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Sorption Kinetics, Intraparticle Diffusion and Equilibrium Partitioning of Azo Dyes on Great Millet (*Andropogon sorghum*) Waste Biomass

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Abstract: Azo dyes are environmental pollutants and they are recalcitrant to decolorization by photo degradation and other conventional methods of treatment. The adsorption kinetics, intraparticle diffusion and equilibrium partitioning of Methyl Orange (MO), Methyl Red (MR) and Methyl Blue (MB) onto *andropogon sorghum* waste biomass was studied. As time increased the amount of the dyes adsorbed increased and equilibrium was reached within 40-50 min. Modification of the adsorbent by carboxymethylation and thiolation enhanced the adsorptive capacity of the adsorbent. The kinetics of sorption was well correlated using the pseudo-second order rate equation. The pseudo second order rate constant ranged from 0.742 (g mg⁻¹-min) for Methyl Orange (MO) on thiolated sorghum to 5.741 (g mg⁻¹-min) for Methyl Blue (MB) on carboxymethylated sorghum. The mechanism of sorption was found to be intraparticle diffusion controlled and the intraparticle diffusion rate constants ranged from 0.0969 min⁻¹ for Methyl Red (MR) on thiolated sorghum to 0.8298 min⁻¹ for Methyl Red (MR) on carboxymethylated sorghum. The boundary layer diffusion effects were calculated. The very high values of correlation coefficients (R²) obtained showed that these models fit the experimental data perfectly. Therefore andropogon sorghum was found to be a good adsorbent for adsorptive decolorization of Azo dyes from waste water.

Key words: Adsorption, kinetics, Azo dyes, agricultural by-product, waste water

INTRODUCTION

The increase in scientific inventions and hence increase in industrialization have brought about an increase in the anthropogenic sources of pollutants in our environment. The issue of environmental cleanliness has reached the stage of sourcing cost effective and renewable resources in environmental management. Most conventional methods used in waste water treatment such as ion exchange, ultra filtration, chemical precipitation etc., are very expensive to perform, therefore, cheap methods for waste water treatment is being sought for. In our laboratory, the use of non-conventional agricultural by-products which are composed mainly of cellulose in the adsorptive treatment of waste waters is going on. These includes the use of maize cob and husk (Igwe and Abia, 2003, 2005; Abia *et al.*, 2005), coconut fibre and sawdust (Igwe *et al.*, 2005), tiger nuts, sugar cane bagasse, etc. Other agricultural by-products have also been reported such as; cassava waste (Abia *et al.*, 2003), wild cocoyam (Horshfall and Spiff, 2005), sphagnum moss peat (Gardea-Torresday *et al.*, 1996), banana pith (Low *et al.*,

1995), peanut skin (Randall *et al.*, 1994) and so on. Hence, in this study, we investigated the use of Great millet waste biomass in the adsorptive removal of Azo dyes from aqueous solutions.

Azo dyes are synthetic compounds characterized by the presence of one or more azo group (-N=N-) bound to aromatic rings. They are mostly used in the textile, paper, food, cosmetics and pharmaceutical industries (Chen *et al.*, 1999). Considerable amount of dyes are discharged everyday into waste water. This corresponds to the release of some 128 tons per day to the environment (Hepel *et al.*, 2004). The release of azo dyes into the environment is of great concern due to the coloration of natural waters, the toxicity, mutagenicity and the carcinogenicity of biotransformation products thereof (Ibrahim *et al.*, 1996; Mana *et al.*, 2003; Oh *et al.*, 1997). They are also tetratogenic in various living organisms (Hepel *et al.*, 2004).

The removal of dyes from effluents is therefore a major environmental problem. Azo dyes are poorly biodegradable because of their structure (Kim and Shoda, 1999) and though they represent a potentially important

class of organic pollutants, little is known about their fate (Chivukula and Renganathan, 1995). Usual methods of decolorization include physical/chemical methods coagulation, precipitation adsorption by activated charcoal, oxidation by ozone, ionizing radiation and ultrafiltration. These methods are not only costly but also generates waste which are difficult to dispose of, are less efficient and of limited application (Chen *et al.*, 1999). Photo-catalytic and photochemical methods have been employed in the degradation of azo dyes (Hepel *et al.*, 2004). Microbial degradation of azo dyes has also been reported (Chen *et al.*, 1999; Oranusi and Ogugbue, 2001; Plumb *et al.*, 2001; Hu, 1998; Jones and Falkinham, 2003). Most of these dyes, especially diazo dyes are stable and are very resistant to photo-degradation as well as microbial attack.

In this study, we report the findings on the adsorptive degradation of three azo dyes; Methyl Orange (MO), Methyl Red (MR) and Methyl Blue (MB), using *Andropogon sorghum* waste biomass as adsorbent. The effects of particle size distribution and modification on the sorption process of the dyes by the adsorbent was also studied.

MATERIALS AND METHODS

Azo dyes: Methyl orange, methyl red and methyl blue were obtained from sigma-Aldrich and were used as received without further purification. All aqueous dye solutions were prepared with de-ionized water.

Adsorbent preparation: The sorghum used was obtained from a local market in Okigwe, Imo State, Nigeria. The grains were soaked for three days, used for preparation of pap and the waste (chaff) was used for the study, it was air dried and sieved, the sieve portions retained on 500 and 250 μm sizes were used for the analysis. These two sizes were then activated using a 2% (v/v) nitric acid and modified by incorporating thiol groups (Okieimen and Okundaye, 1989) and carboxymethyl groups (Ragheb *et al.*, 1989) onto the adsorbent.

Equilibrium sorption of dye onto sorghum: Fifty milliliter portions of the dye solutions were put into conical flasks containing 1 g of the adsorbent. The conical flasks were corked and the solution shaken for various time intervals of 10, 20, 30, 40, 50 and 100 min, at 30°C and pH of 7.5. The initial concentration of the dyes were kept at 100 mg L⁻¹. Decolourization of azo dyes was determined by examining the concentration of dyes using maximum absorbance in a UV-VIS spectrophotometer (Milton Roy, SPECTRONIC GENESYS). The amount of dye adsorbed at any time interval was gotten by difference.

RESULTS AND DISCUSSION

Sorption capacity: The results of the experiment are presented as the amount of dye adsorbed against time. Figure 1 shows the amount adsorbed (Mg g⁻¹) against time (min) for Methyl Orange (MO), Methyl Red (MR) and Methyl Blue (MB) on unmodified sorghum of two particle sizes of 250 and 500 μm . Figure 2 shows the amount adsorbed (Mg g⁻¹) against time (min) for three dyes on thiolated sorghum of two particle sizes. Figure 3 shows

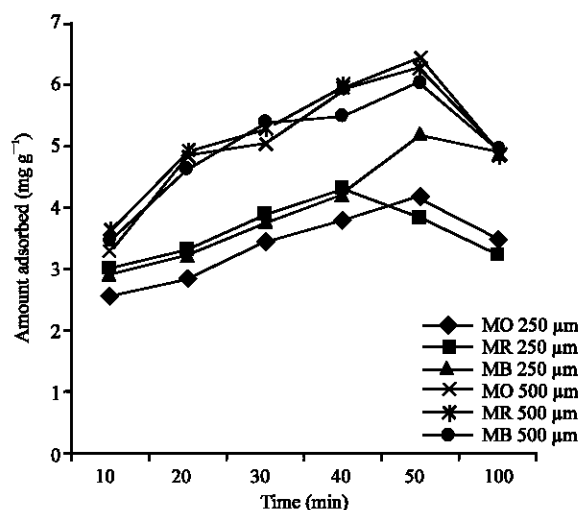


Fig. 1: Amount adsorbed (mg g⁻¹) against time (min) for Methyl Orange (MO), Methyl Red (MR) and Methyl Blue (MB) for unmodified sorghum of two sizes of 250 and 500 μm

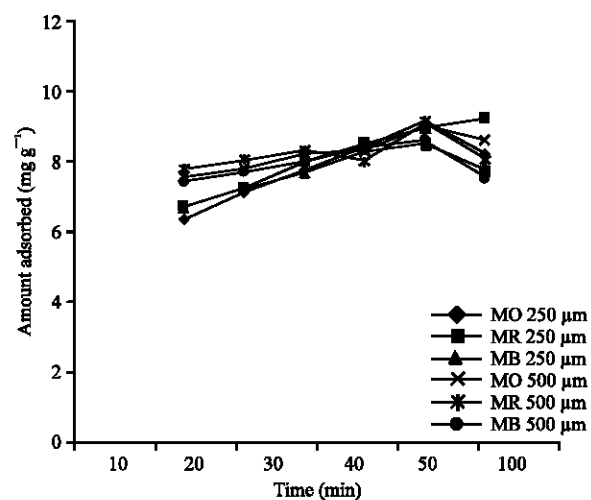


Fig. 2: Amount adsorbed (mg g⁻¹) against time (min) for Methyl Orange (MO), Methyl Red (MR) and Methyl Blue (MB) for thiolated sorghum of two sizes of 250 and 500 μm

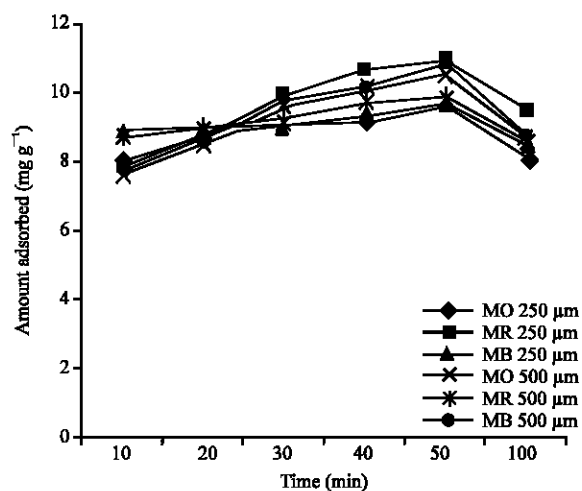


Fig. 3: Amount adsorbed (mg g^{-1}) against time (min) for Methyl Orange (MO), Methyl Red (MR) and Methyl Blue (MB) for thiolated sorghum of two sizes of 250 and 500 μm

amount adsorbed (mg g^{-1}) against time (min) for the three dyes on carboxymethylated sorghum of two particle sizes.

In each case, the amount of dye adsorbed increases steadily from ten minutes to a maximum at about 50-60 min and then decreases. From these result we gathered that.

- Andropogon sorghum is capable of adsorbing and hence decolorizing the azo dyes.
- Equilibrium was established at about 50-60 min.
- Methyl Red (MR) was adsorbed more than Methyl Orange (MO), followed by Methyl Blue (MB).
- The trend of the sorption process is $\text{MR} > \text{MO} > \text{MB}$.

Again the modification carried out on the adsorbent increased the adsorption capacity of the adsorbent. Modification by carboxymethylation adsorbed more than that by thiolation and the unmodified adsorbent. Also the particle size of 250 μm adsorbed more than the 500 μm .

The adsorption capacity of the dyes could be correlated to the structure of the dyes and also the functional groups incorporated on the adsorbent. The structures of the dyes are shown on Fig. 4. Methyl orange is given as I, that of methyl red is II and that of methyl blue is III. From the structures we can see that the point of attachment for methyl blue is three where as the other two have only one. This is why methyl blue has the highest adsorption on the adsorbent. Modification also increases the number of sites for attachment on the adsorbent and hence increases the adsorption capacity on modification of the adsorbent. Results from previous workers shows that desulphonation of the aromatic moiety of the dye molecule coupled within reductive

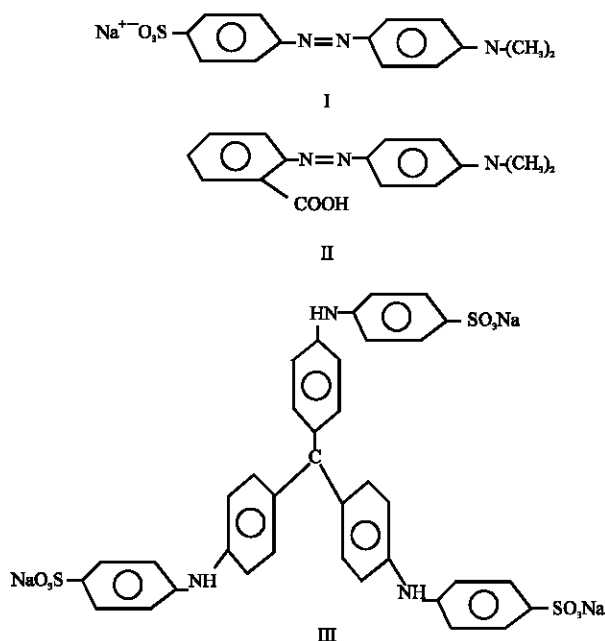


Fig. 4: Chemical structures of the azo dyes. I is Methyl Orange (MO), II is Methyl Red (MR) and III is Methyl Blue (MB)

cleavage of the azo bond will prohibit aromatic amine formation, thereby, detoxifying the aromatic amines (Oranusi and Ogugbue, 2005). Adsorption of dye molecules has been implicated in decolorization of dyes in microbial cultures (Yuxin and Jian, 1998).

Sorption kinetics: It is seen from Fig. 1 to 3 that the sorption process of the dyes on sorghum was rapid at first (10-40 min), after which equilibrium starts to set in at about 40 min and finally at 50 min where the sorption process decreased showing the final equilibrium beyond which no further adsorption takes place. These results complement those obtained by Al-Asheh *et al.* (2003) and Hu *et al.* (2006), using bentonite as adsorbent.

The Lagergren Equation, pseudo-first-order model, has been used to describe dye adsorption kinetics (Walker and Weatherley, 1999), but here a pseudo-second-order model development by Ho *et al.* (2001), fits the adsorption kinetics data better. The pseudo-second-order equation is given as

$$t/qt = I/h_0 + I/qe (t) \quad (1)$$

where, q_e and q_t are the amount of dyes adsorbed per unit mass of adsorbent at equilibrium and time t (mg g^{-1}) and h_0 is the initial sorption rate. In the limit of $t \rightarrow 0$, then;

$$h_0 = K_2 qe^2 \quad (2)$$

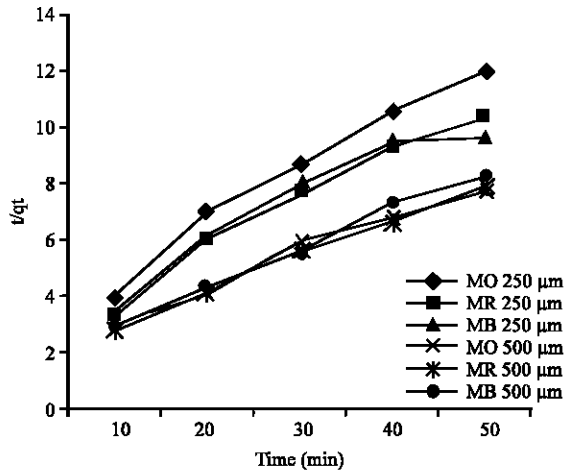


Fig. 5: Pseudo-second order rate equation plot of Methyl Orange (MO), Methyl Red (MR) and Methyl Blue (MB) on unmodified sorghum of two sizes of 250 and 500 μm

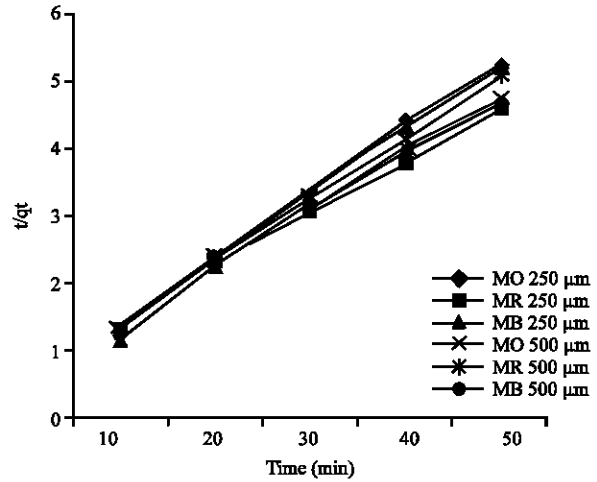


Fig. 7: Pseudo-second order rate equation plot of Methyl Orange (MO), Methyl Red (MR) and Methyl Blue (MB) on carboxymethylated sorghum of two sizes of 250 and 500 μm

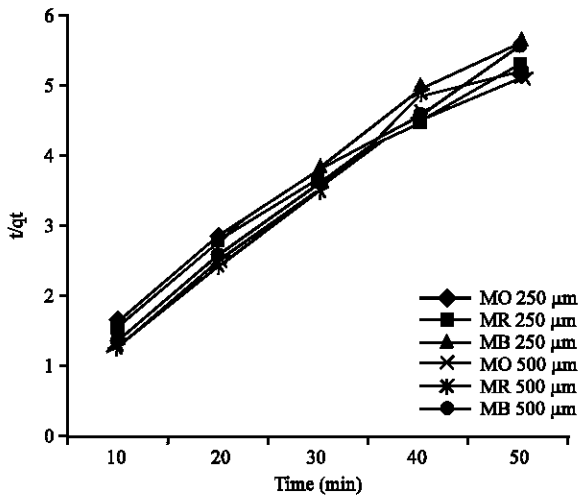


Fig. 6: Pseudo-second order rate equation plot of Methyl Orange (MO), Methyl Red (MR) and Methyl Blue (MB) on thiolated sorghum of two sizes of 250 and 500 μm

Table 1: Regression equations and R² values for pseudo second order equation plot or sorption of azo dyes on sorghum

Azo dye	250 μm	500 μm
Unmodified		
MO	Y = 1.962X + 2.546 R ² = 0.9771	Y = 1.216X + 1.868 R ² = 0.9814
MR	Y = 1.738X + 2.122 R ² = 0.9733	Y = 1.295X + 1.533 R ² = 0.9959
MB	Y = 1.569X + 2.621 R ² = 0.9188	Y = 1.366X + 1.554 R ² = 0.9945
Thiolated		
MO	Y = 0.862X + 1.008 R ² = 0.9818	Y = 0.998X + 0.444 R ² = 0.9901
MR	Y = 0.924X + 0.774 R ² = 0.9916	Y = 1.019X + 0.371 R ² = 0.9746
MB	Y = 1.025X + 0.675 R ² = 0.9905	Y = 1.044X + 0.402 R ² = 0.9972
Carboxymethylated		
MO	Y = 1.004X + 0.29 R ² = 0.9984	Y = 0.85X + 0.574 R ² = 0.9961
MR	Y = 0.81X + 0.57 R ² = 0.9958	Y = 0.97X + 0.262 R ² = 0.9982
MB	Y = 1.019X + 0.181 R ² = 0.9980	Y = 0.829X + 0.579 R ² = 0.9951

Where, K² is the second order rate constant. Linear plots of t against t/qt is shown on Fig. 5 for unmodified sorghum, Fig. 6 for thiolated sorghum and Fig. 7 for carboxymethylated sorghum. From these figures, we found out that we have very good straight lines especially for the carboxymethylated and thiolated sorghum. The regression equations and R² values for the pseudo second order plots is shown on Table 1. With the least value of R² being 0.9188 for MB on 250 μm unmodified sorghum we see that we have very high correlation. From the slope and intercept of the plots for pseudo second

order, the value of the kinetic constants were generated and presented on Table 2. The rate constant K₂ gives a measure of how fast the reaction proceeds. This higher values of k₂, gives higher reaction rates, hence, higher adsorption rate.

Intraparticle diffusion: The mechanism of sorption is either film diffusion controlled or particle diffusion controlled (Okieimen and Orhororo, 1986). Before adsorption takes place, several diffusion processes known to affect the adsorption process takes place. The sorbate, will have to diffuse through the bulk of the solution to the film surrounding the adsorbent and then into the micro pores and macropores of the adsorbent.

Table 2: Kinetic constants for pseudo second-order rate plot for the sorption of the azo dyes on sorghum

Azo dye	250 µm			500 µm		
	qe (mg g ⁻¹)	ho (mg g ⁻¹ min)	K ² (g mg ⁻¹ -min)	qe (mg g ⁻¹)	ho (Mg g ⁻¹ -min)	K ² (g mg ⁻¹ min)
Unmodified						
MO	0.510	0.393	1.511	0.822	0.535	0.792
MR	0.576	0.471	1.420	0.772	0.652	1.094
MB	0.637	0.382	0.941	0.732	0.644	1.202
Thiolated						
MO	1.160	0.998	0.742	1.002	2.252	2.243
MR	1.082	1.292	1.104	0.981	2.695	2.800
MB	0.976	1.482	1.556	0.958	2.488	2.711
Carboxymethylated						
MO	0.996	3.448	3.476	1.177	1.742	1.258
MR	1.235	1.754	1.150	1.031	3.817	3.591
MB	0.981	5.525	5.741	1.206	1.727	1.187

The first one is bulk diffusion resistance which of course is reduced if there is enough agitation to reduce the concentration gradient. The second is external mass transfer resistance and the third is intraparticle mass transfer resistance. When this last one is the rate limiting step, than sorption mechanism is intraparticle diffusion controlled.

Several models have been development for the study of mechanism of sorption processes. The model proposed by Chanda *et al.* as reported by Okieimen and Orhorhoro, (1986), was used to analyze the mechanism of sorption of azo dyes on sorghum. The Eq. is gives as

$$\ln(1-\alpha) = -kpt \quad (3)$$

Where, α (alpha) is the fractional attainment to equilibrium (FATE) given by

$$\alpha = [\text{Dye}]_t / [\text{Dye}]_{eq} \quad (4)$$

Kp is the intraparticle diffusion constant. The plots of $\ln(1-\alpha)$ against time (not shown) giving straight lines means that the sorption is intraparticle diffusion controlled. From these plots, the regression equation and R²-values were calculated and shown on Table 3. High values of R² above 80% were recorded except for Methyl Red (MR) on 500 µm thiolated sorghum. The values of the intraparticle diffusion constant Kp are shown on Table 4. Higher values indicate higher intraparticle mass transfer such as for methyl red on 250 µm carboxymethylated sorghum with the highest value of 0.8298 min⁻¹.

Another model for intraparticle diffusion developed by McKay and Poots (1980), was used to establish the mechanism of sorption. The model is given as

$$qt = X_i + K^1 t^{0.5} \quad (5)$$

Where, qt is the amount of dye adsorbed at time t. The slope of the linear part of the curve (i.e., qt Vs t^{0.5}) (not shown), gives the initial rate of sorption (here taken

Table 3: Regression equation and R² values for intraparticle diffusion plot for sorption of the azo dyes on sorghum.

Azo dyes	25 µm	500 µm
Unmodified		
MO	Y = -0.489X-0.3245 R ² = 0.9578	Y = -0.5473X-0.1685 R ² = 0.9267
MR	Y = -0.423X-0.4535 R ² = 0.9602	Y = -0.6822X-0.103 R ² = 0.9474
MB	Y = -0.2861X-0.4765 R ² = 0.9698	Y = -0.5329X-0.384 R ² = 0.9393
Thiolated		
MO	Y = -0.4589X-0.4195 R ² = 0.9683	Y = -0.2734X-1.3275 R ² = 0.963
MR	Y = -0.5548X-0.4825 R ² = 0.946	
MB	Y = -0.6869X-0.381 R ² = 0.8968	Y = -0.5998X-0.9805 R ² = 0.9041
Carboxymethylated		
MO	Y = -0.423X-1.4455 R ² = 0.9766	Y = -0.6019X-0.566 R ² = 0.9783
MR	Y = -0.8298X-0.1885 R ² = 0.9264	Y = -0.5527X-1.3285 R ² = 0.8939
MB	Y = -0.3068X-2.061 R ² = 0.8052	Y = -0.5402X-0.631 R ² = 0.9846

Table 4: Values of Kp for intraparticle diffusion for sorption of the azo dyes on sorghum

Azo dyes	Unmodified		Thiolated		Carboxymethylated	
	25 µm	500 µm	250 µm	500 µm	250 µm	500 µm
MO	0.4894	0.5473	0.4589	0.2734	0.4230	0.6019
MR	0.4230	0.6822	0.5540	0.0969	0.8298	0.5527
MB	0.2861	0.5329	0.6869	0.5998	0.3068	0.5402

between 10 and 30-40 min before equilibrium was reached), controlled by intraparticle diffusion K' (mg g⁻¹ min^{-0.5}). The initial curve portion of the plot is attributed to boundary layer diffusion effects (i.e., external film resistance). The extrapolation of the linear straight lines to the time axis gives intercepts Xi, which are proportional to the boundary layer thickness. The regression equations and R² values for the McKay and Poots plots is shown on Table 5. The values of the diffusion rate constant and the boundary layer thickness is given on Table 6. High values of the regression coefficients (R²) indicates that the model fits the experimental data very well and also confirms that the

Table 5: Regression equation and R² values for Mckay and Poots intraparticle diffusion equation plot for sorption of the azo dyes on sorghum

Azo dyes	250 μm	500 μm
Unmodified		
MO	Y = 0.4203X+2.1023 R ² = 0.9912	Y = 0.7339X+2.9079 R ² = 0.9361
MR	Y = 0.2588X+2.8982 R ² = 0.6522	Y = 0.644X+3.2946 R ² = 0.9378
MB	Y = 0.5539X +2.2106 R ² = 0.9597	Y = 0.6101X+3.1807 R ² = 0.9069
Thiolated		
MO	Y = 0.9246X+5.1276 R ² = 0.9997	Y = 0.4496X+7.1186 R ² = 0.9492
MR	Y = 0.7463X+5.8227 R ² = 0.9908	Y = 0.3597X+7.4801 R ² = 0.6707
MB	Y = 0.6422X+5.8526 R ² = 0.9849	Y = 0.3989X +7.0563 R ² = 0.9895
Carboxymethylated		
MO	Y = 0.3613X+7.7809 R ² = 0.9496	Y = 0.7447X +6.9623 R ² = 0.9736
MR	Y = 0.8009X +7.1715 R ² = 0.9581	Y = 0.328X +8.2772 R ² = 0.992
MB	Y = 0.199X+8.5424 R ² = 0.9193	Y = 0.7762X +7.0258 R ² = 0.9776

Table 6: kinetic constants for McKay and Poots intraparticle diffusion equation plot for sorption of the azo dyes on sorghum

Azo dyes	250 μm		500 μm	
	K ¹	Xi	K ¹	Xi
Unmodified				
MO	0.4203	2.1023	0.7339	2.9079
MR	0.2588	2.8982	0.6444	3.2946
MB	0.5539	2.2106	0.6101	3.1807
Thiolated				
MO	0.9246	5.1276	0.4496	7.1186
MR	0.7463	5.8227	0.3597	7.4801
MB	0.6422	5.8526	0.3989	7.0563
Carboxymethylated				
MO	0.3613	7.7809	0.7447	6.9623
MR	0.8009	7.1715	0.3280	8.2772
MB	0.1990	8.5424	0.7762	7.0258

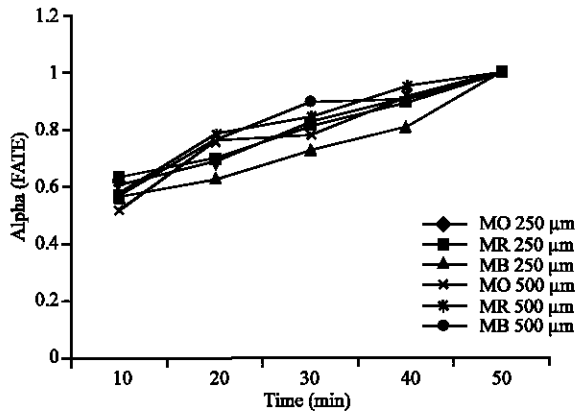


Fig. 8: Fractional Attainment to Equilibrium (FATE) alpha against time (min) for Methyl Orange (MO), Methyl Red (MR) and Methyl Blue (MB) adsorption on unmodified sorghum of two sizes of 250 and 500 μm

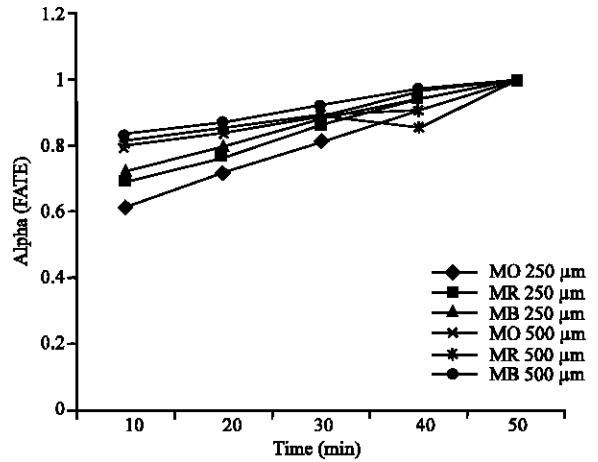


Fig. 9: Fractional Attainment to Equilibrium (FATE) alpha against time (min) for Methyl Orange (MO), Methyl Red (MR) and Methyl Blue (MB) adsorption on thiolated sorghum of two sizes of 250 and 500 μm

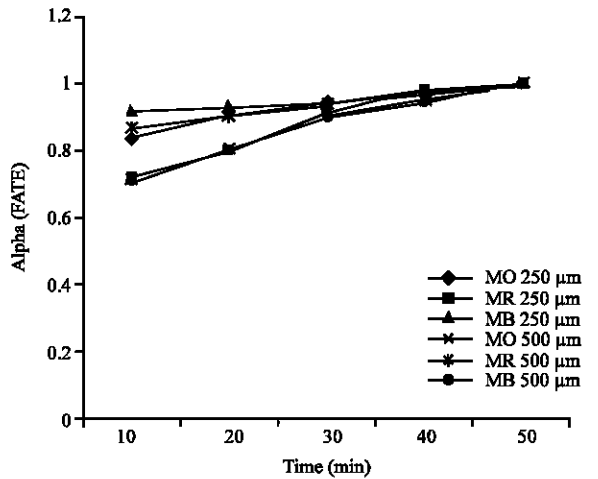


Fig. 10: Fractional Attainment to Equilibrium (FATE) alpha against time (min) for Methyl Orange (MO), Methyl Red (MR) and Methyl Blue (MB) adsorption on carboxymethylated sorghum of two sizes of 250 and 500 μm

sorption process is intraparticle diffusion controlled. Thus, the boundary layer acts as a viscous drag to the sorption process.

The plot of the Fractional Attainment to Equilibrium (FATE) is shown on Fig. 8 for unmodified sorghum, Fig. 9 for thiolated sorghum and Fig. 10 for carboxymethylated sorghum. FATE, helps to ascertain in detail how equilibrium was approached by the three azo dyes on the adsorbent. All values of alpha converge to 1

(one), showing that equilibrium was reached. Thus it means that the higher the sorption rate, the faster the approach to equilibrium.

CONCLUSIONS

The kinetics of sorption, intraparticle diffusion, equilibrium partitioning of three azo dyes; Methyl Orange (MO) Methyl Red (MR) and Methyl Blue (MB); on *Andropogon sorghum* have been studied. It was found out that as time increased, the amount of the dyes adsorbed also increased. The modification employed increased the adsorption capacity of the adsorbent, that of carboxymethylation being higher than thiolation.

The sorption process could be seen as a reaction whereby the azo dyes distribute itself between the aqueous solution and the adsorbent. Thus, the azo dyes at equilibrium will partition themselves and when a greater amount of the dyes cling to the adsorbent, then adsorption has been achieved following partitioning.

The mechanism of sorption was found to be particle diffusion controlled as against film diffusion controlled. Also, the sorption was found to follow the pseudo second order rate equation. The McKay and Poots model was also introduced to calculate the boundary layer diffusion effects. Therefore, it has been adduced that *Andropogon sorghum* could be used to decolorize azo dyes from waste water.

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