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ADSORPTION ISOTHERM STUDIES OF BOD, TSS AND COLOUR REDUCTION FROM PALM OIL MILL EFFLUENT (POME) USING BOILER FLY ASH

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Article

The effluent discharged from an oil mill is still objectionable and the situation in many countries is quite different and much attention has been given to the subject of effective disposal [2]. The quantity of POME produced is about 60% for every tonne of fresh fruit bunches (FFB) processed [3]. Apart from the sludge water itself, which amounts to about 300 kg per tonnes of bunches milled (or about 1.5 tonnes per tonne of palm oil), there are also about 175kg of sterilizer condensate and between 40 and 140kg of effluent from hydro cyclone or clay bath separators per tonne of bunches [4]. The total amount of effluent is therefore more than half a tonne per tonne of bunches or 2.5 tonnes per tonne of oil produced in a typical mill [5]. Hence, an average of 30 tonne FFB per hour mill will generate about 18 tonnes of effluent per hour. In milling 20 tonnes of bunches per hour, more than 200 tonnes of effluent may be discharged over 24 hours and this may contain up to a tonne of oil and 9 tonnes of dissolved or suspended solids. This effluent has a biochemical oxygen demand (BOD) of about 20,000 mg/L or 20% for 5 days, which is extremely high.

Fibre and shell are termed as by-products of the oil mill and they are used as boiler fuel to produce steam for electricity generation for the mill and domestic consumption within the mill complex. Boiler fly ash is produced in palm oil mills from the burning of the fiber and shell. Every tonne of FFB produces about 4kg to 6kg of boiler ash. This porous ash, which contains about 0.28% - 1.33% phosphorus, 1.02% - 4.31% potassium, 0.39% - 3.24% calcium and 0.29% - 2.60% magnesium [6], can be used as a soil conditioner. Currently, this under utilized waste is mainly used as landfill.

Adsorption of heavy metals from aqueous solution by fly ash from palm oil mill and other sources has been reported [7-12]. In view of the maximizing waste utilization and with the prospect of Federal Environmental Protection Agency (FEPA) imposing more stringent BOD limits on palm oil mill, an adsorption method using boiler fly ash may need to be introduced. Therefore, in this study, we investigated the use of boiler fly ash for the reduction of biochemical oxygen demand (BOD), Total suspended solid (TSS) and colour from palm oil mill effluent (POME). Also, adsorption isotherms were used to correlate and model the adsorption studies.

MATERIALS AND METHODS

Materials

Samples of effluent water were collected from a palm oil mill in Okigwe, Imo State Nigeria. 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.

METHODS

Sample Collection and Adsorbent Preparation

Samples of effluent water were collected in different containers of about 5 liters 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 will. 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 425µm and 850µm 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 (425µm and 850µm). The specific surface area of the fly ash was determined using the methylene blue absorption test (MBT) method described by Santamarina *et al* (2002) [13]. The moisture con-

Analyses of Various Parameters

The pH of the solution was determined using pH meter (HACH 51750 – 60) [14]. The pH meter was first standardized using a buffer solution of about 7.0 and then the other solutions were analyzed for their various pH values.

All samples were analyzed for the other parameters as described in the standard methods for the Examination of water and wastewater [15] and standard methods for water and effluents analysis [16].

RESULTS AND DISCUSSION

The particle sizes of the fly ash used were 450µm and 850µm. The specific surface area of the boiler fly ash calculated from the methylene blue absorption test method was 241.4m^2g^{-1} for 850µm and 280.6m^2g^{-1} for 425µm. The fly ash was found to have moisture content of 1.7%.

Sorption Capacity

The experimental results for the adsorptive removal of BOD, colour and TSS using boiler fly ash are presented. The pH of the palm oil mill effluent was found to be 6.4. The amount adsorbed was calculated from equation (2) below:

$$qe = Co - Ce \qquad (2)$$

here qe is the amount adsorbed in mg/g for BOD and TSS and in Hz for colour adsorption; Co is the initial concentration and Ce is the residual amount (concentration) after sorption process

Figure 1 shows the amount adsorbed for BOD, colour and TSS from POME as weight (g) of boiler flay ash was varied for particle size of 425µm, while that for particle size of 850µm is shown on Figure 2.

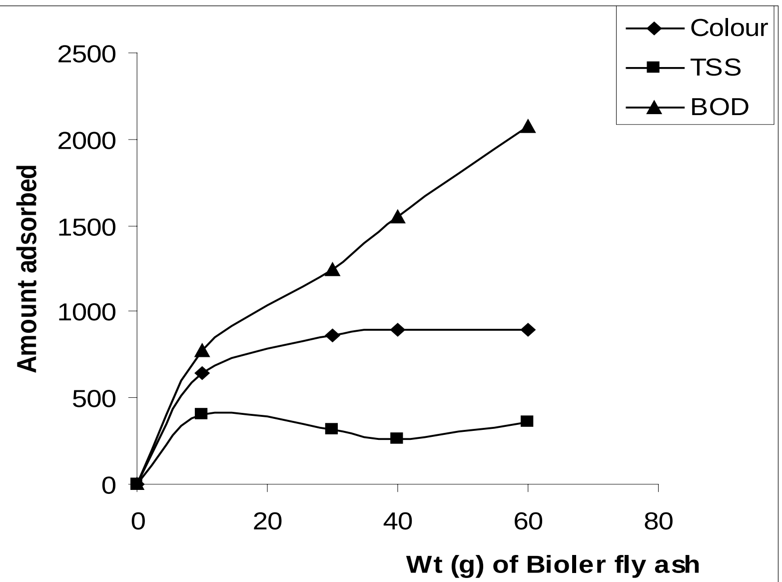

Figure 1: Influence of adsorbent dosage on adsorption of Colour (Hz), TSS (mg/g), and BOD (mg/g) from palm oil mill effluent using boiler fly ash of particle size 425µm.

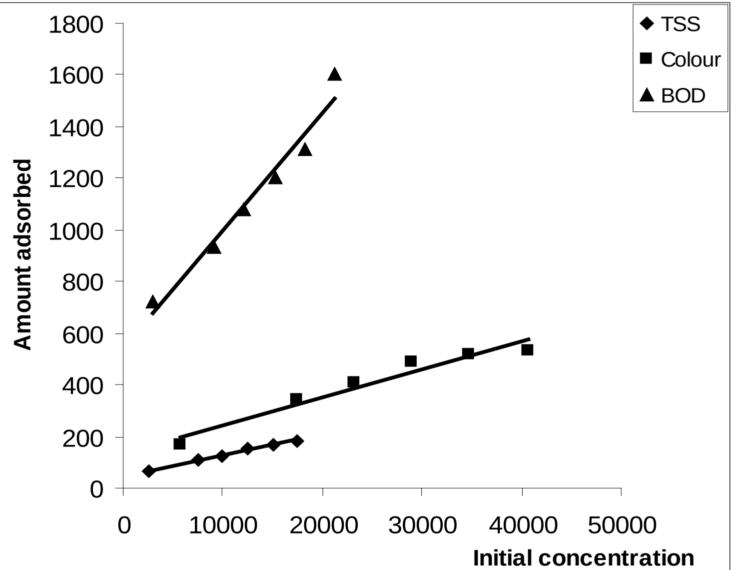

Figure 3: Influence of initial Concentration on adsorption of TSS (mg/g), Colour (Hz) and BOD (mg/g) from Palm oil mill Effluent using Boiler fly ash of 850µm particle size

$$y = 0.0458x + 536.43 \quad (R^2 = 0.9668) \qquad (3)$$

$$y = 0.0108x + 137.5 \quad (R^2 = 0.9422) \qquad (4)$$

$$y = 0.0081x + 46.571 \quad (R^2 = 0.9962) \qquad (5)$$

The amount adsorbed against the percentage of wastewater for BOD, colour and TSS from palm oil mill effluent using boiler fly ash is shown on Figure 4. It could be seen that the amount adsorbed increased as percentage of wastewater was increased. The amount of BOD adsorbed was highest, followed by colour and then TSS.

stewater. Also, it has a fixed range of values, that is, the pH scale.

Sorption Isotherm

When an adsorbent is in contact with the surrounding fluid of a certain composition, adsorption takes place and after a sufficiently long time, the adsorbent and the surrounding fluid reach equilibrium. Generally, an adsorption isotherm is an expression or diagram, which provides information about the fraction of a surface that is covered by adsorbed molecules in equilibrium at constant temperature as a function of pressure or concentration [20]. Adsorption isotherms are described in many mathematical forms, some of which are based on a simplified physical picture of adsorption and desorption, while others are purely empirical relationship intended to correlate the experimental data in simple equation with two or at most three empirical parameters, the more the number of empirical parameters, the better the fit between experimental data [21]. Three isotherms; Freundlich, Langmuir and Dubinin–Radushkevich isotherms were chosen to analyze the adsorption process. The Freundlich and Langmuir isotherms are the earliest and simplest known relationships.

The Freundlich isotherm model was chosen to estimate the adsorption intensity. It is an empirical equation after Freundlich in 1926, used to describe the isotherm data by;

$$Qe = K_F \quad (Ce)^{1/n} \qquad (6)$$

Where K_F and n are empirical constants [22]. Equation (6) may be linearized by taking logarithms as follows:

$$\log Qe = \log K_F + 1/n \log Ce \qquad (7)$$

Where;
K_F = Constant in Freundlich isotherm
n = Freundlich exponent
Ce = Equilibrium liquid phase concentration
Qe = Equilibrium solid phase concentration

The plot of log Qe against log Ce is linear and constants K_F and n were evaluated from the intercepts and slopes respectively. The Freundlich isotherm plots are shown on Figure 5 for TSS, BOD and colour. The regression equations and the coefficient of regression (R^2) are shown as equations 8, 9 and 10 for BOD, Colour and TSS respectively.

TABLE 1. Adsorption isotherm constants for Freundlich, Langmuir and Dubinin-Radushkevich isotherm for adsorption of BOD, Colour and TSS using boiler fly ash.

Fruendlich isotherm				
Parameter	$^1/_n$	K_F(L/g)	R^2	
TSS	0.53	1.00	0.9893	
Colour	0.62	0.80	0.9898	
BOD	0.34	49.11	0.8975	
Langmuir isotherm				
Parameter	As(mg/g)	K(L/g)	R^2	
TSS	277.78	$1.0X10^{-4}$	0.9118	
Colour	909.09	$4.29x10^{-5}$	0.9824	
BOD	2000.00	$1.47X10^{-4}$	0.8851	
Dubinin-Radushkevich isotherm				
Parameter	β(KJ/mol)	q_D(mg/g)	E(KJ/mol)	R^2
TSS	0.82	152.81	0.06	0.8102
Colour	5.44	478.81	0.03	0.9101
BOD	0.47	1233.24	0.02	0.6235

The Langmuir equation was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface. The Langmuir isotherm is represented by the following equation [24];

$$qe = K_L\ Ce / (1 + a_L\ Ce) \qquad (11)$$

The linearized form of equation (11) could be written as;

$$Ce/qe = 1/K_L \quad + (a_L\ /K_L)Ce \qquad (12)$$

Where;

Ce is the equilibrium concentration of the parameter; qe is the amount of parameter adsorbed. The constants K_L and a_L are the Langmuir constant (L/g) and Langmuir isotherm constant (L/mg), respectively. The ratio of a_L/K_L represents the maximum adsorption capacity, Q_{max}. Another form of the Langmuir equation [25], shown below was used to model the adsorption data.

$$Ce/Qe = 1/KAs \quad + Ce/As \qquad (13)$$

Where As is the sorbent binding capacity and K is the binding constant. The plots of Ce/Qe against Ce gave straight lines and are shown on Figure 6 for TSS, BOD and colour adsorption on fly ash. The regression equations and the linear coefficient of regression (R^2) are shown on the plots. The plots and the R^2 values show that the Langmuir model gave did not give a very good fit to the sorption process for BOD and TSS. The values of the Langmuir constants are show on Table 1. It is well known that the Langmuir equation is intended for a homogeneous surface. A good fit of this equation reflects monolayer adsorption [22]. Therefore, the higher the adsorption, the greater the value of the sorbent binding capacity (As).

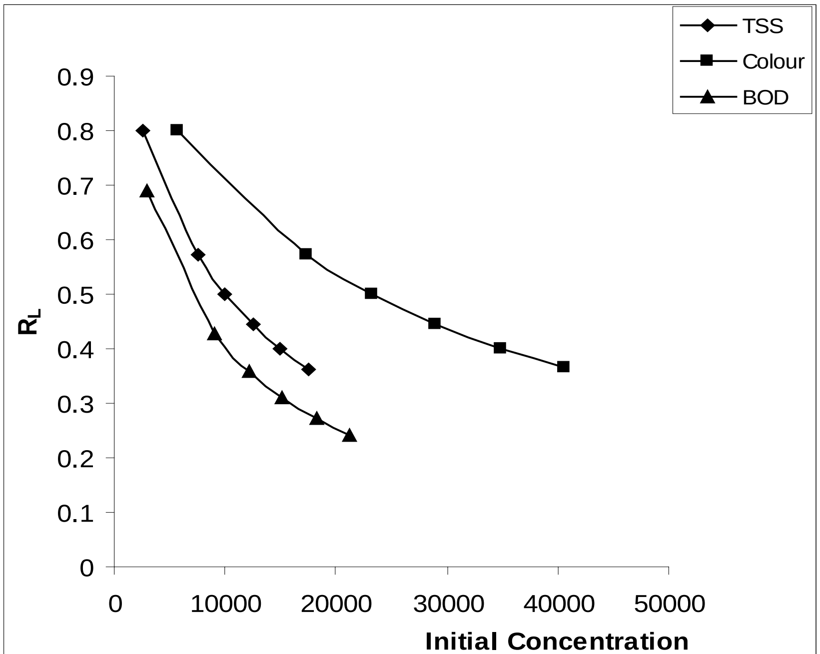

Figure 7: Dimensionless separation factor (R_L) against initial concentration for BOD,Colour and TSS adsorption on boiler fly ash.

The Dubinin-Radushkevich isotherm was chosen to estimate the characteristic porosity of the fly ash and the model is represented by equation (15) [27];

$$qe = q_D \ \exp(-\beta \ [RT \ln(1 + 1/Ce]^2) \qquad (15)$$

Where β is related to the free energy of sorption per mole of the sorbate as it migrates to the surface of the adsorbent from infinite distance in the solution and q_D is the Dubinin – Radushkevich isotherm constant related to the degree of sorbate sorption by the sorbent surface. The linear form of equation (15) is given as;

$$\ln qe = \ln q_D - \beta \varepsilon^2 \qquad (16)$$

Where, ε is the Polanyi potential [28,29] which is related to the equilibrium concentration as;

$$\varepsilon = RT \ln(1+1/Ce) \qquad (17)$$

The plots of ln qe against $[RT \ln (1 + 1/Ce)]^2$ gave fairly straight lines and are shown on Figure 8 for TSS, BOD and colour adsorption on fly ash. The Linear regression equations and R^2 values show that the isotherm model does not describe BOD and TSS removal process very well (Table 1). The apparent energy of adsorption from the Dubinin–Radushkevich isotherm model can be computed using the relationship [27], tion (R^2) for the three isotherms, we can compare their fitness to the experimental data as Freundlich > Langmuir > Dubinin-Radushkevich. From the results of this study, it means that boiler fly ash can be used as an adsorbent to further reduce the concentration of BOD, colour and TSS from POME. Therefore, because boiler fly ash is a waste in the palm oil industry, this is a good step in the right direction to industrial waste management.

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