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Dye Removal from Waste Water by Adsorption onto Boiler Fly Ash

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ABSTRACT

The treatment of wastewater is essential not only to achieve an environment devoid of pollution but also to meet up with the water needs of the community. Dyes have been in use mainly in the textile industry for dyeing fabrics. This introduces dyes and dye products into the effluent water, which must be removed for water re-use and recycling and also for environmental pollution control. The use of waste boiler fly ash derived from a palm oil mill for the adsorptive removal of methyl orange and Congo red was studied in this paper. As time increased, the amount of dye removed increased to a maximum at 20 minutes for methyl orange (249.9 mg/L) and 60 minutes for Congo red (249.999 mg/L) and later decreased to 249.83 mg/L at 60 minutes for methyl orange and 249.99 mg/L at 120 minutes for Congo red. Therefore, Congo red was adsorbed more than methyl orange. The sorption process was modeled using Langmuir and Freundlich isotherm models. The Freundlich isotherm gave a better fit than the Langmuir isotherm although both did not give an excellent correlation. The experiment was also modeled using pseudo-first and pseudo-second order equations. The pseudo-second order gave a better fit with an R^2 value of 1.00 for both dyes. The rate constant K_2 was found to be 1.6 g mg^{-1} min^{-1}. This means that waste boiler fly ash could be used as an excellent adsorbent for removal of Congo red and methyl orange from waste water.

Keywords: Congo red, isotherm, methyl orange, sorption, treatment

INTRODUCTION

A dye can generally be described as a coloured substance that has an affinity to the substrate to which it is being applied (Banerjee *et al*. 1997). The textile, paper, food, cosmetics and pharmaceutical industries extensively use dyes (Chen *et al*. 1999). There is no general method for the removal of colour from dye waste waters. Methods of primary clarification including sedimentation and floatation are not effective for the removal of colour without simultaneous chemical treatment (Chang 1981). Processes such as membrane separation, coagulation and ion exchange are also used for the removal of colour from dye waste waters but the cost of these processes is the main drawback of these techniques (Mishra and Tripathy 1993). Combined methods such as activated sludge and coagulation, activated sludge and adsorption and chemical oxidation are being used by most industries (Lin and Chen 1997).

Dyes are synthetic and aromatic molecular structural compounds. The group producing the colour is the chromophore and the other non-coloured groups that influence or intensify the colour are called auxochromes (Daintith 2004). According to their dissociation in aqueous solution, dyes can be classified as acid, direct reactive dyes (anionic), basic dyes (cationic) and disperse dyes (nonionic). Solutions retain them by physical adsorption by making compounds with metals and salts using covalent bonds (Sathiya *et al*. 2007). Because they are inert and non-toxic when discharged into waste streams, people always overlook their undesirable nature. Some have been reported to be harmful to aquatic life in rivers where they are discharged (Ho and Chiang 2001).

Experimental studies by Erdem *et al*. (2004) and Singer and Little (1975) using textile waste waters in the adsorption of textile dyes (Sıf Blau BRF, Everzol Brill Red 3BS, and Int Yellow 5GF) by diatomite earth shows that values of the removal efficiency of the dyes ranged from 28.60 to 99.23%. Textile dyes are slowly degraded and some authors have reported that colour removal is due to the adsorption on microorganisms (Pagga and Brown 1986). The economical decolourization of effluents by removal of dyes remains an important problem although recently a number of successful systems using adsorption techniques have been developed (Kamal *et al*. 1991; Choy *et al*. 1999; Keith *et al*. 1999; Khattri and Singh 2000; Low *et al*. 2000).

Adsorbents are materials that have been useful in the removal of dyes from waste water or materials that adsorb dyestuff at the surface (Rai *et al*. 2005). Activated carbon has been useful as an adsorbent for the removal of dyes. The performance of an activated carbon treatment process depends on the type of carbon and characteristics of the waste water in addition to the operating condition. Different types of carbon include granular activated carbon, fly ash, coal and Brazilian coal. Saw dust (Igwe *et al*. 2005), coconut fiber maize husk/cob (Igwe and Abia 2005), cocoa pods and boiler fly ash (Okoronkwo *et al*. 2006), etc. have also been used as adsorbents (Mckard *et al*. 1980).

Boiler fly ash is derived from palm oil mills as a waste by burning fibers and shells. Every tonne of Fresh Fruit Bunch (FFB) produces about 4 to 6 kg of boiler fly ash (Majid *et al*. 1999). The composition of this porous ash have been reported as 0.28-1.33% phosphorous, 1.02-4.31% potassium, 0.39-3.24% calcium and 0.29-2.60% magnesium (Rusnani and Ma 1999). Boiler fly ash has been used as a soil conditioner but currently, this under utilized waste is mainly used as landfill. Also, boiler fly ash from palm oil mill has been reported as a good adsorbent for removal of heavy metals from aqueous solution (Panday *et al*. 1985; Mathur and Rupainwar 1988; Weng and Huang 1994; Hashim *et el*. 1996). Boiler fly ash has also been used for reduction of BOD, TSS (Total Suspended Solids) and colour from palm oil mill effluent (POME) (Majid *et al*. 1999; Igwe *et al*. 2007).

Molecules adsorb on boiler fly ash due to the adsorption

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caused by a London dispersion force (LDF), a type of van der Waals force which exists between molecules (de John and Hurchins 1976). It has also been suggested that organic molecules are adsorbed on carbons due to the van der Waal's force between benzoic arrays of carbons and organic molecules (Singh and Rawat 1994).

This paper therefore investigated the extent of adsorption of two dyes (methyl orange and Congo red) from aqueous solution onto boiler fly ash, an agricultural waste and a natural adsorbent.

MATERIALS AND METHODS

Boiler fly ash was collected from Ukelu Oil Mill in Umulolo Okigwe, Local Government Area of Imo State, Nigeria. It was crushed and sieved through a 150 µm mesh then activated by soaking for 24 hours in 2% (v/v) nitric acid, rinsed with deionized water and sun dried. The stock solutions of each of the dyes were prepared with deionized water. All other working solutions were prepared by diluting the stock solution with deionized water. All readings were performed in triplicates, a total of 84 readings were obtained, i.e. 21 readings for each parameter of concentration and time that was varied for the two dyes Methyl Orange and Congo Red. The averaged data were used in the result data with an average standard error of less than 5%. The significance of the results were tested using a one way analysis of variance (ANOVA) at the 0.05 level of significance to ascertain whether the difference among the results were significant.

To determine the effect of contact time and concentration, a fixed concentration (250 mg/L) was used. Then 100 ml of each of the dyes was put into 7 different reagent bottles containing 2 g of the activated boiler fly ash. They were left for different time intervals: 10, 20, 30, 40, 50, 60 and 120 min in a constant temperature rotary shaker at a speed of 150 rpm. The contents were filtered after each time interval and the concentration of dyes left in the filtrates were analyzed.

Also, the concentrations were varied within a fixed time of 60 min. Two g of the activated boiler fly ash was put in 7 different reagent bottles, into which 100 ml of each of the dye solutions at different concentrations (50, 100, 150, 200, 250, 300 and 500 mg/L) were placed. The solutions were shaken after each addition and were left for 60 min in a constant temperature rotary shaker. Thereafter they were filtered using a Whatman No 41 filter paper to separate the adsorbent from the solution. All the filtrates were analyzed using a UV/Visible-spectrophotometer model 200A. The amount of dye absorbed was calculated from the difference between the initial concentration (C_o) of the dye used and amount remaining in solution (C_e).

RESULTS AND DISCUSSION

The maximum wavelengths of the two dyes used in this study were 488 nm and 560 nm for methyl orange and Congo red, respectively. Methyl orange is often used in titration and is toxic while Congo red is a secondary diazo dye.

The amounts of both dyes adsorbed (in mg/L and percentage amount adsorbed) given in **Table 1** indicates that the adsorption of the dye increased then later decreased. This means that at the beginning of the experiment, at time zero, no dyes were adsorbed. As time increased from zero to 10 min, a certain amount of dye (249.995 mg/L for Congo red and 249.890 for methyl orange) were adsorbed. The sorption of the dyes increased further as time increased reaching a maximum (equilibrium) at 20 min for methyl orange and 60 min for Congo red. Thus, this could be taken as the maximum monolayer adsorption site coverage resulting in a further decrease as time increased. Thus, the maximum shows saturation of the sites. This is caused by strong attractive forces between the dye molecules and the sorbent and fast diffusion onto the external surface is followed by fast pore diffusion into the intraparticle matrix to attain rapid equilibrium (Ho and Chiang 2001).

For Congo red, maximum absorption was observed at 60 min and that of methyl orange was observed at 20 min. This means that the sorption of methyl orange approached equilibrium faster than that of Congo red, taking that the equilibrium amount adsorbed is the maximum amount of dye adsorbed. Quantitatively, Congo red was adsorbed by the boiler fly ash more than methyl orange.

Table 1 Amount adsorbed (mg/L and percentage) of dye adsorbed by the boiler fly ash at an initial concentration of 250 mg/L.

Time	Amount adsorbed			
(Min)	Congo red		Methyl orange	
	mg/L	%	mg/L	%
10	249.995 ± 0.03	99.9980	249.89 ± 0.04	99.958
20	249.992 ± 0.04	99.9968	249.90 ± 0.04	99.960
30	249.997 ± 0.02	99.9988	249.83 ± 0.04	99.932
40	249.998 ± 0.01	99.9992	249.86 ± 0.06	99.944
50	249.998 ± 0.01	99.9992	249.87 ± 0.06	99.948
60	249.999 ± 0.01	99.9996	249.83 ± 0.03	99.932
120	249.991 ± 0.02	99.9964	249.86 ± 0.02	99.944

Table 2 Amount adsorbed (mg/L) and percent dye adsorbed after 60 min by boiler fly ash at various concentrations.

Conc	Amount adsorbed			
(mg/L)	Congo red		Methyl orange	
	mg/L	%	mg/L	%
50	49.99 ± 0.08	99.980	49.92 ± 0.03	99.840
100	99.99 ± 0.08	99.990	99.89 ± 0.06	99.890
150	149.99 ± 0.08	99.993	149.70 ± 0.02	99.799
200	199.99 ± 0.08	99.995	199.80 ± 0.02	99.900
250	249.98 ± 0.08	99.992	299.81 ± 0.03	99.924
300	299.96 ± 0.02	99.986	299.79 ± 0.04	99.921
500	499.96 ± 0.02	99.992	499.79 ± 0.02	99.995

Table 3 One way ANOVA without replication between agitation time against amount adsorbed and initial dye concentration against amount adsorbed.

Source of variation	SS	df	MS	F_{cal}	F_{Tab}
Congo red					
Time	133694.67	6	22282.45	3.120×10^8	2.85
Error	0.001	14	7.143×10^{-5}		
Total	133694.67	20			
Methyl Orange					
Time	7000.044	6	1166.674	148.485	2.85
Error	0.011	14	7.85714		
Total	7000.0554	20			
Congo red					
Co	380531.242	6	63421.873	1.199×10^8	2.85
Error	0.0074	14	5.29×10^{-4}		
Total	380531.294	20			
Methyl Orange					
Co	402635.674	6	67107.280	1.174×10^5	2.85
Error	8.0043	14	0.5717		
Total	402643.678	20			

Table 2 shows the varying amount of dye adsorbed when boiler fly ash is added at different concentrations, which indicates that the adsorption of each of the dyes by boiler fly ash was strongly dependent on the initial concentration of the dye, i.e. as concentration increased there was a corresponding increase in the amount of dye adsorbed. The standard deviations of the mean are also shown in **Table 2**.

A one way analysis of variance (ANOVA) without replication between the time of agitation against amount adsorbed and initial dye concentration against amount adsorbed at the 0.05 level of significance revealed significant differences (**Table 3**), i.e. the amount adsorbed which increased and later decreased differ significantly.

The mode of adsorption of these dyes on the adsorbent could be explained based on the mode of adsorption of coloured effluents, hence the mode of decolourization of dye effluents and also on certain properties of the dyes. The structures of the dyes are given as **I** for methyl orange and **II** for Congo red in **Fig. 1**. As can be seen from their structures, both dyes have similar points of attachment to the

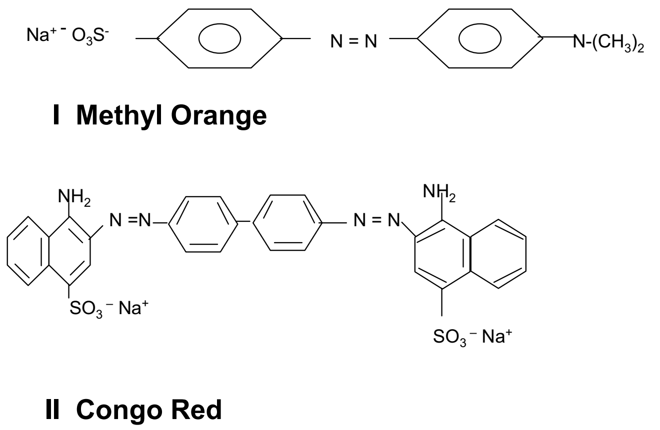

Fig. 1 Structure of methyl orange (I) and Congo Red (II).

adsorbent which is the group SO_3Na. On ionization gives SO_3^- and Na^+, meaning that a possible mechanism is by ion–exchange. Methyl orange, which is less bulky, has only one point of attachment compared to two points in Congo red, which is bulkier.

It is our opinion that the bulky nature of Congo red may have introduced steric hindrance which counteracts the effects of two points of attachment. Hence, the adsorption capacities of both dyes are almost equal. Similar results have been observed and reported that the decolorization or adsorption of the dyes were dependent on the structure of the dyes, that is, the number of azo groups on the dye structure (Oranusi and Ogugbue 2005; Igwe *et al.* 2007). While Oranusi and Ogugbue (2005) investigated the effect of pH and nutrient starvation on the decolorization of Orange II and Direct Blue 71 using *Pseudomonas* sp., Igwe *et al.* (2007) investigated the kinetics, mechanism and equilibrium partitioning of methyl orange, methyl red and methyl blue using sorghum waste biomass. Sathiya *et al.* (2007) used two white rot fungi (*Trametes hirsute* and *Pleurotus florida*) in the decolourization of textile dyes namely Blue CA, Black B133 and Corazol Violet SR and discovered that decolourization depended upon laccase production, media and the properties of the dyes. The adsorption of Acid blue 9 was reported to be because of the strong attractive forces between the dye molecules and the sorbent, fast diffusion onto the external surface followed by fast pore diffusion into the intraparticle matrix to attain equilibrium (Ho and Chiang 2001).

Other studies have also reported similar results such as in the use of *Proteus mirabilis* in the decolourization of deep red azo dye (RED RBN) from textile effluent (Chen *et al.* 1999). They reported that the microorganism exhibited a remarkable color removal capability, even at a high concentration of azo dye. More than 95% of azo dye was reduced within 20 h at a dye concentration of 1.0 g L^{-1}. Also that decolorization appears to proceed primarily by enzymatic reduction associated with a minor portion, 13-17%, of biosorption to inactivated microbial cells. In the removal of methylene blue dye from aqueous solution using activated and non-activated bentonites, it was reported that an increase in sorbent concentration or initial pH value of the solutions resulted in a greater removal of methylene blue dye from the solution (Al-Asheh *et al.* 2003). Again, in their work Bulut *et al.* (2007) reported that the adsorption of direct blue 71 from aqueous solution using wheat shells decreased with increasing adsorbent dosage and also increased with increasing contact time, temperature, and concentration in solution.

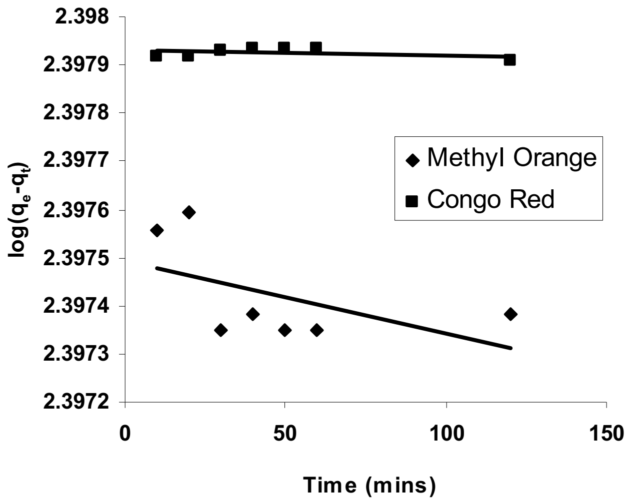

Fig. 2 Pseudo first order plot for adsorption of methyl orange and Congo red using boiler fly ash.

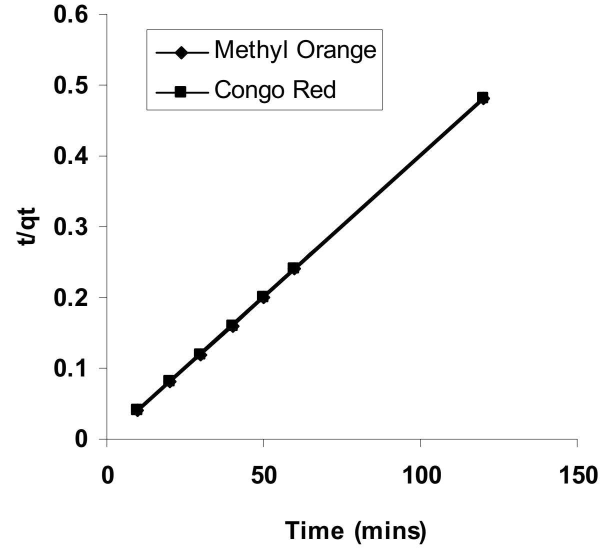

Fig. 3 Pseudo second order plot for adsorption of methyl orange and Congo red using boiler fly ash.

The rate constant (K_{ad}) of adsorption for the removal of each dye in this study was determined using the pseudo-first and pseudo-second order rate, expressed as:

$$\log (q_e-q_t) = \log q_e - (K_{ad}\, t /2.303) \qquad (1)$$

for the pseudo-first order and

$$t/q_t = 1/h_o + 1/q_e\, (t) \qquad (2)$$

for the pseudo-second order rate (Okoronkwo *et al.* 2006)

where
q_t = amount adsorbed at time (t)
q_e = equilibrium amount ($q_o - q_t$)
q_o = initial concentration
k_{ad} = rate constant for pseudo-first order
$k_2 = h_o/qe^2$ for pseudo-second order (rate constant)

Table 4 Parameters for the pseudo-first and pseudo-second order equations.

Dyes	**Pseudo-first order**			**Pseudo-second order**			
	K_{ad}	**q_e**	**R^2**	**K_2**	**q_e**	**h_o**	**R^2**
Methyl orange	4.606×10^{-6}	249.75	0.2749	1.6	250	1×10^5	1.00
Congo red	2.07×10^{-7}	249.98	0.1101	1.6	250	1×10^5	1.00

h_o = sorption rate
t = time

Table 4 shows the rate constant k, the equilibrium sorption q_e and initial sorption rate h_o of the sorption of the various dyes on boiler fly ash for the pseudo-first and pseudo-second order models.

The pseudo-first and second order plots at an initial concentration of 250 mg/L are shown in **Figs. 2** and **3**, respectively for both dyes. The pseudo-second order gave a better fit with an R^2 value of 1.00 for both dyes and a rate constant of 1.60 g $mg^{-1}min^{-1}$

Sorption isotherm

Equilibrium studies that give the capacity of the adsorbent and the equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms which are usually the ratio between the quantity adsorbed and that remaining in solution at a fixed temperature at equilibrium. The earliest and simplest known relationships describing the adsorption equation are the Freundlich and the Langmuir isotherms (Jalali *et al.* 2002). These two isotherms were used to access the different isotherms and their ability to correlate the experimental data.

The Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases. The following equation can be used to model the adsorption isotherm.

$$q = (q_{max} b\ Ceq)/(1 + b\ Ceq) \qquad (3)$$

where q is milligrams of dye accumulated per gram of the biosorbent material; C_{eq} is the dye residual concentration in solution at equilibrium, q_{max} is the maximum specific uptake corresponding to the site saturation and b is the ratio of adsorption and desorption rates (Chong and Volesky 1995). The Langmuir isotherm is based on these assumptions (Langmuir 1918).

- adsorbates are chemically adsorbed at a fixed number of well defined sites;
- each site can hold only one adsorbate;
- all sites are energetically equivalent and;
- there is no interaction between the adsorbates.

When the initial dye concentration rises, adsorption increases while the binding sites are not saturated. The linearized Langmuir isotherm allows the calculation of adsorption capacities and the Langmuir constants and is equated by the following equation.

$$C_{eq}/q = 1/q_{max}b + C_{eq}/q_{max} \qquad (4)$$

From the linear plots of Ceq/q vs Ceq (not shown), we calculated the linear regression equations for the Langmuir isotherm for the sorption process shown in **Table 5**. From these regression equations and the linear plots, the values of the Langmuir constants were calculated and are shown in **Table 6**. q_{max} and b were obtained from the slope and intercept of the plots.

The essential characteristic of the Langmuir isotherms can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L, which was defined by Ahalya *et al.* (2005):

$$R_L = 1/(1 + bC_o) \qquad (5)$$

where b is the Langmuir constant and C_o is the initial concentration of the dyes. The R_L value indicates the shape of the isotherm. According to McKay *et al.* (1982), R_L values between 0 and 1 indicate favourable absorption. Also $R_L > 1$ is unfavorable. From our study, R_L values for methyl orange ranged from 0.03 to 0.23 and Congo red adsorption ranged from 0.00012 to 0.0012. This is for an initial concentration of 50-500 mg/l of the dyes. Therefore, the sorption process was favourable, going by the R_L values.

The Freundlich isotherm was chosen to estimate the adsorption intensity of the sorbent towards the adsorbate. It is represented by the following equation (Freundlich 1957):

$$q = \text{In}\ K_F\ C_{eq}^{1/n} \qquad (6)$$

where C_{eq} is the equilibrium concentration (mg/l), q is the amount adsorbed (mg/g) and k_F and n are constants incorporating all parameters affecting the adsorption process, such as adsorption capacity and intensity, respectively. The linearized form of the Freundlich adsorption isotherm was used to evaluate the sorption data as represented by Ahalya (2005):

$$\ln q = \text{In}K_F + 1/n\ln C_{eq} \qquad (7)$$

The Linear regression equation for the Freundlich adsorption isotherm is also shown in **Table 5**. The values of K_F and n were calculated from the intercepts and slopes of the Freundlich plots respectively and are shown in **Table 6**. According to Kadiruein and Namasivayam (2000), who reported on the sorption of lead (II) ions from aqueous solution onto coir-pith carbon, n values between 1 and 10 represent beneficial adsorption. Malkoc and Nuhoglu (2007) investigated the kinetic and equilibrium parameters of the batch adsorption of Cr (VI) onto Waste Acorn of *Quercus ithaburensis* (WAQI) and reported n values of 7.93, 2.50 and 5.68 at different temperatures of 25, 45 and 60°C respectively. Their n values lie between 1 and 10 and they reported that it indicates favorable adsorption of Cr (VI) onto WAQI. Ho *et al.* (2002) investigated the equilibrium sorption isotherm for Zn, Cu and Pb ions on tree fern (*Cyatheales dicksoniaceae*) and obtained n values of 4.50 for Zn and Pb ions and 3.83 for Cu ion. In their research, Abia *et al.* (2003) reported values of n below 1.0. Chemical modification of the adsorbent by thiolation increased the value of n to be above 1.0. Hence, they concluded that the modification of the adsorbent increased the adsorption capacity since n values were increased (Abia *et al.* 2003). Other workers have also reported values for the Freundlich exponent n less than 1.0 (Sun and Shi 1998; Igwe and Abia 2003). Also, Akgerman and Zardkoohi (1996) stated that the values of K_F and n determine the steepness and curvature of the isotherm. They concluded that n values extrapolated from the slope and the Freundlich isotherm constant K_F help to determine the shape of the isotherm and the fitness of the isotherm to sorption data. From our studies, the values of n are 0.78 and 1.44 for methyl orange and Congo red, respec-

Table 5 Values of regression equations and co-efficient of determination (R^2) for Langmuir and Freundlich isotherms for adsorption of methyl orange and Congo red on boiler fly ash.

Langmuir		**Freundlich**	
Methyl orange	**Congo red**	**Methyl ornage**	**Congo red**
Y = 0.0118x +0.1732	Y =0.0244x + 0.0015	Y =12831x - 3.7937	Y=0.6958x - 3.3502
(R^2 = 0.0078)	(R^2 = 0.386)	(R^2 =0.6111)	(R^2= 0.6386)

Table 6 Langmuir and Freundlich isotherm parameters for adsorption of methyl orange and Congo red on boiler fly ash.

Langmuir				**Freundlich**			
Methyl orange		**Congo red**		**Methyl orange**		**Congo red**	
q_{max}	k_L	q_{max}	k_L	k_F	n	k_F	n
86.21	0.067	40.98	16.27	1.61×10^{-4}	0.78	4.47×10^{-4}	1.44

tively. This represents beneficial adsorption because the values of n did not exceed 10. The results of this study correlates well with these findings. The Freundlich equation frequently gives an adequate description of adsorption data over a restricted concentration range, even though it is not based on any theoretical background. Apart from homogeneous surfaces, the Freundlich equation is also suitable for a highly heterogeneous surface (i.e. considering solid-liquid phase adsorption) and an adsorption isotherm lacking a plateau, indicating a multi-layer adsorption (Juang *et al.* 1996). The values of 1/n, less than unity is an indication that significant adsorption takes place at low concentration but the increase in the amount adsorbed with concentration becomes less significant at higher concentration and *vice versa* (Teng and Hsieh 1998).

The magnitude of K_F and n shows easy separation of the dyes from wastewater and high adsorption capacity. Also, the higher the K_F value, the greater the adsorption intensity. Therefore, the higher K_F values for Congo red confirm that its adsorption capacity was greater than that of methyl orange.

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