**Research Article**

# Removal of Dyes from Synthetic Effluents by Adsorption onto Thiolated boiler fly ash

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**Abstract** The batch adsorption of methyl orange (MO) and Congo red (CR) from synthetic dye effluents using thiolated boiler fly ash was studied by monitoring the dye concentration using UV- spectrophotometer. The amount of dye adsorbed increased as initial concentration and time was increased. MO was adsorbed more than CR. The sorption process was found to be influenced by initial concentration, time, dye structure and properties and thiolation on the surface chemistry of the adsorbent. The kinetic data were subjected to pseudo-first, pseudo-second order, penetrant transport, fractional attainment to equilibrium (FATE) and intraparticle diffusion models. The pseudo-second order model gave a better fit with rate constant ($K_2$) value of $5.33 \times 10^{-2}$ g/mg-min and $R^2$ value of 1.0000, while the Boyd model was used to confirm that film diffusion was the predominate mechanism. The equilibrium data was treated by Langmuir, Freundlich, Dubinin-Raduskevich (D-R) and Temkin isotherms. A normalized standard deviation $\Delta q$ (%) of root mean square sum of residual errors was used to compare the validity of each of the isotherm models and it was found that none of the isotherms gave values less than 10% for the sorption of MO while Freundlich isotherm with $\Delta q$ value of 0.0043% gave a better fit to sorption of CR. Therefore, boiler fly ash which has been shown as a good adsorbent for dye removal was enhanced by thiolation, hence could be used for the design of an effective adsorber for dye removal from effluents.

**Keywords** environment, dyes, pollution, surface chemistry, adsorption

## Introduction

Man has devised several methods for the removal of colour from dye wastewater. Methods of primary clarification which include sedimentation and flotation are not effective for the removal of colour with simultaneous chemical treatment [1]. Processes such as membrane separation, coagulation and ion exchange are also used for the removal of colour from dye wastewater but cost is the major draw-back of these techniques [2-4]. Combined methods such as activated sludge and coagulation; activated sludge and adsorption; and coagulation and chemical oxidation have also been used [5]. The dyes slowly degrade and the colour removal is due to adsorption. Also ozonation of dyes have been reported [6-9].

The economics of decoulorization of effluents by removal of dye remains an important problem, although recently a number of successful systems using adsorption techniques have been developed [10-15]. Adsorption is the accumulation of particles at a surface by loose association [16]. The adsorbent is the solid that bind molecules by physical attractive force, ion-exchange or chemical bonding [17]. The extent of adsorption depends on the nature, particle size, temperature and pH of the adsorbate [15].

Activated carbon has been successfully used as an adsorbent for removal of dyes from wastewater [18-20]. The performance of an activated carbon treatment process depends on the type of carbon and the characteristics of the wastewater in addition to the operating conditions and cost [2, 21]. Furthermore, studies that have been carried out

on the removal of colour using mixtures of fly ash and coal in different proportion showed high adsorption capacity for cationic dyes. A comparative study of adsorption capacity and costs of adsorbent have shown that a fly ash and coal mixture could be used to replace the activated carbon [1]. Studies on the removal of dyes from wastewater by natural sorbents and agricultural by-products have been reported such as Quaternized wood for reactive dyes [22]; sugar beet pulp for Gemazol turquoise blue-G reactive dye [23]; rice husk for Safranin [24]; Carbonaceous adsorbent prepared from waste tires for methyl orange [25]; sugarcane bagasse for Foron Blue E-BL [26]; spruce wood (*Picea abies)* for Egacid Orange and Egacid Yellow [27].

Boiler fly ash is derived from palm oil mills as a waste by burning fiber and shells. Majid *et al* [28], reported that every tonne of fresh fruits Bunch (FFB) produces about 4 to 6 kg of boiler fly ash. This ash which is a porous substance has been reported to contain phosphorous (0.28-1.33%) potassium (1.02-4.31%), calcium (0.39-3.24%) and magnesium (0.29-2.60%) [29]. As a result of this mineral content, boiler fly ash has been used as a soil conditioner. Many other prospects of applying this waste have been investigated, for example, it has been reported as a good adsorbent for removal of heavy metals form aqueous solutions [30-32].

Also the feasibility of utilizing boiler fly as an adsorbent for removal of Congo red and methyl red have been reported [33]. It was found to be a very good adsorbent for dye removal. In this work therefore the aim was to investigate the effect of chemical modification of the boiler fly ash by thiolation on the sorption profile of the adsorbent. Modification of adsorbents has been reported to enhance the sorption capacity of adsorbents [34-38]. Various other types of modification have also been investigated by many other researchers [34, 39, 40]. Also, Wan Ngah and Liang [41], reported on carboxymethylation of chitosan; Igwe and Abia [36], reported on EDTA modified maize husk; Urik *et al* [42], reported on urea and ferric Fe (III) oxyhyroxide modification of spruce (*Picea abies*) sawdust; Adeyemo et al [43], reported on adsorption of dyes using different types of modified and unmodified clay and Sauprasearsit *et al* [44], reported on 0.5 NaOH modified *Luffa cylindrical* fibre. Also, thiolation of other adsorbents have been reported [45-48].

## Materials and Methods
### Adsorbent Preparation
The boiler fly ash was obtained from Ukelu oil mill in Umulolo Okigwe, Imo State Nigeria. The lumps among the sample were crushed and sieved through 2 mm mesh size. The boiler fly ash was then activated by soaking for 24 h in 2% (v/v) nitric acid, filtered and rinsed with deionized water and air-dried.

### Adsorbent Modification
The adsorbent was modified by method of thiolation [49]. 50g of the air-dried activated boiler fly ash was soaked in 500 mL of 0.3M solution of thioglycolic acid for 24 h. The mixture was then filtered and the fly ash was rinsed with deionized water and air-dried. The extent of thiolation was estimated titrimetrically by reaction of the thiolated adsorbent with iodine and back-titration of the unreacted iodine with standard sodium thiosulphate solution [50]. About 0.5 g portions of the thiolated boiler fly ash was reacted with 200 mL aliquots of 1.0 M iodine solution. The unreacted iodine was back titrated with standard thiosulphate solution. The amount of SH groups incorporated onto the boiler fly ash were calculated using the relationship:

$$\%SH = (V_o - V_t) \times 33.07M \times 100/(w \times 1000) \tag{1}$$

Where $V_o$ is the volume of standard thiosulphate solution used in the blank titration (unthiolated adsorbent); $V_t$ is the average volume of the standard thiosulphate solution used in the test titration (thiolated adsorbent). M is molarity of thiosulphate solution and w is the weight of adsorbent.

### Adsorbate (dye solution) Preparation
Congo red and methyl Orange used in this study was obtained from Sigma-Aldrich Company. The synthetic effluents were prepared by dissolving known amounts of the dyes separately in deionized water to produce stock solutions of 1000 mg/L. All working solutions were prepared by diluting the stock solution with deionized water to

the needed concentration of 500, 300, 250, 200, 150 100 and 50 mg/L. Other reagents used were of analytical grade and used as purchased without further purification.

## Sorption of dyes from aqueous solution

The sorption experiments were carried out in a batch mode. Two sorption parameters were investigated; the effect of contact time and effect of initial concentration of dye solutions. For contact time, 100 mL of 250 mg/L of the dye solutions was transferred into different properly cleaned and dried Erlenmeyer flasks containing 1g of thiolated boiler fly ash. The reagent flasks were left in a constant temperature rotary shaker at $30^{\circ}C$ and pH of 7.5 for different time intervals of 10, 20, 30, 40, 50 60 and 120 min. At the end of each time interval, the contents of the flasks were filtered rapidly through a Whatman filter paper No 41. The filtrates were then analyzed for residual dye concentration.

For effect of initial concentration the contact time was kept constant at 1 h. 100 mL of dye solution of concentrations 500, 300, 250, 200, 150, 100 and 50 mg/L were transferred into Erlenmeyer flasks containing 1g of thiolated boiler fly ash. The flasks were also left in a constant temperature rotary shaker at temperature of $30^{\circ}C$ and pH of 7.5 for 1 h. Thereafter, they were filtered rapidly and the filtrates analyzed for residual dye concentration.

The determination of dye concentration in the filtrates was carried out using a UV-Visible Spectrophotometer model 200A at maximum wavelength of 560 nm for CR and 488 nm for MO. All experiments were conducted in duplicates and average values were used. Control experiments (without thiolated fly ash) were simultaneously carried out to ensure that the sorption capacity was solely by the thiolated boiler fly ash and not by the container or any other interference.

## Results and Discussion

The activation of the fly ash by 2% (V/V) nitric acid was to wash off any debris, remove any soluble biomolecules and then open up the pores ready for subsequent adsorption reactions. The degree of thiolation was calculated as 92.60%. The amount of dyes adsorbed was calculated by a simplified mass balance equation shown below:

$$q_e = (C_o - C_e)V/m \qquad (2)$$

Where V is the volume of solution (L); m is mass of adsorbent (g); $q_e$ is equilibrium amount adsorbed (mg/g); $C_o$ is initial dye concentration (mg/L) and $C_e$ is the amount remaining in solution after adsorption (mg/L). The percent removal of the dyes was calculated by the following equation:

$$\% \text{ dye removed } = 100 \ (C_o - C_e)/C_o \qquad (3)$$

The structures of the dyes used in this study are shown in **Figure 1** for Congo Red (CR) [9] and **Figure 2** for Methyl Orange (MO) [51] while the properties of the dyes are shown in **Table 1**.
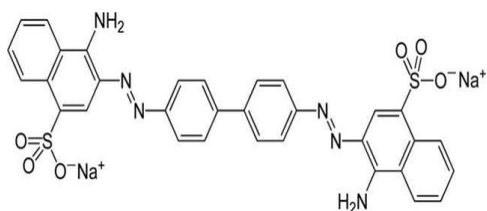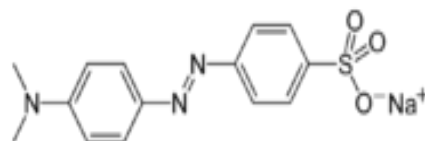
*Figure 1: Structure of Congo Red*          *Figure 2: Structure of Methyl Orange*

**Table 1:** Properties of the Dyes used in this study, Congo red and Methyl Orange

| S/N | Properties | Congo Red (CR) | Methyl Orange (MO) |
|---|---|---|---|
| 1 | Molecular formula | $C_{32}H_{22}N_6Na_2O_6S_2$ | $C_{14}H_{14}N_3NaO_3S$ |
| 2 | Chemical name | 3,3-([1,1-biphenyl)-4,4-diyl) bis (4-aminonaphthalene-1-sulfonic acid | Sodium 4-[(4-dimethyl amino) phenyldiazenyl] |

| | | | benzenesulfonate |
|---|---|---|---|
| 3 | Molar mass | 696.665 g/mol | 327.33 g/mol |
| 4 | Density | 1.0g/cm$^3$ | 1.28 g/cm$^3$ |
| 5 | Melting point | $< 0^oC$ | $> 300^oC$ |
| 6 | Boiling point | $> 100^oC$ | Decomposes |
| 7 | Solubility in water | Water soluble | Water soluble |
| 8 | $\lambda_{max}$ | 560 nm | 488 nm |

**Effect of contact time and initial concentration**

The experimental results obtained for the effect of contact time is shown in **Figure 3**. It could be seen that the percent of the dyes adsorbed increased as time was increased. The amount of CR adsorbed was greater than that of MO. The maximum percent of CR adsorbed was 99.99% while that of MO was 99.56%. Generally, the amount of dyes adsorbed was very high and thiolated boiler fly ash served as a good adsorbent for MO and CR adsorption from aqueous solutions. This trend of sorption could be explained by the theory that in the process of dye adsorption initially the dye molecules have to first encounter the boundary layer effect and then diffuse from the boundary layer film onto adsorbent surface and then finally diffuse into the porous structure of the adsorbent [52, 53].

Again, from **Figure 3**, it could be seen that the adsorption of the dyes was rapid at the initial contact time of 0 to 60 min and then decreased slightly. At this point it could be said that the sorption process have reached saturation or equilibrium. This pattern have also been observed [54, 55]. The amount of dye adsorbed at equilibrium time reflects the maximum adsorption capacity of the adsorbent under the operating condition [15, 33, 53]. Also, the adsorption trend of the dyes could be explained on the properties and structures of the dyes. From the structures of the dyes shown above, it could be seen that CR is more bulky than MO but both dyes have similar points of attachments, that is, the -SO$_3$Na group. It appears that the bulky nature of CR introduced steric hindrance, and this has an effect on the two points of attachment, hence reducing its sorption capacity. Similar results have been reported [33, 56, 57].

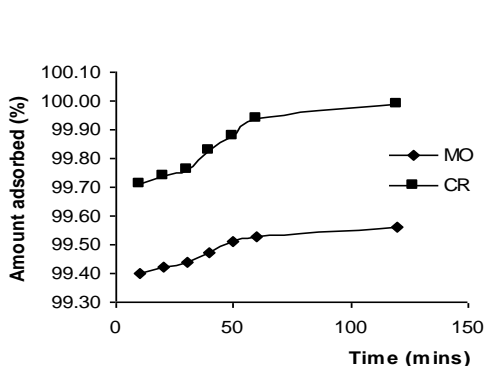The effect of initial concentration on the adsorption of MO and CR is shown in **Figure 4**.



Figure 3: Amount adsorbed (%) against time (mins) for adsorption of methyl orange (MO) and congo red (CR) using thiolated bioler fly ash
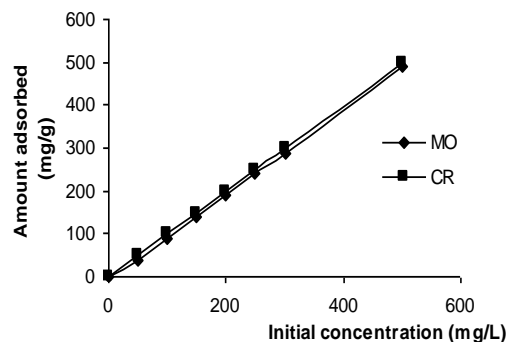


Figure 4: Amount adsorbed (mg/g) against initial concentration for adsorption of methyl orange (MO) and congo red (CR) using thiolated bioler fly ash

It could be seen that the amount of dye adsorbed increased proportionally as the initial concentration was increased and that the amount of CR adsorbed was slightly higher than that of MO. It has been reported that the concentration of dye adsorbed usually increased with increase in initial concentration [33, 58, 59]. This could be explained that when the initial concentration is increased, there is an increase in the mass driving force of the concentration gradient of the dye molecules and this result in increased sorption capacity [15, 53]. Vadivelan and Vasanth Kumar [60], reported that at lower dye concentration the available biosorption sites are relatively high and consequently the dye species can find easily the accessible biosorption sites. On the other hand, Ben Hamissa *et al*, [14], reported that at higher concentration the available site for biosorption become fewer and consequently the dye take more time in order to reach the last available sites.

## Sorption Kinetics and Dynamics

The rate at which sorption takes place have been reported as one of the very important factors for adsorber design. Also, kinetics has been reported as the controlling factor for sorbate residence time and reactor dimensions [61]. The kinetics of MO and CR adsorption from aqueous solution using thiolated boiler fly ash was analyzed using pseudo-first and pseudo-second order kinetic models [62]. The pseudo-first order kinetic equation is given as:

$$dq_t/dt \;=\; K_1\,(q_e - q_t) \tag{4}$$

The integrated form of the equation is given as:

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

The pseudo-first order rate constant values for the sorption process were determined from the slope and intercepts of the plot of $\log(q_e - q_t)$ against t shown in **Figure 5**.

The pseudo-second order kinetic equation is given as:

$$dq_t/dt \;=\; K_2\,(q_e - q_t)^2 \tag{6}$$

The integrated form of the equation is given as:

$$t/q_t \;=\; 1/h_o + t/q_e \tag{7}$$

Where the initial sorption rate $h_o$ is given as:

$$h_o \;=\; K_2 q_e^{\,2} \tag{8}$$

The pseudo-second order rate constant values were determined from the slopes and intercepts of the plot of $t/q_t$ against t shown in **Figure 6**.

The rate constants $K_1$, $K_2$ and $h_o$; $q_e$ and correlation coefficients ($R^2$) are shown in **Table 2**. From Table 2, the data showed a good compliance with pseudo-second order model with squared correlation coefficient of 1.0000 for both MO and CR. The predicted values of $q_e$ were 250 mg/g for MO and CR as against the experimental values of 248.89 and 249.98 mg/g for MO and CR respectively. This shows very good agreement with the pseudo-second order kinetic model. It has been reported that the pseudo-second order model is more likely to predict kinetic behaviour of sorption with chemical sorption being the rate-limiting or determining step [62-64]. Pseudo-second order model predicting correctly the sorption experimental data for coloured or dye effluents have been reported [15, 53, 55, 61].
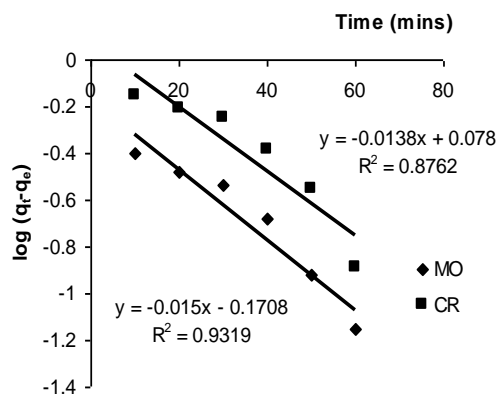


Figure 5: Pseudo -first order plots for adsorption of methyl orange (MO) and congo red (CR) using thiolated bioler fly ash
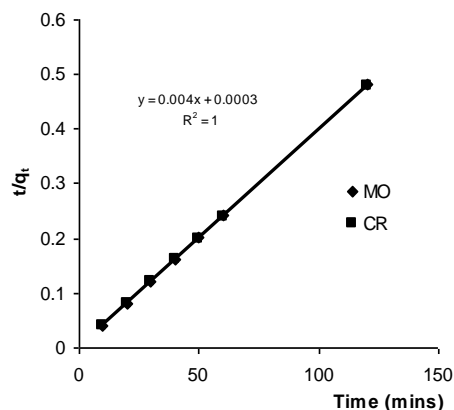
Figure 6: Pseudo-second order plots for adsorption of methyl orange (MO) and congo red (CR) using thiolated bioler fly ash

The above kinetic models do not identify the diffusion mechanism of the sorption process. Adsorption is usually preceded by diffusion; hence the diffusion mode that is prevalent tends to govern the sorption mechanism. Diffusion has been divided into four, namely; bulk diffusion, external diffusion, surface or pore diffusion and adsorbate uptake

[47, 65]. Adequate agitation makes bulk diffusion non-existence and adsorbate uptake could involved such processes as physico-chemical sorption; ion-exchange, precipitation on complexation. Sorption dynamics have been broadly divided into film diffusion or intraparticle diffusion mechanisms, although these two mechanisms most times can not be sharply demarcated [66]. Film diffusion mechanism is predominant when external diffusion is the rate limiting step whereas, intraparticle diffusion mechanism is predominant if the pore diffusion mass transfer resistance is the rate limiting step.

Sorption dynamics and the diffusion mechanism were evaluated using two particle diffusion equations. The first one is called penetrate transport equation and is given by [46]:

$$\log R = \log K_{id} + n \log t \qquad (9)$$

Where R is the percent adsorbed and $K_{id}$ is the rate constant for intraparticle diffusion. The penetrate transport plot is shown in **Figure 7**.

The second equation used is the intraparticle diffusion equation which was developed using the linear driving force concept and was reported by Abia and Igwe, [66]. The equation is given as:

$$\ln (1 - \alpha) = - K_p t \qquad (10)$$

Where $K_p$ is the intraparticle rate constant and $\propto$ is the fractional attainment to equilibrium (FATE) given by:

$$\alpha = [X]_t^{n+} / [X]_\infty^{n+} \qquad (11)$$

[X] represents the concentration of the adsorbate (dye molecules). FATE is the ratio of the amount of dye removed from solution after a certain time to that removed when sorption equilibrium is attained. The plot of FATE for the sorption process is shown in **Figure 8**. It could be seen that MO gave higher fractions than CR. The plot of intraparticle diffusion is shown in **Figure 9**.

The constants for the penetrant transport and the intraparticle diffusion are also shown in **Table 2**. From Table 2, it could be seen that penetrant n <1, and penetrant $K_{id}$ >1. Penetrant n- values represents the likelihood and degree of strive. n >1 indicates the presence of high strive, n ≈1 depicts moderate strive while for n <1, the adsorption process may not be due to adsorbate core strive [46]. Again, penetrate $K_{id}$ value of an adsorption system is usually less than 1 for an interaction between adsorbent and adsorbate which is dominated by ion- exchange [46]. From the results of this study, n values are <1 and $K_{id}$ >1. This means that there is an indication that dipole induced dipole interactions are dominant.
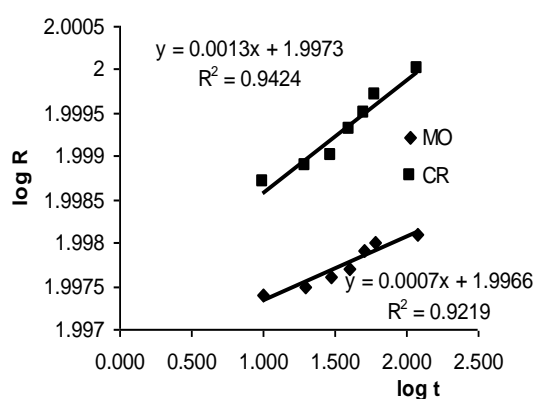


**Figure 7: Penetrant transport plots for adsorption of methyl orange (MO) and congo red (CR) using thiolated bioler fly ash**
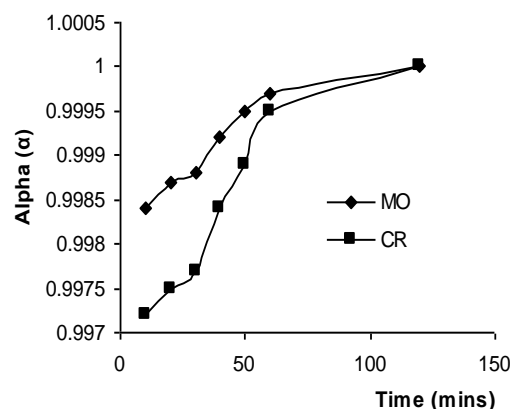
**Figure 8: Fractional attainment to equilibrium (FATE) plots for adsorption of methyl orange (MO) and congo red (CR) using thiolated bioler fly ash**

**Table 2**: Constants for sorption kinetics and dynamics for adsorption of Methyl orange and Congo red onto thiolated boiler fly ash

| Dyes | Sorption kinetics | | Sorption dynamics | |
|---|---|---|---|---|
| | Pseudo-first order | Pseudo-first order | Penetrant transport | Intraparticle diffusion |
| MO | $K_1 = 0.0346$ | $K_2 = 0.0533$ | $K_{id} = 99.22$ | $K_p = 0.0333$ |
| | $q_e = 0.675$ | $h_o = 3.33 \times 10^3$ | $n = 0.0007$ | Intercept = -5.94 |
| | $R^2 = 0.9319$ | $q_e = 250.0$ | $R^2 = 0.9219$ | $R^2 = 0.9396$ |
| | | $R^2 = 1.0000$ | | |
| CR | $K_1 = 0.0318$ | $K_2 = 0.0533$ | $K_{id} = 99.38$ | $K_p = 0.0327$ |
| | $q_e = 1.197$ | $h_o = 3.33 \times 10^3$ | $n = 0.0013$ | Intercept = -5.32 |
| | $R^2 = 0.8762$ | $q_e = 250.0$ | $R^2 = 0.9424$ | $R^2 = 0.8767$ |
| | | $R^2 = 1.0000$ | | |

Again, the linear regression coefficient ($R^2$) values for the penetrant transport and intraparticle diffusion equation are all less than 0.95. This shows poor correlation and indicates that the sorption process was not intraparticle diffusion controlled but was of film diffusion mechanism. This means that external diffusion was the rate determining step in the sorption process.

Furthermore, in order to confirm the actual slow step involved in the adsorption process, the kinetic data were analyzed using the Boyd model [53] given as:

$$B_t = -0.4977 - \ln(1 - F) \qquad (12)$$

Where F represents the fraction of solute adsorbed at any time t (min) and is given by $q_t/q_o$. The calculated values of $B_t$ were plotted against time as shown in **Figure 10**.
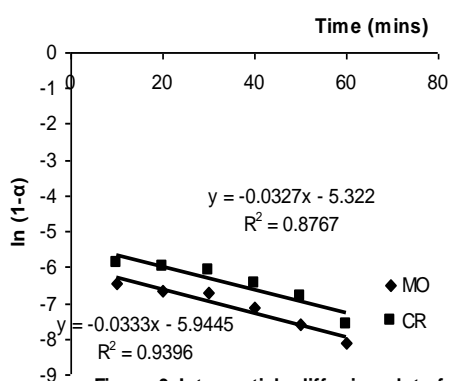


Figure 9: Intraparticle diffusion plots for adsorption of methyl orange (MO) and congo red (CR) using thiolated bioler fly ash
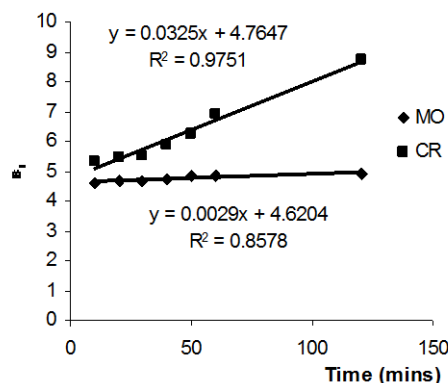
Figure 10: Boyd plots for adsorption of methyl orange (MO) and congo red (CR) using thiolated bioler fly ash

The linear lines did not pass through the origin and the points were scattered. This confirms that the sorption of MO and CR on thiolated boiler fly ash was mainly governed by external mass transport where film diffusion is the rate determining step [67].

**Adsorption isotherm**

Adsorption isotherm is basically important to describe how solutes interact with adsorbent and it is crucial in optimizing the use of adsorbents [53]. The analysis of the adsorption equilibrium data by fitting them into different isotherm models is an important step to find the suitable model in order to optimize the design of sorption systems to remove dyes from effluents. It is also important to establish the most appropriate correlation for the equilibrium curve [68].

In this study, four adsorption isotherms namely Langmuir, Freundlich, Dubinin-Radushkevich (D-R) and Temkin were used to model the equilibrium sorption data. The linear correlation coefficient ($R^2$) values were used to judge the applicability of the isotherm equation to describe the adsorption process. The Langmuir equation is intended for

homogeneous type of biosorption which means that maximum sorption corresponds to a saturated monolayer of sorbate molecules on the sorbent surface; that the energy of sorption is constant and there is no transmigration of the sorbate in the plane of the surface [37]. The Freundlich isotherm is empirical, considered suitable for highly heterogeneous surface and used to model multilayer adsorption [58]. The D - R isotherm is more general than the Langmuir isotherm because it does not assume a homogenous surface or constant sorption potential [69]. The D - R isotherm is intended to estimate the characteristic porosity of the biomass to the dye molecules and also to estimate the apparent energy of adsorption which gives insight to the mechanism of sorption. The derivation of the Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic as implied in the Freundlich equation [70].

The Langmuir, Freundlich, D - R and Temkin isotherms [71] are given by Eqs. (13) – (16):

$$\textbf{Langmuir}: \quad q_e = q_m K_L C_e / 1 + K_L C_e \qquad (13)$$

$$\textbf{Freundlich}: \quad q_e = K_F C_e^{1/n} \qquad (14)$$

$$\textbf{D – R}: \quad q_e - q_D e^{-\beta \varepsilon^2} \qquad (15)$$

$$\textbf{Temkin}: \quad q_e = (RT/b)\ln(AC_e) \qquad (16)$$

The linear forms of the isotherms can be expressed by Eqs. (17) – (20) respectively:

$$\textbf{Langmuir}: \quad C_e/q_e = 1/q_m K_L + C_e/q_m \qquad (17)$$

$$\textbf{Freundlich}: \quad \log q_e = \log K_F + 1/n(\log C_e) \qquad (18)$$

$$\textbf{D – R}: \quad \ln q_e = \ln q_D - \beta \varepsilon^2 \qquad (19)$$

$$\textbf{Temkin}: \quad q_e = B \ln A + B \ln C_e \qquad (20)$$

Where $K_L$ is Langmuir constant (L/g), $q_m$ is maximum monolayer adsorption capacity (mg/g), $K_F$ and n are Freundlich constant (L/g) and exponent respectively; $q_D$ is D-R constant related to monolayer capacity; B (=RT/b) and A are Temkin constants; $\varepsilon$ is the Polanyi potential given by:

$$\varepsilon = RT \ln(1 + 1/C_e) \qquad (21)$$

$\beta$ is a constant related to the apparent biosorption energy E (KJ/mol) given by:

$$E = (2\beta)^{-1/2} \qquad (22)$$

The results of the isotherm treatment is shown by plotting equilibrium solid phase concentration ($q_e$) against equilibrium liquid phase concentration ($C_e$) for the experimental and calculated values for each of the isotherm in **Figure 11** for MO and **Figure 12** for CR. It could be seen that the Temkin isotherm $q_e$ values gave better plots much closer to the experimental plot for MO, whereas Freundlich isotherm resulted in better plot for CR.
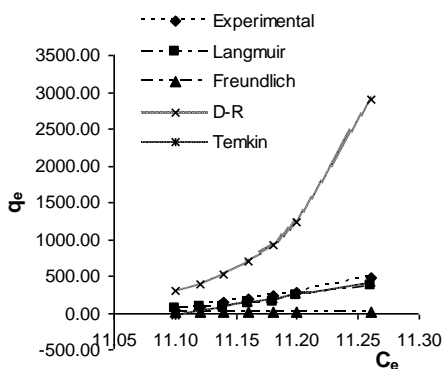


**Figure 11: Isotherm plots for adsorption of methyl orange (MO) from aqueous solution using thiolated bioler fly ash**
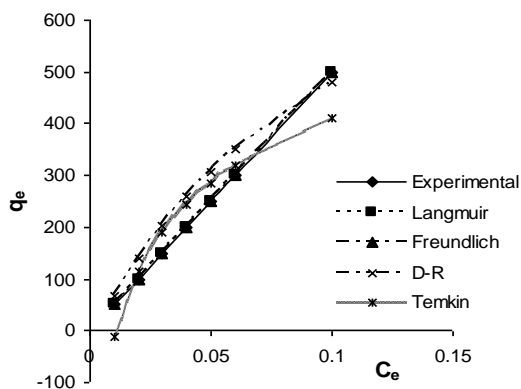
**Figure 12: isotherm plots for adsorption of congo red (CR) from aqeuous solution using thiolated bioler fly ash**

The isotherm constants and the coefficient of linear regressions ($R^2$) are shown in **Table 3**. From this table it could be seen that the $R^2$ value for Temkin isotherm (0.9943) was highest for MO while that for Freundlich (1.0000) was highest for CR. The values of the apparent mean biosorption energy were 16.67 KJ/mol for MO and 5000 KJ/mol fort CR. It has been reported that physiosorption process usually have adsorption energies less than 40 KJ/mol and above this value sorption is of chemisorption mechanism [72]. Therefore, it means that the sorption of MO followed physiosorption mechanism while sorption of CR was of chemisorption mechanism. Many authors have reported on the use of apparent mean biosorption energy to determine the mechanism of sorption of pollutants from aqueous solutions [53, 71, 73-76].

**Table 3**: Adsorption isotherm constants for adsorption of Methyl orange and Congo red onto thiolated boiler fly ash

| Dyes | Langmuir | Freundlich | D-R | Temkin |
|------|----------|------------|-----|--------|
| MO | $q_m = -0.765$ | $n = 0.0061$ | $\beta = 0.0018$ | $A = 0.09$ |
|  | $K_L = -0.089$ | $K_F = 4.27 \times 10^{-171}$ | $q_D = 2.38 \times 10^{39}$ | $B = 31013.00$ |
|  | $R^2 = 0.6017$ | $R^2 = 0.8995$ | $E = 16.67$ | $R^2 = 0.9943$ |
|  | $\Delta q = 39.21$ | $\Delta q = 108.01$ | $R^2\ 0.8976$ | $\Delta q = 82.\ 56$ |
|  |  |  | $\Delta q = 430.93$ |  |
| CR | $q_m = -3.33 \times 10^{17}$ | $n = 1.00$ | $\beta = 2.0 \times 10^{-8}$ | $A = 93.24$ |
|  | $K_L = -1.50 \times 10^{-14}$ | $K_F = 4999.19$ | $q_D = 9.97 \times 10^2$ | $B = 184.68$ |
|  | $R^2 = -4 \times 10^{-16}$ | $R^2 = 1.0000$ | $E = 5000.0$ | $R^2 = 0.8747$ |
|  | $\Delta q = 0.086$ | $\Delta q = 0.0043$ | $R^2\ 0.9867$ | $\Delta q = 54.\ 44$ |
|  |  |  | $\Delta q = 30.92$ |  |

Again a normalized standard deviation $\Delta q$ (%) of root mean square residual error was used to compare the validity of each of the isotherm model more efficiently by the following equation [12, 64]:

$$\Delta q\,(\%) \;=\; 100 \times \sqrt{(\Sigma[(q_e^{\exp} - q_e^{cal})/q_e^{\exp}]^2/n - 1)} \qquad (23)$$

Where the superscripts "exp" and "cal" mean the experimental and calculated values respectively an n is the number of measurements. The values of $\Delta q$ are also given in **Table 3**. It could be seen that the lowest value obtained for MO was 39.21% for Langmuir isotherm and for CR was 0.0043% for Freundlich isotherm. The isotherm model was considered to satisfactorily fit the sorption process if the value of $\Delta q$ (%) was less than 10% [15]. Hence, from the values of $\Delta q$ (%) in **Table 3**, it could be seen that for MO, none of the values of $\Delta q$ were below 10%. For CR, Freundlich isotherm gave $\Delta q$ value of 0.0043% and Langmuir isotherm gave 0.086%. Therefore, for MO none of the isotherms could be said to give a satisfactory fit to the sorption data while for CR, Langmuir and Freundlich models gave satisfactory fit to the sorption experimental data with the lower value for the Freundlich model giving the best fit.

**Conclusion**

In this study, thiolated boiler fly ash was used to remove methyl orange (MO) and Congo red (CR) from synthetic effluents and the following conclusions were made:

1. The percentage of MO adsorbed was higher than that of CR.
2. The adsorption of the dyes was influenced by contact time, initial dye concentration of dye effluents and the structure of the dye molecules.
3. Modification of the adsorbent also influences the sorption properties of the adsorbent.
4. The pseudo-second order kinetic model gave a better fit to the kinetic sorption experimental data and diffusion was found to follow film diffusion mechanism.
5. The sorption equilibrium data was modeled by Langmuir, Freundlich, D-R and Temkin adsorption isotherms.
6. Therefore thiolated boiler fly ash was found to be an effective adsorbent for the removal of methyl orange and Congo red from synthetic effluents.

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