Enhanced Adsorption Capacity of Sweet Sorghum Derived Biochar towards Malachite Green Dye Using Bentonite Clay

Elvis Fosso-Kankeu, Frans B. Waanders, and Jalize Potgieter

Abstract**—**The enhanced adsorption capacity of modified sweet sorghum derived biochar using bentonite clay was prepared and systematically studied for its adsorption behaviour towards the removal of cationic dye namely malachite green (MG). A clay biochar composite was prepared by combining clay and biochar in a ratio of 1:5. The composite showed an improvement in the adsorption capacity for the removal of the dye compared to the biochar. The kinetic studies revealed that the adsorption fits both pseudo-first-order and pseudo-second-order kinetic models which indicates both physisorption and chemisorption mechanisms for the interaction between adsorbent and adsorbate molecules. The adsorption isotherm indicated that the Freundlich model best describes the adsorption mechanism.

Index Terms**—**Bentonite, biochar, composite, cationic malachite green adsorption, kinetic, isotherm

I. INTRODUCTION

Climate change and limited water resources are the major factors which are attributes to water shortage. In a case of countries such as South Africa which has limited rainfall and a rapid rate of population and industrial expansion there is an increase in water pollution of the current water sources [1]. Some of industrial activities, mostly manufacturing sector, pose a detrimental effect on the ecosystem. In the present study, the treatment of wastewater which is polluted with dyes is investigated. Dyes are organic, synthetic compounds which have become industrial pollutants during their synthesis as well as their use [2]. The textile industry as well as paper and pulp mills, dyestuff, distilleries, tanneries, among others generate highly coloured wastewaters [2]. The afore-mentioned industries release a variety of different types of dyes into the water-course, each with different chemical and physical properties making it difficult to remove them from wastewater [3]. Industries are compelled by environmental legislation to remove dye from their effluents before they are discharged to the water-course due to the impact on aquatic living plants and creatures, which then extends to humans and ecological systems [4]. The treatment of the wastewaters containing pollutants, such as dyes, depends on the nature of the impurities, the type and the composition of the wastewater [5].

Chemical processes, biological degradation and physical separation techniques have been developed over decades to remove dyes from wastewater. Each process has its own constraints in terms of cost, feasibility and environmental impact [2]. Among the conventional methods adsorption is an effective method in the removal or reduction of the pollutants from the wastewater, and has also proven to be an economical and simple technique [6].

The adsorbents that are investigated in this study include biochar, bentonite clay and a composite combining the two. Biochar is a carbon rich organic substrate, and is synthesized from sweet sorghum bagasse. It has properties such as high porosity, high specific surface area and cation exchange capacity, and it is an effective adsorbent and incur low costs [7]. Natural bentonite clay has properties such as high plasticity, a large surface area and it can swell numerous times larger than its original size. Bentonite clay is in abundance and has porous structure which reduces turbid materials through sorption and intercalation [8]. Bentonite clay mining in South Africa is predominantly of the type which contains both calcium and magnesium montmorillonite [9]. Montmorillonite is composed of a central sheet of octahedral aluminium ions between two tetrahedral sheets of silicone ions, where these sheets are linked with oxygen atoms. The substitution of Al^{3+} by Si^{4+} within the tetrahedral sheet, and Mg^{2+} by Al^{3+} in the octahedral sheet is the attribute to the net negative charge on the clay [10]. Bentonite clay behaves as a flocculent in the adsorption of particles, during ion exchange and in the coagulation-flocculation process [11].

All these properties, including the low cost and high availability, make it an attractive adsorbent to employ in the treatment of the wastewater polluted with dyes [12].

One of the challenges associated with biochar is the limited capacity in the removal of cationic dye because of the presence of positively charged binding sites. A plausible solution to the problem is to combine it with bentonite clay to form clay-biochar composite. The composite clay-biochar synthesised in this study induces a mixture of bentonite clay and sweet sorghum bagasse at a 1:5 ratio. The composite is characterised and tested for the adsorption of cationic dye and compared to the adsorption capacity of natural bentonite clay and biochar respectively. The advantage of this composite is combining the biochar technology and the good sorption ability of clay particles [13]. The behaviour of the sorbent is investigated using kinetic and isotherm models.

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II. METHODOLOGY

A. Materials

1) Dyes

The cationic dye used in this study was malachite green. The dye was used as received and was purchased from Merck Millipore (South Africa). The adsorptive solutions were prepared by dissolving the dye in distilled water.

2) Bentonite clay

Bentonite clay was used during the course of the experiments with particle sizes smaller than 150 μm.

3) Biomass

The biomass was sweet sorghum bagasse and was chosen due to its high availability and low cost. The biomass from the same origin and harvest was then grinded and sieved to achieve a particle size smaller than 150 μm before further use.

B. Characterisation

1) Bentonite Clay

A scanning electron microscopy (SEM) analysis was performed with the aid of a model FEI Quanta 200 ESEM Scanning Electron Microscope, integrated with an Oxford Inca 400 energy dispersive x-ray spectrometer to determine the surface morphology of each adsorbent.

C. Preparation of adsorbent

1) Bentonite-biochar composite

A stable clay suspension was prepared by adding 1 g of bentonite clay to 200 mL of deionized water (DI), the mixture was then mixed using an orbital shaker for 30 min at 180 rpm before adding 5 g of the biomass. The mixture was then stirred for a further 1 h before the excess water was drained and the modified feedstock was dried in an oven at 40°C for 12 hours. The clay-treated biomass feedstock was then placed inside a furnace in the presence of nitrogen for 1 h at 400°C to produce a powdered mass. The powder was then crushed and sieved to a particle size smaller than 150 μm.

2) Biochar

The biomass underwent slow pyrolysis at 400°C (in the presence of nitrogen) for an hour to convert the biomass to biochar. After pyrolysis, the sample was crushed and sieved again to obtain a particle size smaller than 150 μm.

D. Adsorption experiments

The adsorption experiments were carried out in a batch system. The adsorbents, bentonite clay, biochar and the bentonite-biochar composite were each added separately to 100 mL of dye solution and mixed on an orbital shaker at 160 rpm for a specific time. The suspension was centrifuged at 4000 rpm for 5 min. The supernatant was removed with a pipette and analyzed with the UVmini-1240 UV-VIS spectrophotometer. Two parameters were considered to determine the adsorption capacity of each of the adsorbents respectively. The parameters which were considered included the contact time (10 min, 20 min, 30 min, 40 min, 60 min, 80 min, 100 min, 120 min) of the adsorbents with the dye solutions and the initial dye concentration (10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L, 60 mg/L, 70 mg/L, 80 mg/L, 100 mg/L) in the dye solution.

E. Mathematical modelling

1) Determining the adsorption capacity

The adsorption capacity is determined once the equilibrium concentration is obtained experimentally using the following equation:

$$q_i = \frac{(C_0 - C_i)V}{m} \ ; \ i = e, t \qquad (1)$$

Where q_i is the amount of dye adsorbed per unit mass of adsorbent (mg/g); C_o is the initial dye concentration in the solution (mg/L); C_i is the dye concentration (mg/L); *m* is the amount of adsorbent (g) and *V* is the solution volume (L). The subscript “*i*” denotes the state of either the system at equilibrium (*e*) or at a time interval (*t*) [11].

2) Isotherm modeling

Langmuir and Freundlich isotherms were used to determine the adsorption affinity of the adsorbents for the dyes.

The Langmuir isotherm assumes a monolayer adsorption onto a surface containing a finite number of active sites and is expressed by:

$$q_e = \frac{KQC_e}{1 + KC_e} \qquad (2)$$

or in linearised form:

$$\frac{C_e}{q_e} = \frac{1}{KQ} + \frac{C_e}{Q} \qquad (3)$$

Where C_e is the dyes’ equilibrium constant (mg/L), q_e is the amount of adsorbed dye at equilibrium (mg/g), *Q* is a langmuir constant associated with the adsorption capacity (mg/g) and *K* is a Langmuir constant associated with the energy released during adsorption (L/mg) [12].

The Freundlich isotherm takes heterogeneous systems into account and is not restricted by a monolayer [10]. It is described by:

$$q_e = k_f C_e^{\frac{1}{n}} \qquad (4)$$

or in linearised form:

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \qquad (5)$$

Where, C_e (mg/L) is the concentration of dye at equilibrium, q_e is the amount of dye adsorbed at equilibrium (mg/g), k_f is the Freundlich adsorption capacity parameter in (mg/g) and n indicates the deviation of adsorption from linearity.

3) Kinetic modeling

Before applying the kinetic models, the adsorption capacity at diffirent times need to be calculated according to the previously described equation.

The pseudo first-order is expressed by the following equation:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (6)$$

The pseudo second-order can be described by the following equation:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (7)$$

Where q_e is the adsorbed amount of the dye at equilibrium (mg/g), q_t is the adsorbed amount of dye at a certain time t (mg/g) and $k_1 \, and \, k_2$ is the rate constant for the first and second order adsorption kinetics, respectively [13]. Non-linear regression methods were used to determine these rate constants.

III. RESULTS AND DISCUSSION

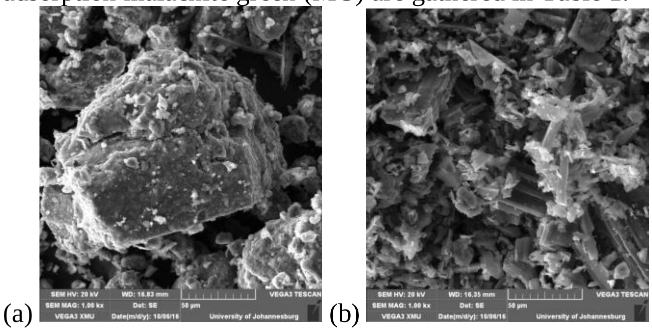
A. *Adsorbent Characterisation*

The morphology of the bentonite clay, biochar and composite was determined by a scanning electron microscope (SEM) at an electron acceleration voltage of 20 kV. From Figure 1 (a) it can be seen that the bentonite has a porous structure indicating a larger surface area, whereas the biochar has a non-spherical rod-like structures that have many alcoves and protrusions, seen in Figure 1 (b).

It can be seen from Figure 2 that after modification the biochar still has a rod-like structure along with little lumps showing the presence of the bentonite particles. These findings were similar to those of Fosso-Kankeu et al. [14]

B. *Adsorption Isotherm modeling*

The Langmuir and Freundlich isotherm models have been used to describe the adsorption of malachite green. It was observed that the initial uptake of the dye increased linearly with increasing initial concentrations of dye and then surface saturation was reached at higher concentrations. This may be the result of achieving adsorption equilibrium quickly due to all the binding sites being occupied. The isotherm parameters and the correlation coefficients (R^2) for the adsorption malachite green (MG) are gathered in Table 1.



(a) (b)

Fig. 1 SEM image of bentonite clay (a) and biochar (b) magnified a 1000 times.

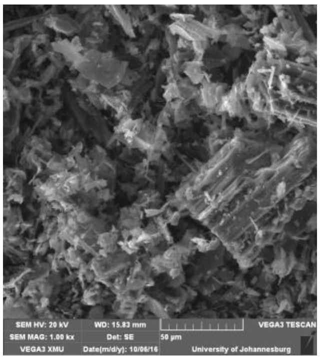


Fig. 2 SEM image of the bentonite-biochar-composite magnified a 1000 times

TABLE I

ISOTHERM MODEL PARAMETERS FOR MALACHITE GREEN ADSORPTION

Malachite Green Isotherm Study

Adsorbent	**Best model**	**Model Parameters**		**Adsorption Potential (q_e) (mg/g)**
Bt	Freundlich	kf	121.3520	2834.840
		n	1.2415	
		R^2	0.7840	
Bc	Freundlich	kf	1.9290	4638.388
		n	0.5025	
		R^2	0.9105	
Composite	Freundlich	kf	10.3050	218.701
		n	1.2805	
		R^2	0.9515	

From Table 1 it is clearly seen that the Freundlich isotherm model best describes the adsorption of MG by all adsorbents. The R^2 value obtained from the fit of the data to the theory of MG was favorable for two of the adsorbents, implying that the Freundlich model was suitable only for the prediction of the adsorption of MG on the biochar and composite. The affinity of the adsorbent towards the uptake of the dye is indicated by the value of n. It can be seen from Table 1 that n > 1 for the composite indicating that the adsorbent is good over the entire range of concentrations, and n < 1 for the biochar indicating that the adsorbent is good only for higher concentrations studied and less at lower concentrations [7].

C. *Adsorption Kinetics Modeling*

The pseudo-first-order and pseudo-second-order kinetic models of different initial times were used to fit the experimental data. The values of $k_i \, ; i = 1, 2$ and $q_{e_{cal}}$ were calculated from the intercept $(1/k_i q_e^2)$ and slope $(1/q_e)$ of the plot $t/q_t \; vs. t$ in Fig. 3 and presented in **Error! Reference source not found.**. The $q_{e_{exp}}$ was found to be in good agreement with the $q_{e_{cal}}$ values for both pseudo-first-order and pseudo-second-order models. The values of R^2 for both kinetic models are relatively close to each other, however the higher correlation coefficient suggests the applicability of the pseudo-second-order model for the adsorption of MG onto the various adsorbents. It can be observed from **Error! Reference source not found.** that the adsorption capacity ($q_{e(\text{exp})}$) of the composite is higher compared to that of the biochar, which implies that the composite has a higher affinity for MG dye. It can therefore be said that the negative net charge of the composite is suitable for the attraction of cationic dyes.

TABLE II
KINETIC MODEL PARAMETERS FOR MALACHITE GREEN ADSORPTION

Adsorbent		Kinetic Model and Parameters			
		Pseudo 1st order		Pseudo 2nd order	
Biochar					
qe(exp) (mg/g)	**9.8400**				
		q_{e1}	9.5953	q_{e2}	10.0616
		k_1	0.1634	k_2	0.0369
		R^2	0.9705	R^2	0.9953
Bentonite Clay					
qe(exp) (mg/g)	**16.6087**				
		qe_1	16.5552	q_{e2}	16.5841
		k_1	0.5562	k_2	0.9007
		R^2	0.9997	R^2	0.9999
Composit					
qe(exp) (mg/g)	**12.1255**				
		q_{e1}	11.8973	q_{e2}	12.1788
		k_1	0.2434	k_2	0.0710
		R^2	0.9864	R^2	0.9975

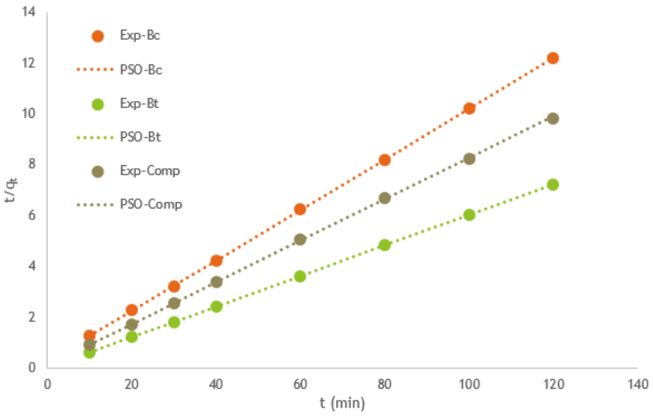


Fig. 3. Fit of kinetic data to pseudo-second-order rate model for the adsorption of MG onto biochar, bentonite and the composite.

IV. CONCLUSION

From the characterization of the adsorbents it was seen that the synthesis of the composite was performed successfully. The composite and the biochar both removed cationic dye from the aqueous phase. The adsorption isotherm can be fitted by the Freundlich model, implying that adsorption occurs on the heterogeneous surface. The adsorption kinetics can be well described by the pseudo-second order model equation. Due to the observation that the adsorption capacity of the composite was higher than the biochar, it could be concluded that the composite has a higher affinity for cationic dyes and does thus enhance the adsorption of derived biochar towards cationic dyes.

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