Studies on the kinetics and intraparticle diffusivities of BOD, colour and TSS reduction from palm oil mill effluent (POME) using boiler fly ash

J. C. Igwe¹*, C. O. Onyegbado² and A. A. Abia³

¹Department of Industrial Chemistry, Abia State University, P. M. B. 2000, Uturu, Abia State, Nigeria.
²Department of Chemical Engineering, University of Port Harcourt, River State, Nigeria.
³Department of Pure and Industrial Chemistry, University of Port Harcourt, River State, Nigeria.

Accepted 20 January, 2010

The palm oil industry has been identified as one of the main contributors of organic pollution. These industries generate large volumes of effluent and solid waste including boiler fly ash. The kinetics and intraparticle diffusivities of BOD, TSS and colour reduction from palm oil mill effluent (POME) using boiler fly ash was reported in this paper. The amount of BOD, colour and TSS adsorbed increased as the weight of the boiler fly ash was increased. Also, the smaller adsorbent particle size of 425 μm adsorbed more than the 850 μm size. Attempts were made to fit the experimental data with the pseudo - first order and pseudo-second order kinetic equations. The pseudo - second order model gave a better fit to the sorption process. The rate constants obtained for the pseudo-second order model are 2.26 x 10⁻⁵ mg/g-min for BOD, 6.48 x 10⁻⁴ mg/g-min for colour and 9.55 x 10⁻⁴ mg/g-min for TSS at 30°C. The mechanism of sorption was investigated by using the intraparticle diffusion model. The regression coefficient for the intraparticle diffusion model showed that BOD with a value of 0.9744 was well correlated than TSS (R² = 0.1018) and colour (R² = 0.1450). This means that BOD adsorption was particle diffusion controlled while colour and TSS were film diffusion controlled. Therefore, this study reveals that boiler fly ash can effectively be used as an adsorbent for POME treatment and also established the kinetic and mechanisms of the sorption process. Also, the results of this study could serve as effective design parameters for a treatment plant to further reduce BOD, colour and TSS from POME.

Key words: Adsorption, boiler fly ash, kinetics, pome, wastewater.

INTRODUCTION

Increasing urbanization and industrialization have resulted in a dramatic increase in the volume of wastewater produced around the world. Palm oil mill industries are large industrial consumers of water as well as producers of wastewater. Palm oil mill effluent (POME) is a colloidal suspension of 95 - 96% water, 0.6 - 0.7% oil and 4 - 5% total solids including 2 - 4% suspended solids originating from the mixing of stabilizer condensate, separator sludge and hydro cyclone wastewater that are mostly debris from palm fruit mesocarp (Ahmad et al., 2005). Most industries in Nigeria still discharge their effluent directly into nearby streams, rivers and seas and even on land without prior analysis and possible treatment. Most palm oil mill industries still discharge their waste indiscriminately, particularly the numerous small-scale palm oil mills scattered all over the towns and villages of South East and West of Nigeria and other developing countries of Africa. Unfortunately, operators of such mills are not aware that the liquid discharges from oil palm fruit processing in the untreated form are very high strength wastes. Tightening environmental standards have meant that much of these wastewaters have to be treated before it can safely be discharged (Asia et al., 2006)

The oil palm mills generate many by - products and wastes besides the liquid wastes that have been mentioned, that may have a significant impact on the
environment if they are not properly dealt with. The most common among these by-products is the empty fruit bunch (EFB). The empty bunch is a solid waste product of the oil palm milling process and has a high moisture content of approximately 55 - 56% and high silica content; from 25% of the total palm fruit bunch (Ken, 2005). The treated empty bunches are mechanically crushed (de-watered and de-oiled) in the process, but are rich in major nutrients and contains reasonable amounts of trace elements. They have a value when returned to the field to be applied as mulch for the enrichment of soil (Zakaria and Murdi, 2000). However, it was noted that over application of the effluent must be avoided as it may result in anaerobic conditions in the soil by formation of an impervious coat of organic matter on the soil surface (Ken, 2005; Henson, 1994). Air emission from the oil palm mills are from the boilers and incinerators, and are mainly gases with particulates such as tar and soot droplets of 20 - 100 microns and a dust load of about 3000 to 4000 mg/µm (Ken, 2005).

Incomplete combustion in the boiler and incinerator produce dark smoke resulting from burning a mixture of solid waste fuels such as shell, fiber and sometimes empty bunches. These boiler fly ashes are also a waste themselves and also pose problems of disposal. Since boiler fly ash is a waste and poses disposal problems, then there is huge economic advantage in the use of a waste (boiler fly ash) to treat another waste (POME) from palm oil mills. Thus, using a waste to clean-up another waste, hence achieving a zero discharge layout of the palm oil mill industry.

In the bid to achieve a zero discharge of the palm oil mill, various methods have been employed in POME treatment. Physico - chemical technique involves coagulation of finely dispersed and suspended solid particles, adsorption of dissolved impurities such as heavy metals (Namasivayanan and Senthilkumaran, 1998; Okoronkwo et al., 2006; Saifuddin and Kumaran, 2005) selective crystallization, reverse osmosis and ion-exchange processes (Chow et al., 1981). Reverse osmosis is most often used at the final stage of effluent treatment. Secondary treatment is biological process following primary treatment. The forms of secondary biological processes include activated sludge, trickling filters, contact stabilization, etc (Borja et al., 1996; Chin et al., 1996; Hoe and Dam, 1981; Ma et al., 1996; Katzenberg and Marchaim, 1993; Lin and Hsiu, 1997; Schobar et al., 1999).

The goal of all biological wastewater treatment systems is to remove the non-settling solids and the dissolved organic load from the effluents by using microbial populations. The micro-organisms used are responsible for the degradation of the organic matter and the stabilization of organic wastes. Amongst the various practical biological treatment methods, anaerobic digestion is often the most attractive option for treatment of wastewater due to the following advantages: a high BOD and COD reduction, production of energy as biogas, production of a bio-fertilizer, small production of already stabilized biological sludge that can be used as a nutrient and lower capital cost.

The effluents from these biological treatment plants still contain a high percentage of BOD and other contaminants. Therefore, this work focuses on the use of boiler fly ash to further reduce BOD, colour and TSS from POME. The use of industrial solid waste such as boiler fly ash for the treatment of POME has not been extensively studied. The removal of residual BOD, colour and TSS from POME by adsorption using adsorbents is very promising and requires further study. The feasibility of using boiler fly ash as an adsorbent for POME treatment has been reported (Ma et al., 1996). The application of certain sorption isotherms for BOD, TSS and colour reduction (Igwe et al., 2009), the adsorption of residual oil from POME (Ahmad et al., 2005, 2004, 2003) have also been reported. However, there are very few research reported in the literature on the kinetics of sorption and intraparticle diffusion of BOD, TSS and colour reduction from POME using boiler fly ash. Kinetics describes the solute uptake rate which in turn controls the residence time of sorbate uptake at the solute - solution interface (Ho and Wang, 2004). Therefore, it is important to be able to predict the rate at which pollutant is removed from aqueous solutions in order to be able to design appropriate sorption treatment plants. Therefore, in this paper, the emphasis is on the kinetics of sorption, the development of the sorption rate model constants and the mechanism of the diffusion processes in BOD, colour and TSS reduction from POME using Boiler fly ash.

MATERIALS AND METHODS

Samples of effluent water were collected from a palm oil mill in Okigwe, Imo State. Boiler fly ash was also collected from the same mill. All reagents used were of analytical reagents grade and were used as purchased without further purification.

Sample collection and adsorbent preparation

Samples of effluent water were collected in different containers of about 5 L in volume. The containers were properly washed and rinsed with the effluent before collection to avoid contamination and dilution. The containers were labeled showing time of collection and temperature at collection. Boiler fly ash was also collected from the same mill. To do this, a large quantity was collected using polyethylene bags. The boiler fly ash was first washed with distilled water and then air-dried. The particle size distribution was determined using a Fritsch sieve shaker. This properly sieved the boiler fly ash into two particular mesh sizes of 425 and 850 µm for the purpose of the experiment. Therefore, two samples of boiler fly ash were obtained and placed in different sample containers and labeled according to their mesh sizes (425 µm and 850 µm). The fly ash was activated by soaking in dilute (2% v/v) HNO₃ over night. It was then rinsed with distilled water and air-dried, ready for the experiments. The reason for soaking in nitric acid was to wash off soluble contaminants and activate the boiler fly ash. The specific surface area of the activated fly ash was determined using the methylene blue absorption test (MBT) method described by Santamarina et al (2002). The moisture content of the sample was determined using a Fritsch sieve shaker. This properly sieved the boiler fly ash into two particular mesh sizes of 425 and 850 µm for the purpose of the experiment. Therefore, two samples of boiler fly ash were obtained and placed in different sample containers and labeled according to their mesh sizes (425 µm and 850 µm). The fly ash was activated by soaking in dilute (2% v/v) HNO₃ over night. It was then rinsed with distilled water and air-dried, ready for the experiments. The reason for soaking in nitric acid was to wash off soluble contaminants and activate the boiler fly ash. The specific surface area of the activated fly ash was determined using the methylene blue absorption test (MBT) method described by Santamarina et al (2002).
measured by heating the fly ash in an oven at 135°C for two h (Majid et al., 1999).

**Determination of specific surface area (\(S_{AA}\))**

The specific surface area of the adsorbent was determined using the methylene blue absorption test (MBT) method (Santamarina et al., 2002). 2.0 g of each adsorbent was dissolved in 200 mL of deionized water and 10 ppm of the methylene blue solution was added to the adsorbent suspension and agitated in a shaker for 2 h. Thereafter, it was kept for 24 h to reach equilibrium, after which 10 mL aliquot was taken and centrifuged. The centrifuged aliquot was then analyzed using a UNICAM - 8700 UV/Visible spectrophotometer to determine the amount of methylene blue absorbed. Also, 20, 30, 40, 50, 60 and 70 ppm solutions of methylene blue were then added sequentially and the previous steps repeated. A graph of concentration of methylene blue added versus the amount of absorbed methylene blue (not shown) was used to identify the break-point. The specific surface area was calculated from the amount of absorbed methylene blue at the optimum point of cation replacement as follows:

\[
\text{Specific surface area} = \left( \frac{m_{MB} \times Av \times AMB}{319.98 \times (1/M_s)} \right)
\]

Where;

- \(m_{MB}\) = Amount of methylene blue absorbed at the point of complete cation replacement.
- \(M_s\) = Mass of adsorbent
- \(Av\) = Avogadro's number, 6.02 \(\times\) 10\(^{23}\)
- \(AMB\) = Area covered by one methylene blue (assumed to be 130Å\(^2\))

**Batch adsorption studies**

**Effect of weight of fly ash**

The adsorption experiments were conducted in a batch system by preparing various amounts of fly ash (10, 30, 40 and 60) in grams of the two different mesh sizes in series of 300 mL waste water. The various mixtures of fly ash and wastewater were allowed to stand with continuous stirring for 60 min contact time, at a constant temperature of 30°C. After the contact time of 60 min had elapsed, the fly ash was removed by suction filtration using a filter paper (Whatman No.41) and funnel into labeled sample bottles for analysis. A control sample was prepared by filtering the wastewater without the fly ash. The filtrates were then analyzed for BOD, TSS and colour as described later.

**Effect of contact time**

To investigate the effect of contact time and hence, the kinetics of the sorption process, 30g of boiler fly ash of 850 μm size was put into 300 mL of wastewater at 30°C, at a constant initial concentration. Various samples were allowed to stand with continuous stirring for 10, 40, 60 and 120 min. After each contact time, the samples were filtered and the filtrate was also analyzed for BOD, TSS and colour by the same methods stated below.

**Analyses of various parameters**

The pH of the solutions was determined using pH meter (HACH 51750 – 60). The pH meter was first standardized using a buffer solution of about pH 7.0 and then the other solutions were analyzed for their various pH values (Igwe, 2006; APHA, 1985). All samples were analyzed for the other parameters as described in the standard methods for the examination of water and wastewater (Schobar et al., 1999) and standard methods for water and effluents analysis (Ademoroti, 1996).

The amounts of these parameters adsorbed were calculated by difference in the initial concentrations and that remaining in the filtrates according to the simplified mass balance equation below:

\[
q_e = V (C_0 - C_e)/m
\]

Where \(q_e\) is the amount adsorbed, \(C_0\) is initial concentration, \(C_e\) is the final concentration after adsorption, \(V\) is the volume of solution and \(m\) is the mass of adsorbent used.

**RESULTS AND DISCUSSION**

The particle sizes of the fly ash used were 450 μm and 850 μm. The specific surface area of the boiler fly ash calculated from the methylene blue test method was 241.4 m\(^2\)g\(^{-1}\) for 850 μm and 280.6 m\(^2\)g\(^{-1}\) for 425 μm. The pH ranged from 5.3 to 6.9. The experimental results for the adsorptive removal of BOD, Colour and TSS using boiler fly ash are presented. Figure 1 show the amount adsorbed for BOD, colour and TSS from POME as dose (g) of boiler fly ash was varied. Figure 2. From these figures, it can be seen that for BOD, both for 425 μm and 850 μm sizes of boiler fly ash, the amount adsorbed increased steadily as the dose (g) of fly ash was increased. For TSS and colour, there were little changes. Also, it can be seen that particle size of 425 μm gave higher sorption capacity than particle size of 850 μm. This could be attributed to the higher specific surface area of the 425 μm particle size compared to the 850 μm particle size. This is expected due to the fact that the higher specific surface area, the greater availability of exchangeable sites for the solutes in solution.

**Sorption kinetics**

The rate law is determined by experimentation and it cannot be inferred by mere examination of the overall chemical reaction equation (Ho and Wang 2004; Majid et al., 1999). Therefore, predicting the rate at which sorption takes place for a given system is probably the most important factor for sorbent design, with sorbate residence time and the reactor dimensions controlled by the system's kinetics. However, sorption kinetics shows a large dependence on the physical and/or chemical characteristics of the sorbent material which also influences the sorption mechanism (Ho and Chiang 2001).

The kinetics of sorption for the adsorption of BOD, TSS and colour from palm oil mill effluent using boiler fly ash was studied by finding the amount adsorbed at various time intervals. The result for the experiments of amount
adsorbed against time for BOD, colour and TSS using boiler fly ash is shown in Figure 3. The amount of BOD adsorbed was highest and also increased rapidly as time increased from 0 to 120 min. This was followed by colour and then TSS. The kinetics of the sorption process was studied using pseudo - first order and pseudo - second order kinetic models. The Pseudo - first order as developed by Lagergren is given by (Lagergren 1898):
\[
dq_t/dt = K_1 (q_e - q_t) \tag{3}
\]

Where \( q_e \) (mg/L) and \( q_t \) (mg/g) are the adsorption capacity at equilibrium and at time \( t \) respectively; \( K_1 \) is the rate constant for pseudo-first order adsorption (min\(^{-1}\)). Integrating Equation (3) for the boundary conditions \( t = 0 \) to \( t = t \) and \( q_t = 0 \) to \( q_t = q_t \), gives:

\[
\log (q_e/q_e - q_t) = K_1 t/2.303 \tag{4}
\]

This is the rate law for pseudo-first order reaction. Equation (4) can be rearranged to obtain a linear form given as:

\[
\log (q_e - q_t) = \log q_e - K_1 t/2.303 \tag{5}
\]

When the values of \( \log (q_e - q_t) \) are linearly correlated with \( t \) and a plot of \( \log (q_e - q_t) \) against \( t \), gives a straight line, then we have a good fit to the pseudo-first order kinetic model. \( K_1 \) and \( q_e \) can be determined from the slope and intercept of the plot respectively. The pseudo-first order model plot is shown on Figure 4. From this figure, it can be seen that straight lines were obtained for the graphs. The values for Colour were higher followed by BOD and then TSS. The linear regression equations were obtained and given below as equations (6), (7) and (8), for BOD, colour and TSS respectively.

\[
y = -0.0002x + 4.4665 \quad (R^2 = 0.8983) \tag{6}
\]

\[
y = 5E-06x + 4.7547 \quad (R^2 = 0.0695) \tag{7}
\]

\[
y = 5E-06x + 4.3897 \quad (R^2 = 0.0695) \tag{8}
\]

The kinetic constants for pseudo-first order model and the coefficient of determination (\( R^2 \)) are shown on Table 1. The pseudo-first order rate constant is higher for BOD, followed by both TSS and colour which have the same value. Although this model gave straight lines for the three parameters, the regression coefficient for TSS and colour are very poor (\( R^2 = 0.0695 \)), and the \( R^2 \) value for BOD is 0.8983, which is still low. This means that the pseudo-first order rate model gave a better fit to the BOD sorption process than colour and TSS. Also, the equilibrium amount adsorbed (\( q_e \)) was determined from the plots and are shown on Table 1. The highest value was obtained for colour, followed by BOD and then TSS. It has been reported that the higher the rate constant, the higher the rate of adsorption (Igwe et al., 2006; Ho, 2006; Demirbas et al., 2004.)

The pseudo-second order kinetic model is expressed as (Ho and McKay, 1998.)

\[
dq_t/dt = K_2 (q_e - q_t)^2 \tag{9}
\]

Where, \( K_2 \) is the rate constant for pseudo-second order model (g/mg-min). For the boundary conditions \( t=0 \) to \( t=t \) and \( q_t=0 \) to \( q_t=q_t \), the integrated form of equation (9) becomes:

\[
1/ (q_e - q_t) = 1/q_e + K_2 t \tag{10}
\]
Equation (10) can be rearranged to obtain Equation (11) which has a linear form as;

\[ \frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \]  

(11)

If the initial adsorption rate \( h_0 \) (mg/g-min) is;

\[ h_0 = K_2 q_e^2 \]  

(12)

Then, equation (11) and (12) becomes;

\[ \frac{t}{q_t} = \frac{1}{h_0} + \frac{t}{q_e} \]  

(13)

Equation (13) was used to analyze the experimental data for fitness to the pseudo-second order kinetic model. A plot of \( \frac{t}{q_t} \) against \( t \) using equation (13), which gives a straight line, confirms the model. \( K_2 \) and \( q_e \) can be determined from the intercept and slope of the plots respectively.

From the pseudo-second order plot shown on Figure 5, it could be seen that fairly straight lines were obtained for BOD, colour and TSS. The values of the linear regression equations are shown on equations (14), (15) and (16) for BOD, colour and TSS respectively.

\[ y = 0.0006x + 0.0159 \quad (R^2 = 0.9855) \]  

(14)

\[ y = 0.0018x + 0.005 \quad (R^2 = 0.9940) \]  

(15)

\[ y = 0.0041x + 0.0176 \quad (R^2 = 0.9892) \]  

(16)

The values of the kinetic constants are shown on Table 1. The \( R^2 \) values for analysis of the parameters were very high. Colour gave 0.9940; that of BOD was 0.9855 and for TSS was 0.9892. Thus, this model gave very good fit to the sorption of BOD, Colour and TSS from palm oil mill effluent. Also, the pseudo-second order rate constant was higher for TSS \((9.55 \times 10^{-4} \text{ mg/g-min})\), followed by colour \((6.48 \times 10^{-4} \text{ mg/g-min})\) and then BOD \((2.26 \times 10^{-5} \text{ mg/g-min})\). Therefore, sorption was higher for TSS followed by colour and then BOD.

The initial sorption rate \( (h_0) \) was higher for colour, followed by BOD and then TSS. This means that at the initial time as \( t \) tends to zero, the sorption rate for colour was higher, but as time increased and equilibrium was approached, the sorption of TSS became more pronounced over the other rates. Thus, the pseudo-second order model gave good fits to sorption of BOD, colour and TSS. Therefore, these kinetic models are concerned with the effect of the observable parameters on the overall rate of sorption (Ho, 2006).

**Intraparticle diffusion**

The sorption rate is known to be controlled by several factors including the following processes (Findon et al., 1993; Weber and Digiana, 1996). (i) diffusion of the solute solute from the solution to the film surrounding the particle, (ii) diffusion from the film to the particle surface (external diffusion), (iii) diffusion from the surface to the internal sites (surface diffusion or pore diffusion) and (iv) uptake which can involve several mechanisms; physicochemical sorption, ion-exchange, precipitation or complexation. Bulk diffusion (i) is non-limiting when agitation is sufficient to avoid concentration gradients in solution; sorption is seen as a quasi-instantaneous mechanism. External mass transfer resistance (ii) and intraparticle mass – transfer resistance (iii) are likely to be rate controlling. Fick’s law may be applied to describe mass transfer rates.

Now, as stated above, if the intraparticle mass transfer is rate controlling, it means that the rate of sorption of the parameters may depend on particle diffusion. The rate of attainment to equilibrium may either be film diffusion controlled or particle diffusion controlled (Okieimen and Orhorhoro, 1986; Weber and Moris, 1963; Srivastava et al., 1989; Igwe and Abia, 2005) even though these two
Figure 5. Pseudo second order plot for adsorption of colour, BOD and TSS using boiler fly.

<table>
<thead>
<tr>
<th>Equation constants</th>
<th>BOD</th>
<th>Colour</th>
<th>TSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first order</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_1$</td>
<td>$4.61 \times 10^{-4}$</td>
<td>$1.15 \times 10^{-5}$</td>
<td>$1.15 \times 10^{-5}$</td>
</tr>
<tr>
<td>$q_e$</td>
<td>$2.93 \times 10^{4}$</td>
<td>$5.68 \times 10^{4}$</td>
<td>$2.45 \times 10^{4}$</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.8983</td>
<td>0.0695</td>
<td>0.0695</td>
</tr>
<tr>
<td>Pseudo-second order</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_2$</td>
<td>$2.26 \times 10^{-5}$</td>
<td>$6.48 \times 10^{-4}$</td>
<td>$9.55 \times 10^{-4}$</td>
</tr>
<tr>
<td>$h_o$</td>
<td>62.89</td>
<td>200.00</td>
<td>56.82</td>
</tr>
<tr>
<td>$q_e$</td>
<td>1666.67</td>
<td>555.56</td>
<td>243.90</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9855</td>
<td>0.9940</td>
<td>0.9892</td>
</tr>
<tr>
<td>Intraparticle diffusion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K$</td>
<td>110.51</td>
<td>7.28</td>
<td>3.13</td>
</tr>
<tr>
<td>$X_i$</td>
<td>215.90</td>
<td>593.80</td>
<td>253.30</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9744</td>
<td>0.1450</td>
<td>0.1018</td>
</tr>
</tbody>
</table>

Table 1. Kinetics and intraparticle diffusion constants for adsorption of colour, BOD and TSS from pome using boiler fly ash.

Figure 6. Intraparticle diffusivity plot for adsorption of colour, BOD and TSS using boiler fly ash.
different mechanisms cannot be sharply demarcated. McKay and Poots (1980) observed that the fraction of solute adsorbed can be expressed in terms of the square root of time. A plot of fraction of solute absorbed against $t^{0.5}$ may be used to estimate the intraparticle diffusion rate in the linear range. This mathematical dependence of concentration in the solid on $t^{0.5}$ has been deduced by considering the sorption mechanism to be controlled by diffusion in the sorbent (as spherical particles) and by convective diffusion in the solution. The solution of the diffusion equation leads to relationship between the concentration in the solid and the parameter $(Dt/a)^{0.5}$ (McKay and Poots 1980). Since D and 'a' are considered constant during the experiment; the concentration varies as a function of $t^{0.5}$ as given by the equation:

$$q(t) = X_i + Kt^{0.5}$$  \hspace{1cm} (17)

The slope of the linear part of the curve (uptake capacity vs. square root of time) gives the initial rate of sorption, controlled by intraparticle diffusion, $K$ (mg/g-min$^{0.5}$). The initial curve portion of the plot is attributed to boundary layer diffusion effects (that is external film resistance) (McKay and Poots 1980).

The extrapolation of linear straight lines to the time axis gives intercepts $X_i$, which are proportional to the boundary layer thickness. The values generated for the intraparticle diffusion is shown on Figure 6. Fairly straight lines were obtained. BOD was higher than colour then followed by TSS. The regression equations and the $R^2$ values are given for BOD, colour and TSS as equations (18), (19) and (20) respectively.

$$y = 110.51x + 215.9 \quad (R^2 = 0.9744)$$  \hspace{1cm} (18)

$$y = -7.2768x + 593.8 \quad (R^2 = 0.1450)$$  \hspace{1cm} (19)

$$y = -3.1277x + 253.3 \quad (R^2 = 0.1018)$$  \hspace{1cm} (20)

The kinetic constants for the intraparticle diffusion are also shown on Table 1. The values of the rate constants for TSS and colour gave negative values whereas, that for BOD is positive. Therefore, one can conclude that the adsorption of BOD was particle diffusion controlled while that of colour and TSS was film diffusion controlled. The values of the boundary layer effects ($X_i$), was higher for colour, followed by TSS and then BOD. The boundary layer acts a viscous drag to the diffusion process before the adsorption takes place. Thus, it could be said that the higher the boundary layer, the slower the diffusion process, hence the lower the sorption process, because diffusion precedes adsorption.

**Conclusion**

The use of boiler fly ash in the adsorptive removal of BOD, TSS and colour from palm oil mill effluent (POME) was investigated. The effect of weight of boiler fly ash and contact time were investigated. The amount adsorbed was found to increase as the adsorbent dose was increased. The smaller particle size of 425 μm was found to adsorb more than the 850 μm size. The experimental data was correlated using the pseudo - first order and pseudo - second order kinetic equations. It was found that the pseudo - second order equation gave a better fit with the rate constant for BOD adsorption being higher than that of colour and TSS. The boundary layer diffusion effect was investigated and the mechanism of sorption was found to be particle diffusion controlled for BOD and film diffusion controlled for colour and TSS.

**REFERENCES**


Ho YS, McKay CC (2001). Sorption studies of Acid Dye by mixed sorbents Adsorption 7:139-147.


Igwe JC, Gbaruko BC, Abia AA (2006). Sorption kinetics and intraparticulate diffusivity of As (III) bioremediation from aqueous...


