	n	R^2
28.49	0.246	0.999	7.028	2.106	0.986

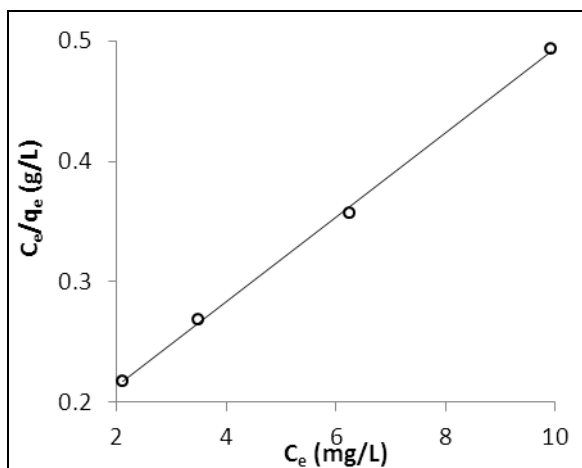


Figure 9. Langmuir isotherm model linearised to equilibrium data for methylene blue

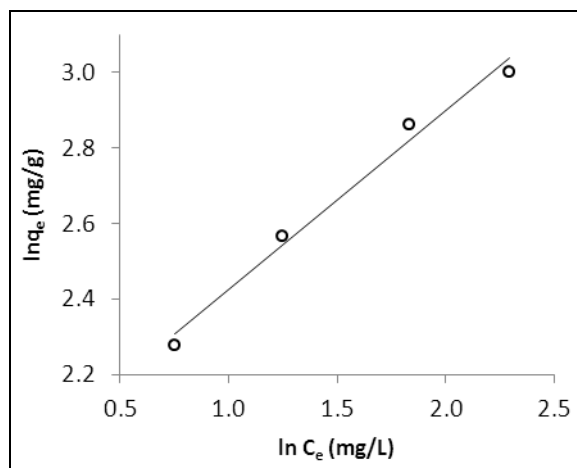


Figure 10. Freundlich isotherm model linearised to equilibrium data for methylene blue

3.7.2 Freundlich isotherm

The Freundlich isotherm model is used to describe heterogeneous adsorption process i.e adsorption which takes place on a heterogeneous surface through a multilayer adsorption mechanism [23]. The Freundlich equation is expressed as follows:

$$q_e = K_f (C_e)^{1/n} \quad (8)$$

The linearised form of Equation (8) is expressed as follows:

$$\ln q_e = \ln K_f + 1/n \ln C_e \quad (9)$$

K_f is the adsorption capacity and n is a dimensionless constant that is related to the extent of adsorption and the adsorption intensity between the dye concentration and adsorbent respectively. A linear plot of $\ln q_e$ against $\ln C_e$ as shown in Figure 10 was employed to obtain the values of K_f and n from the intercept and slope of the plot respectively. The values of these parameters as well as the correlation coefficient (R^2) of the Freundlich equation are given in Table 2. The high values of the correlation coefficients as shown in Table 2 indicates that the data conformed well to both isotherm equations; nevertheless, the Langmuir isotherm equation resulted in a better fit as seen in the higher value of the correlation coefficient.

4. Conclusion

The photocatalytic decolourisation of methylene blue was investigated in this study. The following conclusions can be drawn from the results obtained.

- The photodegradation process was affected by factors such as irradiation time, initial dye concentration and PSA dosage
- The optimum adsorption condition are as follows: irradiation time, 50 minutes; initial dye concentration, 7 mg/L; PSA dosage, 2 g/L
- The kinetics of the decolourisation process was well described by the pseudo first order and Langmuir-Hinshelwood kinetic models with high correlation coefficient values.
- Adsorption equilibrium was well described by the Langmuir isotherm equation.

References

- [1] M. Mehra, T.R. Sharma, *Adv. Appl. Sci. Res.*, 3 (2012) 849-853.
- [2] F.A. Aisien, N.A. Amenaghawon, E.F. Ekpensisi, *J. Eng. Appl. Sci.*, 9 (2013) 11-16.
- [3] M.A. Behnajady, N. Modirshahla, R. Hamzavi, *J. Hazard. Mater.*, 133 (2006) 226-232
- [4] J. Yao, C. Wang, *Int. J. Photoenerg.*, 2010 (2010) 1-6
- [5] Y. Zhiyong, D. Laub, M. Bensimon, J. Kiwi, *Inorganica Chimica Acta.*, 361 (2008) 589–594
- [6] A. Akyol, H.C. Yatmaz, M. Bayramoglu, *Appl. Catal. B: Envir.*, 54 (2004) 19-24.
- [7] M. Saquib, M. Muneer, *Dyes Pigments*, 56 (2003) 37-49.
- [8] V.A. Shrivastava, *Arch. Appl. Sci. Res.*, 4 (2012)1244-1254
- [9] R. Dhodapkar, N.N. Rao, S.P. Pande, S.N. Kaul, *Bioresourc Technol.*, 97 (2006) 877–885.
- [10] D. Georgiou, P. Melidis, A. Aivasidis, K. Gimouhopoulos, *Dyes Pigments*, 52 (2002) 69-78.
- [11] D.E. Gu, B.C. Yang, Y.D. Hu, *Catal. Lett.*, 118 (2007) 254–259.
- [12] R. Bergamini, E.B. Azevedo, L.R. Araújo, *Chem. Eng. J.*, 149 (2009) 215-220.
- [13] X. Chen, S.S. Mao, *Chem. Rev.*, 107 (2007) 2891–2959.
- [14] L. Hua, H. Ma, L. Zhang, *Chemosphere* 90 (2013) 143-149.
- [15] A. Lair, C. Ferronato, J.M. Chovelon, J.M. Herrmann, *J. Photochem. Photobiol A: Chem.*, 193 (2008) 193-203.
- [16] G. Palmisano, V. Augugliaro, M. Pagliaro, L. Palmisano, *Chem. Commun.*, 33 (2007) 3425-3437.
- [17] M. Qamar, M. Saquib, M. Muneer, *Dyes Pigments*, 65 (2005) 1–9.
- [18] A. Akyol, M. Bayramoglu, *Chem. Eng. Proc.: Proc. Intensif.*, 47 (2008) 2150-2156.
- [19] S.B. Gajbhiye, *Int. J. Modern Eng. Res.*, 2 (2012) 1204-1208
- [20] S. Ahmed, M.G. Rasul, W.N. Martens, R. Brown, M.A. Hashib, *Water, Air, & Soil Pollut.*, 215 (2011), 3-29.
- [21] G. Liu, Z. Wang, W. Zheng, S. Yang, C. Sun, *Adv. Condensed Matter Phys.*, 2014 (2014) 1-5
- [22] S.Y. Aku, D.S. Yawas, P.B. Madakson, S.G. Amaren, *The Pacific J. Sci. Technol.*, 13 (2012) 57-63.
- [23] S.A. Umoren, U.J. Etim, A.U. Israel, *J. Mater. Envir. Sci.*, 4 (2013) 75-86.
- [24] Z. Eren, F.N. Acar, *Desalination*, 194 (2006) 1-10.
- [25] U.G. Akpan, B.H. Hameed, *J. Hazard. Mater.*, 170 (2009) 520-529.
- [26] J. Inamdar, S.K. Singh, *Int. J. Chem. Biol. Eng.*, 1 (2008) 160-164.
- [27] M. Saquib, M.A. Tariqa, M. Faisala, M. Muneer, *Desalination*, 219 (2008) 301–311.
- [28] J. Sun, L. Qiao, S. Sun, G. Wang, *J. Hazard. Mater.*, 155 (2008) 312–319.
- [29] C.M. So, M.Y. Cheng, J.C. Yu, P.K. Wong, *Chemosphere*, 46 (2002) 905-912.
- [30] I.K. Konstantinou, T.A. Albanis, *Appl. Catal. B: Envir.*, 49 (2004) 1-14.