

Full Length Research Paper

Removal of methylene blue from aqueous solutions using biochar prepared from *Eichhornia crassipes* (Water Hyacinth)-molasses composite: Kinetic and equilibrium studies

Mupa Mathew*, Rutsito D. Desmond and Musekiwa Caxton

Department of Chemistry, Faculty of Science, Bindura University of Science Education, Private Bag 1020, Bindura, Zimbabwe.

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A biochar based adsorbent prepared from *Eichhornia crassipes*-molasses bio-composite was tested for its ability to remove methylene blue from aqueous solutions. Molasses were used as a granulating media for powdered biomass making it easier to prepare the biochar under set conditions. The Biochar adsorbent was prepared by igniting biomass granules at 400°C. A maximum adsorption capacity of 44.13 mg·g⁻¹ was achieved at an optimum pH 8, with a bio-sorbent dosage of 0.8 g and an initial concentration of 50 mg·L⁻¹. Experimental data fitted well onto Freundlich adsorption isotherm with an R² value of 0.9819. Adsorption processes followed pseudo-second order kinetics with an R² value of 0.9877. FT-IR spectra reveal typical absorption bands around 1563, 1375 and 1028 cm⁻¹. SEM image show the biochar consisted of irregular particles with a microporous structure and appeared to be fibrous. BET results showed that biochar particles had a surface area of 0.8923 m²·g⁻¹, a pore volume of 0.00246 cm³·g⁻¹ and a pore diameter of 10.87 nm.

Key words: Bio-sorbent, biochar, *Eichhornia crassipes*, methylene blue, isotherm.

INTRODUCTION

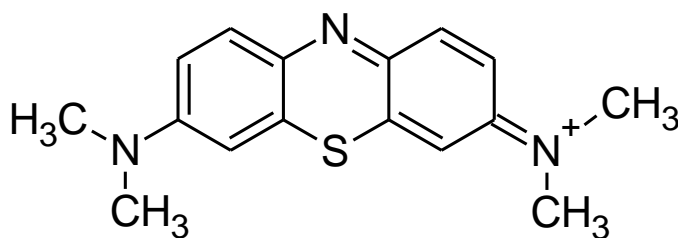
Pollution as a result of industrial and human activity is becoming a concern for local and water authorities due to increased cost of water purification. One of the major contributors to water pollution are dye and pigment manufactures, pulp and paper, printing and textile industries. Reports from various researchers suggest that a total of 7x10⁵ metric tons of dyes are produced annually

worldwide from about 10000 commercially available dyes (Nadhini et al., 2012; Hameed et al., 2008). The dying process produces huge volumes of colored water effluent. Ratna and Padhi (2012) estimated that between 10-15% of dye is disposed of thereby making a highly colorful effluent. Discharge of huge volumes of dye effluent into rivers or lakes interferes with aquatic life and

*Corresponding author. E-mail: mathewmupa@daad-alumni.de.

Table 1. Classification of dye effluent treatment methods.

Biological	Chemical	Physical
Aerobic biological processes	Coagulation-flocculation and precipitation (Yuan et al., 2006; Bidhendi et al., 2007)	Adsorption: adsorption with activated carbon (Namasivayam and Kavitha, 2002), adsorption with activated alumina and other metal oxides, biosorption (Srinivasan and Viraraghavan, 2010), adsorption with biochar (Agarwal et al., 2015)
Anaerobic biological treatment process	Electrocoagulation (Chen, 2004) Oxidative processes: Ozonation, oxidative processes with hydrogen peroxide, oxidative process with sodium hypochlorite, photochemical oxidation process, and electrochemical oxidation processes. (Bautista et al., 2008)	Irradiation (Anjaneyulu et al., 2005) Membrane processes: reverse osmosis, micro-filtration, bio-filtration, ultra-filtration, Nano-filtration (Chen et al., 2005).

**Figure 1.** Chemical structure of methylene blue.

the dye compounds and their degradations products are known to be toxic or carcinogenic due to aromatic nature of most dyes (Kant, 2012; Mathur et al., 2005). This has necessitated the need to develop viable dye effluent treatment methods. Current dye treatment methods can be broadly classified into physical, chemical, biological processes. A summary of reported treatment methods for textile effluent are listed in Table 1.

Eco-friendly dye effluent treatment methods continue to attract the interest of many researchers and these include bio-sorption techniques. Quite a number of bio-sorption techniques and adsorbents based on renewable biobased raw materials have been developed and tested for use in the treatment of dye effluent (Vijayaraghavan and Yun, 2008; Aksu, 2004). In this research article we report a possible environmentally friendly application of an *Eichhornia crassipes-molasses* based biochar in the removal of methylene blue (Figure 1) from synthetic wastewaters. *Eichhornia crassipes* better known as water hyacinth is a highly invasive water weed and poses environmental problems. Application of biochar prepared from different biomasses for textile effluent treatment has been reported by some researchers. Table 2 shows a comparison of adsorption capacity of different biochars for methylene blue. Biochar potential applications have also been demonstrated in heavy metal removal in effluent water (Yang et al., 2013) and soil amendments in

agriculture (Lehmann et al., 2011; Jha et al., 2010).

MATERIALS AND METHODS

Chemicals

Chemical reagents were of analytical grade and were used without further purification. This includes hydrochloric acid purchased from Radchem (Pvt) Ltd, RSA, methylene blue from Skylabs (Pvt) Ltd and sodium hydroxide from Sigma-Aldrich.

Sampling

E. crassipes was harvested from Lake Chivero, 32 km south of Harare and was sun-dried over a period of 30 days. The leafy part was separated from the roots and cut in to smaller pieces. The biomass was ground in a laboratory mill and sieved through 75 μ sieve.

Equipment

A Genesy 10s UV/Vis spectrophotometer supplied by Thermo Fisher Scientific GmbH, Germany was used to determine concentrations of dyes in synthetic effluents. A Thermo Fisher Scientific Nicolet iS5 MIR FT-IR spectrophotometer configured with an ATR accessory and OMNIC software was used to measure spectra of biochar samples. The spectra were scanned within 4000-400 cm^{-1} range in 256 scans at a resolution of 1 cm^{-1} . SEM images were recorded on a Tescan Vega3 SEM instrument.

Table 2. Comparisons of biochars used in the adsorption of methylene blue.

Biochar adsorbent type	Maximum adsorption capacity (mg·g ⁻¹)	References
Water Hyacinth based biochar	44.13	Current study
Palm oil Empty Fruit Bunch biochar	55.25 at 30°C	Rebitamin et al. (2012)
Sawdust-derived biochar	333.33	Ghani et al. (2013)
Biochar from co-pyrolysis of dewatered sludge and pine sawdust	16.75	Cheng et al. (2013)
Wheat straw biochar	12.04 ± 0.41 at 293 K	Liu et al. (2012)

Table 3. Physico-chemical properties.

Parameter	Value
Yield (%)	60±1
Ash content (%)	43±0.01
Density (g·cm ⁻³)	0.132
BET N ₂ surface area (m ² ·g ⁻¹)	0.8925
Pore diameter (nm)	10.87
Pore volume (cm ³ ·g ⁻¹)	0.00246

Preparation of biochar

Ground *E. crassipes* biomass was mixed with molasses in the ratio of 5:1. The composite mixture which predominantly was granular in nature was dried at 80°C overnight. Exactly 50 g of dried biomass granules were ignited in a muffle furnace at 400°C for 5 h. The resultant biochar was ground to a fine powder and sieved through 250 µ sieve.

Adsorption experiments

Dye solutions were prepared by serial dilution from 200 mg·L⁻¹ solution of methylene blue and were 10, 20, 30, 40 50, 60, 80 100, 130, 150 and 200 mg·L⁻¹. Dye solutions in which the biosorbent was suspended, were agitated at 125 rpm for 120 minutes. Dye concentrations before and after adsorption were measured using a UV/Vis spectrophotometer. The adsorption parameters were optimized in terms of pH, contact time, and biosorbent dosage. Removal efficiencies and adsorption capacities were calculated using equations 1 and 2 below.

$$RE = \frac{(c_0 - c_t)}{c_0} \times 100 \quad (1)$$

$$q_t = \frac{(c_0 - c_t)V}{m} \quad (2)$$

where c_0 is the initial concentration in mg·L⁻¹, c_t dye concentration at time t , V volume and m mass of biosorbent in g and q_t adsorption capacity at time t .

RESULTS AND DISCUSSION

Physico-chemical properties of the biochar are shown in Table 3. From the table, it can be observed that *Eichornia crassipes* had a very high ash content of 43%. The yield was however very high, suggesting that the biowaste can be viable raw material for the preparation biochar. The

Biochar had a BET surface area of 0.8925 m²·g⁻¹. Results for BET surface area are similar to biochars prepared from peanut hull, pecan shell and poultry liter under similar condition (Novak et al., 2009). However, literature reports suggest that surface area is heavily dependent upon the temperature and the type of biomass (Mukherjee et al., 2011; Özçimen and Erosoy-Meriçboyu, 2010).

FT-IR spectra help identify functional groups on the adsorbent surface and hence explain the adsorption mechanism. The FT-IR spectrum of water-hyacinth – molasses based biochar is shown in Figure 2. The FT-IR spectrum exhibit a peak at 1563 cm⁻¹ which could be assigned to C=C-C stretch characteristic of the aromatic ring stretch. Another absorption band at 1375 cm⁻¹ is due to C-H stretch. An absorption band at 1029 cm⁻¹ is evidence of a C-O-C stretch associated with cellulose, hemicellulose and lignin. These IR absorption bands have also been observed for other biochars based on other biomasses (Sun et al., 2011, Lee et al., 2010).

The SEM images of biochar samples are shown in Figure 3. The images show that the biochar consisted of particles with an irregular porous structure. The fibrous nature of some of the particles is also evident in the images.

Adsorption experiments

Effect of pH

The effect on methylene blue adsorption capacity was investigated between pH 2 and 9. The result is illustrated in Figure 4. From the diagram, one observes a sharp rise

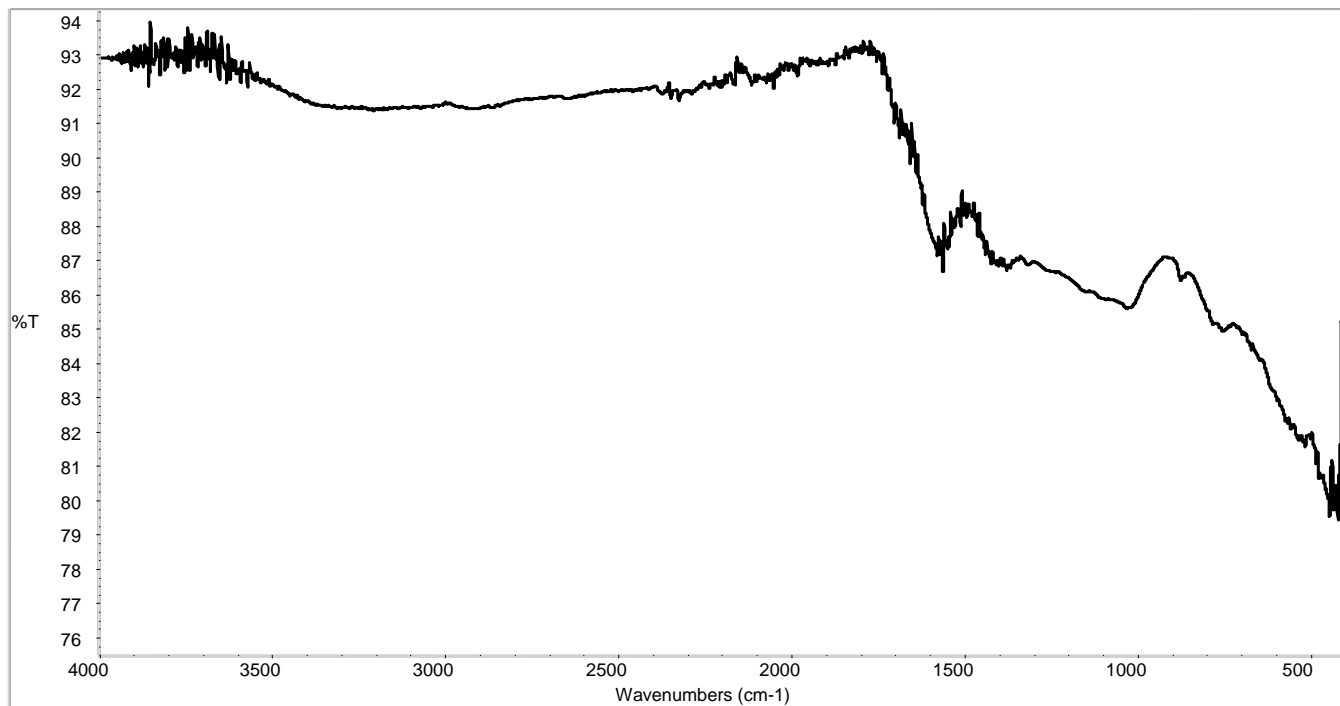


Figure 2. FT-IR Spectra of water hyacinth-molasses based biochar.

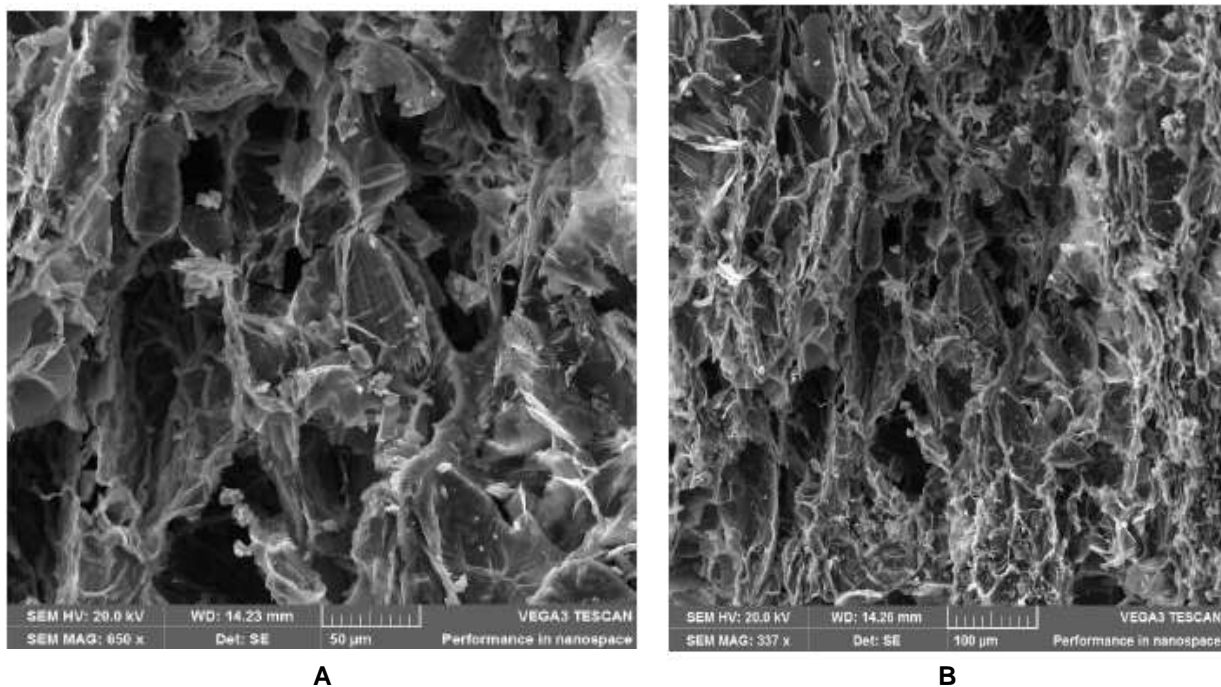


Figure 3. SEM Images of *Eichhornia crassipes*-molasses based Biochar.

in removal efficiency from 47.08% at pH 4 to 88.82% at pH 8. The trend in the removal efficiency is similar to findings by Abdur et al. (2013), who attributed low

removal efficiencies in acidic pH to electrostatic repulsion between protonated bio-sorbent surface and methylene blue.

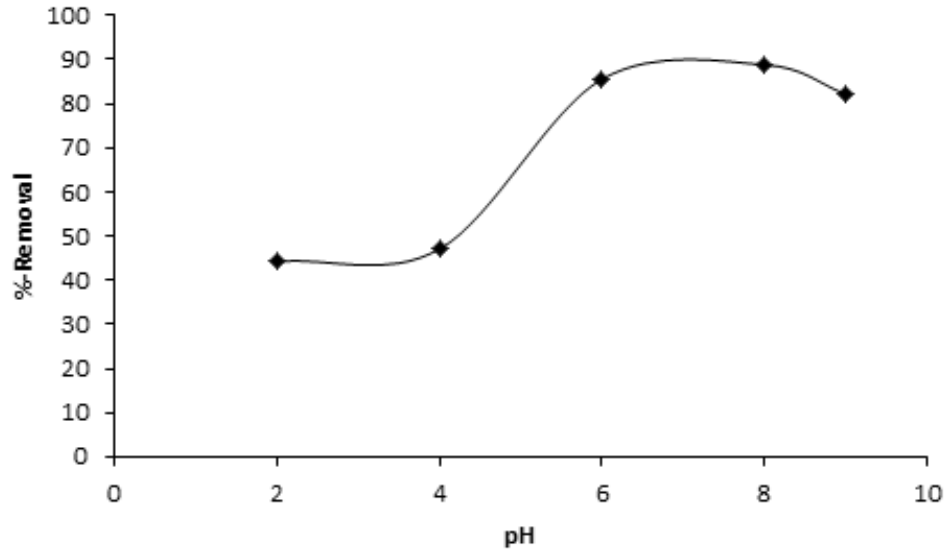


Figure 4. Effect of pH= 8, ($c_0 = 50 \text{ mg}\cdot\text{L}^{-1}$, agitation =125 rpm, bio-sorbent dosage = 0.8 g, $T = 25^\circ\text{C}$).

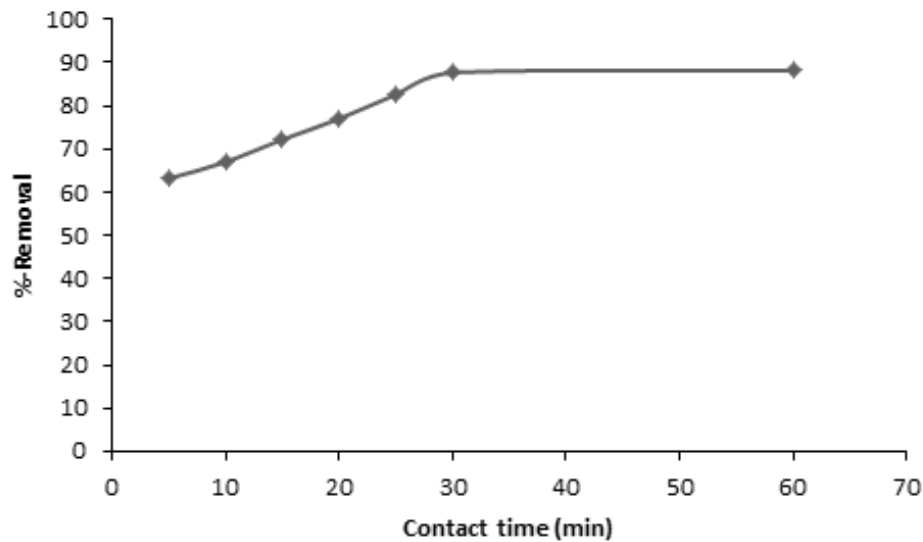


Figure 5. Effect of contact time (pH = 8, $c_0 = 50 \text{ mg}\cdot\text{L}^{-1}$, bio-sorbent dosage= 0.8 g, agitation = 125 rpm, $T = 25^\circ\text{C}$).

Effect of contact time

Contact time is important in the sizing of an adsorption plant. The results for the effect of contact time on adsorption capacity are shown in Figure 5. From the diagram, one observes a steep rise in the removal efficiency in the first thirty minutes up to a maximum of 87.1%. No meaningful improvement in the removal efficiency was observed after this time. This trend can be attributed to the high number of available adsorbent sites in the first thirty minutes.

Effect of adsorbent dosage

Effect of adsorbent dosage is illustrated in Figure 6. From the diagram one can observe that removal efficiency increased sharply between bio-sorbent dosage of 0.2 and 0.4 g and then gradually between 0.4 and 0.8 g. Above 0.8 g, removal efficiency remained steady and was hence considered as the optimum dosage. According to El Jamal and Ncibi (2012), the adsorption trend is due to an increase in surface area and hence the number of active.

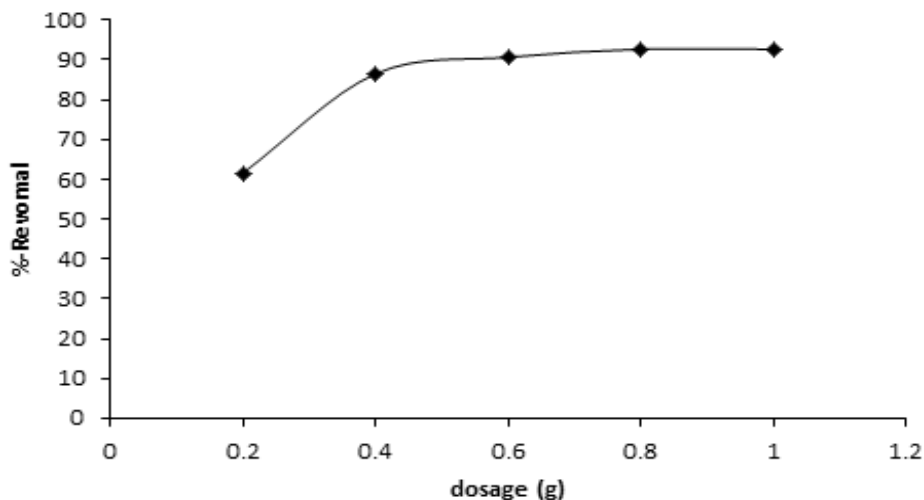


Figure 6. Effect of bio-sorbent dosage ($c_0 = 50 \text{ mg}\cdot\text{L}^{-1}$, agitation = 125 rpm, pH = 7, T = 25°C).

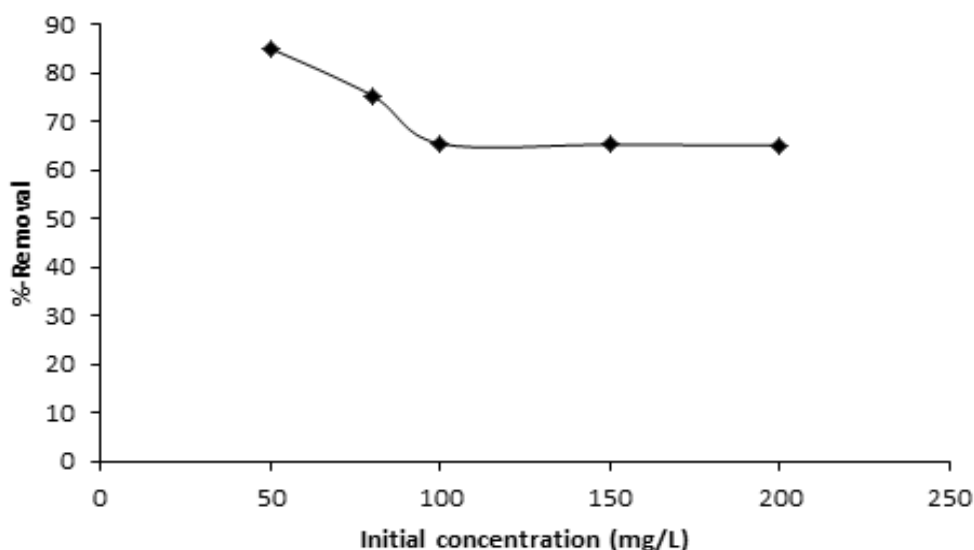


Figure 7. Effect of initial concentration (pH = 7, biosorbent dosage = 0.8 g, t = 125 rpm, T = 25°C).

Effect of initial concentration

Initial concentration is known to have an effect on the removal efficiency. From the removal efficiency as illustrated in Figure 7, one can observe a sharp decrease in the removal efficiency from an initial dye concentration of $50 \text{ mg}\cdot\text{L}^{-1}$ to $100 \text{ mg}\cdot\text{L}^{-1}$. The trend may be due to the limitation of active sites with increase of initial dye concentration.

Kinetic studies

Kinetic studies were carried out in order to establish whether adsorption processes followed the pseudo-first

or pseudo-second order kinetics. The pseudo-first order model can be expressed using Equation 3 below.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

where q_e is adsorbed dye in $\text{mg}\cdot\text{g}^{-1}$ at equilibrium and k_1 the pseudo-first order rate constant. The linearized form of this Equation 3 is given by Equation 4.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

Plotting $\ln(q_e - q_t)$ should generate a straight line with an intercept $\ln q_e$ and a slope of $-k_1$. The pseudo second order can be expressed using Equation 5.

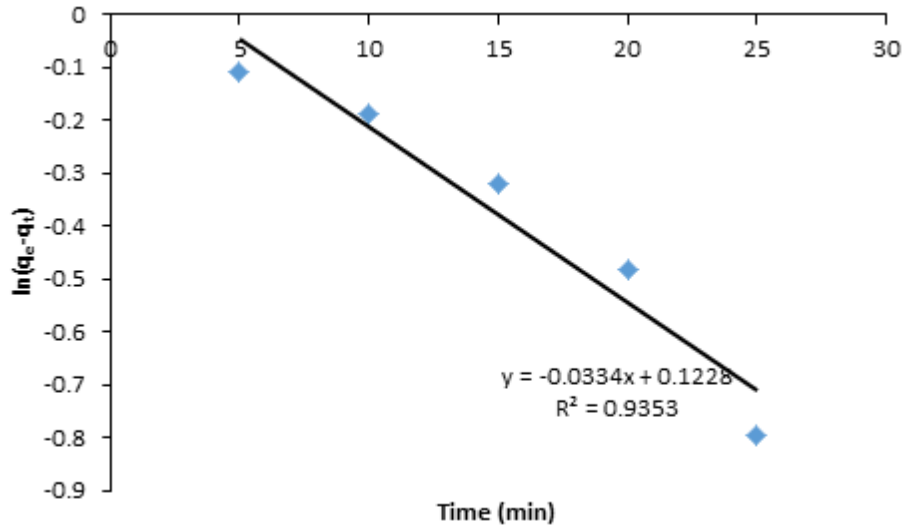


Figure 8. Graph of pseudo-first order rate methylene blue bio-sorption process.

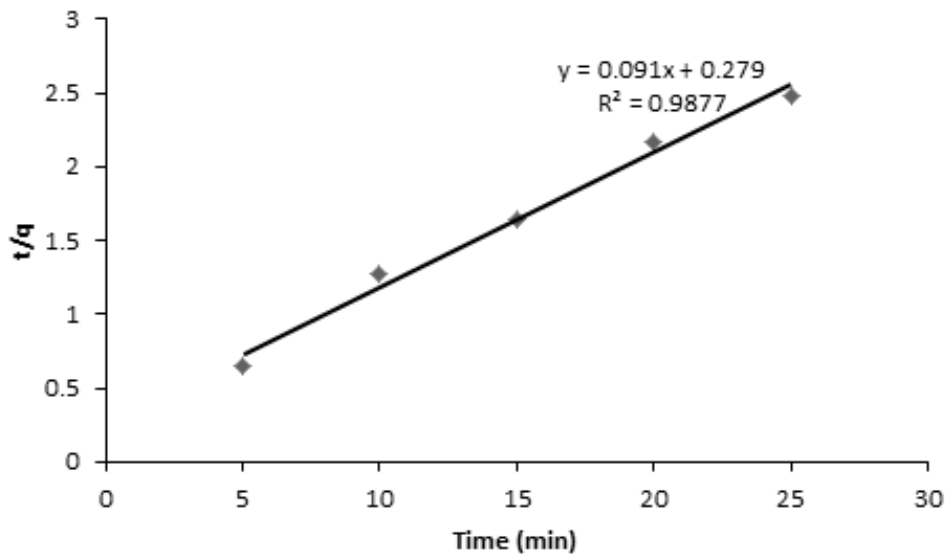


Figure 9. Plot of the pseudo-second order rate for methylene blue bio-sorption process.

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{5}$$

where k_2 is the pseudo-second order rate constant. The linearized form of this equation is given by Equation 6.

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{6}$$

The pseudo-second order rate parameters k_2 and q_e are obtained from the intercept of the $\frac{t}{q}$ versus t . The results of the pseudo-first and pseudo-second order are illustrated in Figures 8 and 9 respectively. A comparison

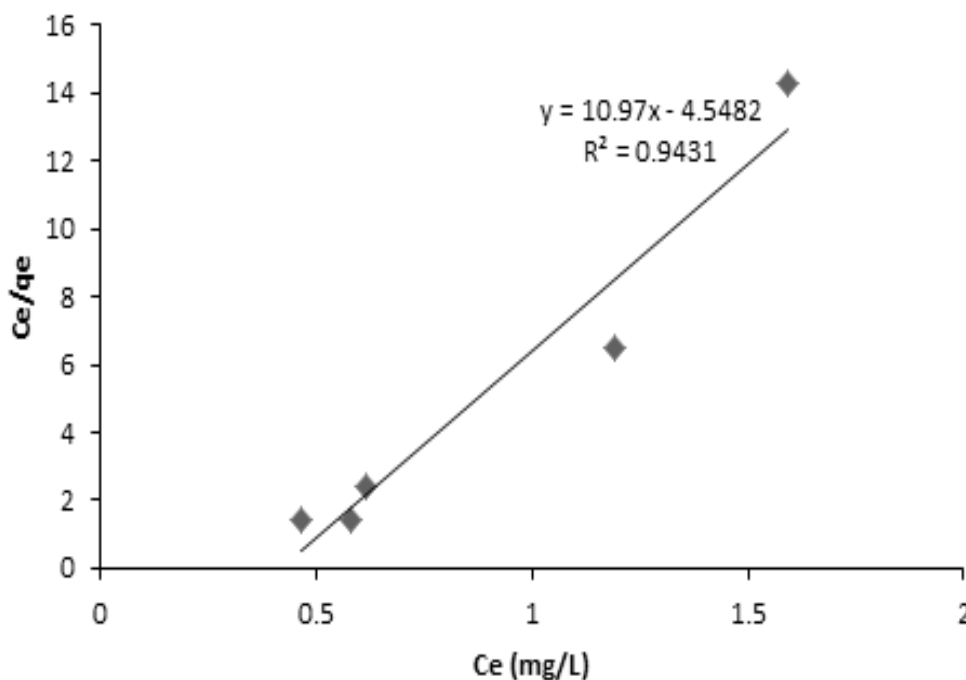
of the R^2 values suggests in table 4 that experimental data fitted well into pseudo-second order adsorption process. This trend has been reported by other researchers who have worked with similar bio-based adsorbents (Han et al., 2015; Tan et al., 2016).

Adsorption isotherms

An adsorption isotherm can be described as the equilibrium relationship between the amount of the adsorbed material and the concentration or pressure in the bulk fluid phase at constant pressure. Parameters for

Table 4. Comparison of pseudo-first and pseudo-second order kinetic parameters.

Parameter	Pseudo-first order			Pseudo-second order		
c_0	k_1	q_e	R^2	k_2	q_e	R^2
50	0.0334	1.3268	0.9353	432.826	10.99	0.9877

**Figure 10.** Plot of Langmuir adsorption isotherm for methylene blue adsorption.

adsorption isotherms are important in the sizing of an adsorber. A number of adsorption isotherm models (Freundlich, Langmuir, BET, Temkin, Dubinin-Radushkevich, Flory-Huggin, etc.) formulated over years have been tested on a different adsorption systems. Experimental data for methylene blue adsorption on to *E. Crassipes*-molasses based bio-sorbent was fitted on to the Langmuir and Freundlich adsorption isotherm models. The Langmuir adsorption isotherm model assumes a mono layer adsorption on a finite number of active sights per unit mass. It further assumes that the adsorbent is structurally homogeneous and that there is no interaction between molecules adsorbed on neighboring sites. The Langmuir adsorption can be expressed using Equation 7.

$$\frac{q}{q_m} = \frac{cK_L}{1+cK_L} \quad (7)$$

where q_m is the maximum adsorption capacity in $\text{mg}\cdot\text{L}^{-1}$, K_L the Langmuir constant. The linearized form of the Langmuir adsorption isotherm is shown in Equation 8.

$$\frac{1}{q} = \frac{1}{q_m c K_L} + \frac{1}{q_m} \quad (8)$$

The Freundlich adsorption assumes a multilayer heterogeneous adsorption with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. The Freundlich adsorption isotherm is represented by Equation 9.

$$q_e = K_F c_e^{\frac{1}{n}} \quad (9)$$

where K_F is Freundlich constant, c_e the equilibrium constant in $\text{mg}\cdot\text{L}^{-1}$. the linearized logarithmic form is expressed using Equation 10.

$$\log q_e = \log K_F + \frac{1}{n} \log c_e \quad (10)$$

The experimental results for fitting into the Langmuir and Freundlich adsorption isotherms are illustrated in Figures 10 and 11 respectively. A comparison of the results is shown in Table 5. From the R^2 values it can be observed that adsorption fitted more into the Freundlich than the

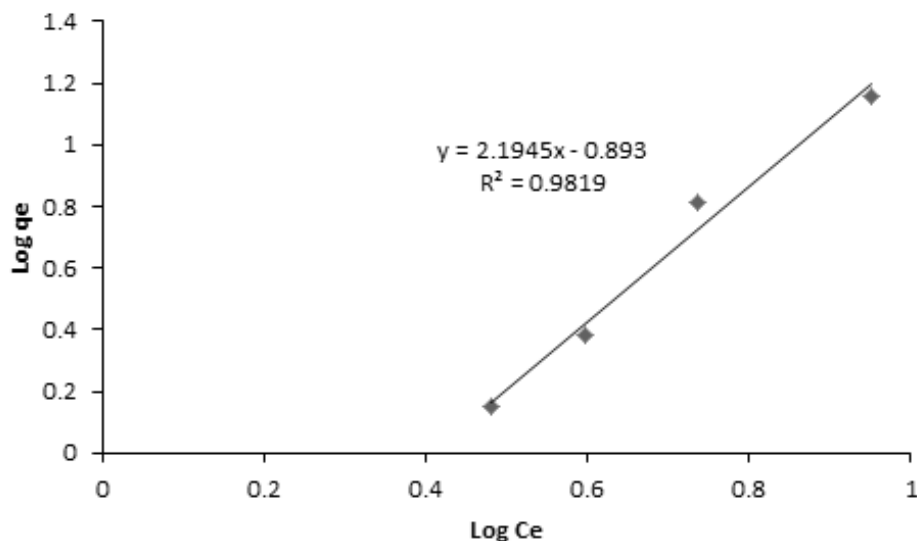


Figure 11. Plot of Freundlich adsorption isotherm for methylene blue adsorption.

Table 5. Comparison of the Langmuir and Freundlich adsorption parameters.

Parameter		Langmuir parameters		Freundlich parameters		
c_0 (mg·L)	q_m (mg·g ⁻¹)	K_L	R^2	K_F	n	R^2
50	44.13	0.201	0.9431	2.583	2.235	0.9819

Langmuir adsorption isotherm model and can be concluded that the adsorption is assumed a multi-layer form.

Conclusion

E. crassipes-molasses based biochar adsorbent was prepared. The adsorbent showed good methylene blue dye adsorption properties, with a maximum adsorption capacity of 44.13 mg·g⁻¹. Experimental data fitted well onto the Freundlich adsorption isotherm and adsorption processes followed the pseudo-second order rate with an R^2 value of 0.9877. FT-IR spectra showed typical IR absorption bands of biochar based materials. The SEM images show that adsorbent had an irregular porous structure.

Conflict of Interests

The authors have not declared any conflict of interests.

REFERENCES

Abdur RFB, Akter M, Zainal Abedin M (2013). Dye removal from textile waste waters using orange peels. *Int. J. Sci. Technol. Res.* 2:47-50.
 Agarwal M, Tardio J, Mohan SV (2015). Pyrolysis biochar from

cellulosic municipal solid waste as adsorbent for azo dye removal: Equilibrium isotherms and kinetic analysis. *Int. J. Environ. Sci. Dev.* 6(1):67-72.
 Aksu Z (2004). Application of Biochemistry for the Removal of organic pollutants. *Process Biochem.* 40:997-1026.
 Anjaneyulu Y, Chary NS, Raj DSS (2005). Decolourization of industrial effluents – Available methods and emerging technologies – a review. *Rev. Environ. Sci. Biol.* 4:245-273.
 Bautista P, Mohedano AF, Casas JA, Zazo JA, Rodriguez JJ (2008). An overview of the application of Fenton Oxidation to industrial wastewaters treatment. *J. Chem. Technol. Biot.* 83:1323-1338.
 Bidhendi GRN, Torabian A, Ehsani H, Razmkhah N (2007). Evaluation of industrial dyeing wastewater treatment with coagulants and polyelectrolyte as coagulant aid. *Iran. J. Environ. Health. Sci. Eng.* 4(1):29-36.
 Chen G (2004). Electrochemical technologies in waste water treatment. *Sep. Purif. Technol.* 38:11-41.
 Chen X, Shen Z, Zhu X, Fan Y, Wang W (2005). Advanced treatment of textile waste water for reuse using electrochemical oxidation and membrane filtration. *Water SA* 3(1):127-132.
 Cheng G, Sun L, Jiao L, Peng L, Lei Z, Wang Y, Lin J (2013). Adsorption of methylene blue by residue biochar from co-pyrolysis of dewatered sludge and pine sawdust. *Desalin. Water Treat.* 51:7081-7087.
 El Jamal MM, Ncibi MC (2012). Biosorption of Methylene blue by *Chaetophora elegans* algae: Kinetics, Equilibrium and Thermodynamic Studies. *Acta Chim. Slov.* 59:24-31.
 Ghani WAWK, Mohd A, Mahmoud DK, Rebitanim NZ, Sanyang L, Zainudin RB (2013). Adsorption of methylene blue on sawdust-derived biochar and its adsorption isotherms. *J. Purity Util. React. Environ.* 2(2):34-50.
 Hameed BH, Mahmoud DK, Ahmad AL (2008). Equilibrium modeling and kinetic studies on the adsorption of basic dye by a low cost adsorbent: *Coconum (Cocos nucifera)* Bunch waste. *J. Hazard. Mater.* 158:65-72.

- Han X, Chu L, Liu S, Chen T, Ding C, Yan J, Ciu L, Quan G (2015). Removal of Methylene Blue from aqueous solution using porous biochar obtained by KOH activation of peanut shell biochar. *Bioresource* 10(2):2836-2849.
- Jha P, Biswas AK, Lakaria BL, Rao AS (2010). Biochar in agriculture: Prospects and Related implications. *Curr. Sci.* 99(9):1218-1225.
- Kant R (2012). Textile dyeing industry an environmental hazard. *Nat. Sci.* 4(1):22-26.
- Lee JW, Kidder M, Evans BR, Paik S, Buchanan III AC, Garten CT, Brown RC (2010). Characterization of biochars produced from cornstivers for soil amendment. *Environ. Sci. Technol.* 44:7970-7974.
- Lehmann J, Rillig MC, Thies J, Masiello CA, Hockday WC, Crowley D (2011). Biochar effects on soil biota: A Review. *Soil Biol. Biochem.* 43:1812-1836.
- Liu Y, Zhao X, Li J, Ma D, Han R (2012). Characterization of biochar from pyrolysis of wheat straw and its evaluation on methylene blue adsorption. *Desalin. Water Treat.* 46:115-123.
- Mathur N, Bhatnagar P, Bakre P (2005). Assessing mutagenicity of textile dyes from Pali (Rajasthan) using AMES bioassay. *Appl. Ecol. Environ. Res.* 4(1):111-118.
- Mukherjee A, Zimmerman AR, Harris W (2011). Surface chemistry variations among series of laboratory produced biochar. *Geoderma* 163:247-255.
- Nadhini R, Vaishnavi V. Koti, Vadanandunari V, Rangabhashiyam S (2012). Decolourization studies of synthetic textile dye using *Aspergillus* species under static and shaking conditions. *Asian J. Sci. Technol.* 4(11):80-82.
- Namasivayam C, Kavitha D (2002). Removal of Congo Red from wastewater on to activated carbon prepared from coir pith, an agricultural solid waste. *Dyes Pigm.* 54:47-58.
- Novak JM, Lima I, Xing B, Gaskin JW, Steiner C, Das KC, Ahmedna M, Rehrh D, Watt DW, Busscher WJ, Schomberg H (2009). Characterization of designer biochar produced at different temperatures and their effects on a loamy sand. *Ann. Environ. Sci.* 3:195-206.
- Özçimen D, Ersoy-Meriçboyu A (2010). Characterization of biochar and biooil sample obtained from carbonization of various biomass materials. *Renew. Energ.* 35:1319-1324.
- Ratna, Padhi PS (2012). Pollution due to synthetic dye toxicity & carcinogenicity studies and remediation. *Int. J. Environ. Sci.* 3(3):940-955.
- Rebitamin NZ, Ghani WAWK, Mahmoud DK, Rebitamin A, Salleh MAM (2012). Adsorption of methylene blue by agricultural solid waste of pyrolyzed EFB Biochar. *J. Purity Util. React. Environ.* 1(7):376-390.
- Srinivasan A, Viraraghavan T (2010). Decoloration of dye wastewaters by biosorbents: A Review. *J. Environ. Manage.* 91:1915-1929.
- Sun K, Ro K, Gao M, Novak J, Mashayekhi H, Xing B (2011). Sorption of bisphenol A, 17 α -ethyl estradiol and phenanthren on thermally and hydrothermally produced biochars. *Bioresour. Technol.* 102:5757-5763.
- Tan X, Liu Y, Zeng G, Wang X, Hu X, Gu Y, Yang Z (2015). Application of biochar for the removal of pollutants from aqueous solutions. *Chemosphere* 123:70-85.
- Vijayaraghavan K, Yun YS (2008). Bacterial biosorbent and biosorption. *Biotechnol. Adv.* 26:266-291.
- Yang Z, Xiong S, Wang B, Li Q, Yang W (2013). Cr(III) adsorption by sugarcane pulp residue and biochar. *J. Cent. South Univ.* 20:1319-1325.
- Yuan Y, Wen Y, Li X, Luo S (2006). Treatment of waste water from dye manufacturing industry by coagulation. *J. Zhejiang Univ-Sci. A* 7(Suppl. II):340-344.