International Journal of Applied Engineering Research
ISSN 0973-4562 Volume 10, Number 3 (2015) pp. 6547-6555

http://www.ripublication.com

Experimental Study of *EM* Based Leaf Waste Compost onto Malachite Green Removal

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ABSTRACT

The discarded materials from different sources can be utilized as effective materials in wastewater remediation. This proposed study was aimed mainly to investigate the possibility of*Effective Microorganisms (EM)*basedcompost, which is derived from the leaf solid waste, as a non-conventional low cost adsorbent for the removal of Malachite Green (Basic Dye) from aqueous solution. Batch experiments were carried out to evaluate the optimum operating parameters of pH (2-9), initial dye concentration (50–1000 mg/L), adsorbent particle size (0.6– 2.36 mm) and adsorbent dosage (2 -12 g/L). The equilibrium adsorption data followed two and three parameter isotherm models were employed for the mathematical description of this study. The results revealed that the Freundlich model offers a better fit than other models.

KEYWORDS: Malachite Green, dye, compost, *Effective Microorganisms*, isotherms

Introduction

Many industries such as textile, paper, food processing, dyeing, and cosmetics use dyes to colour the products. Many dyes and their breakdown products may be toxic for living organisms. Malachite Green (MG) is a type of dye which is most commonly used for dyeing of cotton, silk, paper and also in manufacturing of paints and inks [1]. The Malachite Green is very difficult to remove from aqueous solution. Though the use of this dye is banned in several countries, it is still being used in many places due to its low cost, and availability [2].The dye-contaminated water when consumed will cause ill effects to liver, kidney and intestine [3]. Therefore the treatment is very much necessary in order to save the aquatic and human existence.

Biosorption is a well-established technique for the removal of textile dyes [4] from aqueous solution.Numerous number of inexpensive and abundant biosorbents especially agro waste materials as well as industrial and municipal wastes have been proposed by several researchers for the removal of MG dyes [5]from their aqueous solution.

This study was aimed to investigate the role of *EM*based leaf waste compost (EM_{LC}), as a non-conventional low cost adsorbent in the removal of Malachite Green from aqueous solution.

Materials and Methods

Adsorbent

Compost was preparedfrom neem leafsolid wasteand it was collected from the college campus and nearby areas. The compost bed was prepared by the number of layers with cow dung, kitchen waste and saw dust which are moist by*Effective Microorganisms (EM)*.

EM is a mixture of groups of organisms that has a reviving action on humans, animals and the natural environment [6]and has also been described as a multi-culture of coexisting anaerobic and aerobic beneficial microorganisms [7].*EM* is available in a dormant state which procured from a local vendorand requires activation before application. Activation involves the addition of water, jaggery and dormant *EM*as recommended by[8]. Within 30 days, the volume of compost bed has dropped substantially due to thermophillic process and white mould appeared on the biomass with a sweet smelling. At this point, the matured compost was collected, dried and sieved. This derived EM_{LC}can be used as an adsorbent.The prepared adsorbent was air dried for 24 hours and oven dried at a temperature of 70^0C for 2 hours and sieved.

Characterization of Adsorbent

The physico-chemical compositionof pH, moisture content, organic carbon, nitrogen, phosphorous and potassium for $EM_{LC}$was characterized and summarized inTable 1.The Morphological structure and surface characteristics of EM_{LC}before and after adsorption were determined, by Scanning Electron Microscopy (FESEM S-4700, Hitachi).

Adsorbate

Basic dye Malachite Green Oxalate was purchased from Merck Chemicals with a wavelength of 616 – 620 nm and the structure was shown in Figure 1. The dye was used as commercial salts without further purification.

TheMGstocksolution wasmadeup to aconcentration of 2000mg/L by dissolving an accurately weighed quantity of dye in deionized water andwassubsequentlydilutedtotherequiredconcentrations.The pH of working solutions were adjusted for the desired pH valuesby 0.1 M HCland 0.1 M NaOH.

Equilibrium studies

Batch mode adsorption studies of MG were carried out to optimize and investigate the effect of different parameters such as pH, adsorbate concentration, particle size of adsorbent and adsorbent dose. Batch equilibrium studies were carried outin 100 mL dye solutions, taken into250 mL Erlenmeyer flasks, of different initial concentrations (50–1000 mg/L) at pH 8 by adding fixed amount of sorbent and agitated at 150 rpm in an incubator orbital shaker (Technico) at 30^{0} C for desired time until equilibrium was reached. Later, the samples were centrifuged (Remi, R-8C) at 3500 rpm for 5 min and supernatant liquid was analyzed in UV visible spectrophotometer at 620 nm. The amount of dye adsorbed by the $EM_{LC}$was calculated from the following equation:

$$Q = V \times (C_0 - C_f)/M \quad (1)$$

where Q is the dye uptake (mg/g); V is the volume of dye solution (L); C_0 and C_f are the liquid phase concentrations of dye at initial and equilibrium (mg/L) respectively; and M is the mass of dry biosorbent used (g).Control experiments were done to evaluate the absorption of MG over the container walls with all optimized experimental conditions. It was observed that absorption on the container walls was negligible.

Results and Discussion

SEM study

Scanning Electron Microscopy (SEM) of EM_{LC} before and after adsorption were shown in Figures 2a and 2b. The presences of high number of pores and surface area with an irregular morphology of control $\mathrm{EM_{LC}}$ were observed from the Figure 2a. This morphology indicates the greater number of pores gives the greater biosorption of dye onto the biomass surface [9]. It was clear evident that the Figure 2b had different morphology from Figure 2a. This is due to occupation of Malachite Green on the pores of EM_{LC}. Thus, there is good possibility for the dye to be adsorbed on the surface of *EM* based Leaf waste compost.

Effect of solution pH

The effect of solution pH was investigated by agitating the 100 mL dye solution with initial dye concentration 100 mg/L in contact with the desired amount of adsorbent EM_{LC} at different pH from 2 to 9.Agitation wascarried out for 5h which is adequate to reachequilibrium with an agitation speed of 150 rpm. At equilibrium,the percentage removal of dye at different pH was measured and it waspresented in Figure 3.The binding of Malachite Green by $EM_{LC}$was found to be affected significantly by pH, with a maximum adsorption capacity being observed at pH 8.0. By the observation, the decolouration increases with the increase of pH from 2 to 8 as 9 % to 87.3 % respectively. The removal of MG decreased with decreasing pH is possible because the surface is positively charged.

Effect of Initial Dye Concentration

With the optimum solution pH8,the effect of initial dye concentration was varied from of 100 - 500 mg/L investigated and presented in Figure 4. By the observation, the decolouration decreases with the increase in dye concentration. The removal percentage at initial dye concentration 100 mg/Lwas 87.7 % and for 500 mg/Lwas 18.7%. The initial MG concentration was optimized as 100 mg/L. It can be explained by the fact that the initial concentration of dye had a restricted effect on dye removal capacity; simultaneously the adsorbent media had a limited number of active sites, which would have become saturated at a certain concentration [10].

Effect of Adsorbent Particle Size

With optimum pH, initial dye concentration and desired adsorbent dosage, the adsorbent particle size varies from 0.6 to 2.36 mm was examined and optimized which is shown in Figure 5. The optimum particle size was found as 1.18 mm with percentage removal 88.4. The increase in sorption depends on the large external surface area for small particles.

Effect of Adsorbent Dosage

The dose of adsorbent varied from 2 to 10 g/L was to evaluate the optimum dosage which was analyzed and presented in Figure 6. The maximum percentage removal was attained at 6 g/L because the uptake was decreased due to increase of adsorbent dosage. The percentage removal for 6 g/L of dosage was 89 and for 10 g/L was 82.9.Due to the increase of dosage, the particles tend to accumulate and the active sites in the adsorbent may decrease so that theremoval percentage was decreased.

Sorption Isotherm Modeling

The functional relationship between the adsorbate and adsorbent in constant temperature is given in sorption isotherm which is important in the design of an adsorption system.The five equilibrium isotherm models were used to fit the experimental data for adsorption of MG onto EM_{LC}. The isotherm models were as follows [11, 12]:

Freundlich model: $$Q = K_F C_f^{1/n} \tag{2}$$

Langmuir model: $$Q = \frac{Q_{\max} b C_f}{1 + b C_f} \tag{3}$$

Redlich-Peterson model: $$Q = \frac{K_{RP} C_f}{1 + a_{RP} C_f^{\beta_{RP}}} \tag{4}$$

Sips model: $$Q = \frac{K_S C_f^{\beta s}}{1 + a_S C_f^{\beta s}} \tag{5}$$

Tothmodel: $$Q = \frac{Q_{\max} b_T C_f}{[1 + (b_T C_f)^{1/n_T}]^{n_T}} \quad (6)$$

where K_F is the Freundlich constant (mg/g) $(L/mg)^{1/n}$, n is the Freundlich exponent,Q_{max} is the maximum dye uptake (mg/g), b is the Langmuir equilibrium constant (L/mg), K_{RP} is the Redlich-Peterson isotherm constant (L/g), a_{RP} is the Redlich-Peterson isotherm constant $(L/mg)^{1/\beta}$RP, β_{RP} is the Redlich-Peterson model exponent, KS is the Sips model isotherm coefficient (l/g)βS , a_S is the Sips model coefficient (l/mg)βS, β_S is the Sips model exponent. b_T is the Toth model constant (L/mg), and n_T is the Toth model exponent.All the model parameters were evaluated by non-linear regression using the Sigma Plot (Version 4.0, SPSS, USA) software.

The average percentage error between the experimental and predicted values was calculated using:

$$\% \, Error = \frac{\sum_{i=1}^{N} (Q_{exp,i} - Q_{cal,i}/Q_{exp,i})}{N} \times 100 \quad (7)$$

whereQ_{exp} and $Q_{cal}$are the experimental and calculated dye uptake valuesand N is the number of measurements.

The two parameter models of Freundlich and Langmuir isotherms based on equations 2 and 3 were plotted and the three parameter models of Redlich-Peterson, Sips and Toth isotherms were evaluated. The regression co-efficients and the fitted isotherm parameters are summarized in Table 2. The regression co-efficient (R^2)values were obtained as 0.99 for Freundlich model, 0.96 for Langmuir model and 0.97 for three parameter models of Redlich-Peterson, Sips and Toth isotherms.The calculated1/n value in the Freundlich isotherm was found to be 0.62 which is less than 1 indicates favourable adsorption.Based on the regression co-efficient and the attained theoretical maximum uptake, the Freundlich model fitted the equilibrium data very well compared to the other models. This proves that the dye molecules formed a multilayer coverage of the sorbent surface. A similar observation was reported for the dye adsorption onto activated carbons prepared from sawdust and rice husk [13].

Figure 7 described the equilibrium data of isotherm models and experimental data of Malachite Green and the obtained maximum uptake was 75.35 mg/g from Freundlich model.

Conclusion

- In this study, the sorption capacity of matured thermophillic *EM*based Leaf Waste Compost to remove Malachite Green from aqueous solution was investigated. EM_{LC} had exhibited the maximum MG uptake at optimum experimental conditions such as pH 8, initial dye concentration 100 mg/L, adsorbent particle size 1.18 mm and adsorbent dosage 6 g/L.
- EM_{LC} showed a maximum percentage dye removal of 85.7 and experimental uptake of 20.8 mg/g upon optimized experimental conditions.

- Two (Freundlich, Langmuir) and three (Redlich-Peterson, Sips, Toth) parameter biosorption isotherms were modeled using experimental data.
- Based on dye uptake,regression coefficient and 1/n value, the Freundlich model better described MG adsorption data.
- Since the Leaf waste used for preparing adsorbent was easily, plenty and locally available, the resulting sorbent is expected to be economically viable for removal of basic dye Malachite Green from aqueous solution.
- The adsorbent was prepared from the solid leaf waste which leads to the reduction of solid waste generation.

From this investigation, it wasconcluded that, *EM* based Leaf Waste Compost (EM_{LC}) can be successfully utilized as low cost, alternative, eco-friendly and effective biosorbent for the treatment of Malachite green dye bearing industrial wastewater.

Table 1: Physico-chemical composition of *EM* based Leaf waste Compost

Parameters	**Level**
pH	7.17
Moisture content	50 %
Organic Carbon	11.3 % by dry mass
Nitrogen	0.31 % by dry mass
C:N ratio	36
Phosphorous	0.59 % by dry mass
Potassium	0.5 % by dry mass

Table 2: Isotherm constants for MG adsorption on EM_{LC}

Isotherm Models	**Isotherm Constants, Regression Co-efficient and Percentage Error**				
Freundlich Isotherm		$\mathbf{K_F}$	**1/n**	$\mathbf{R^2}$	**% Error**
		2.18	0.62	0.99	13.5
Langmuir Isotherm		$\mathbf{q_m}$	**Ka**	$\mathbf{R^2}$	**% Error**
		20.37	0.0498	0.96	14.7
Redlich-Peterson model	$\mathbf{K_{rp}}$	$\mathbf{a_{RP}}$	$\mathbf{B_{rp}}$	$\mathbf{R^2}$	**% Error**
	0.9268	0.0492	0.9777	0.97	15.0
Sips Model	**Ks**	$\mathbf{a_S}$	**Bs**	$\mathbf{R^2}$	**% Error**
	1.3973	0.0612	0.8323	0.975	15.0
Toth Model	$\mathbf{Q_{max}}$	$\mathbf{b_T}$	$\mathbf{n_T}$	$\mathbf{R^2}$	**% Error**
	2.3799	0.0404	0.99	0.97	15.9

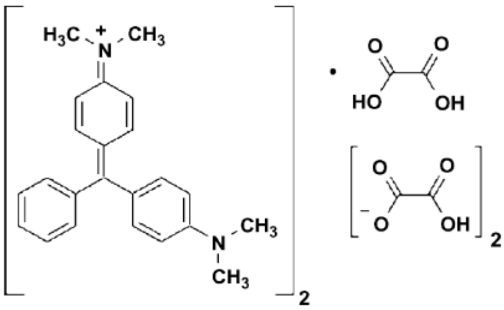

Figure 1: Structure of the MG Oxalate

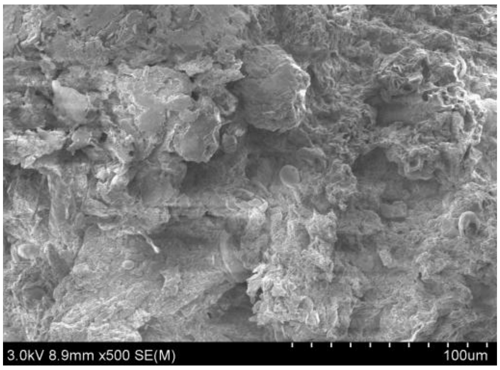

Figure 2a: SEM of *EM*$_{LC}$before adsorption

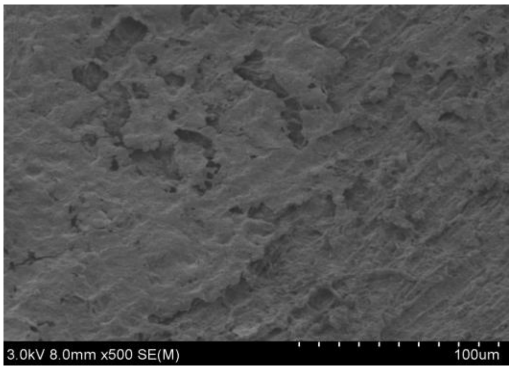

Figure 2b: SEM of *EM*$_{LC}$ after adsorption

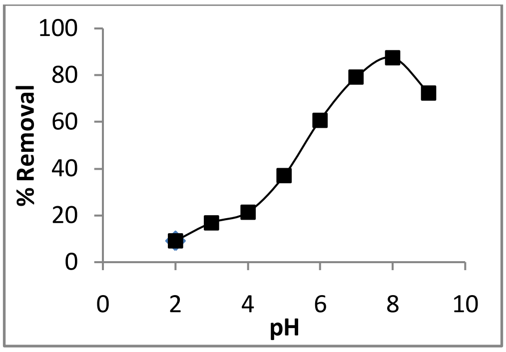

Figure 3: Effect of solution pH

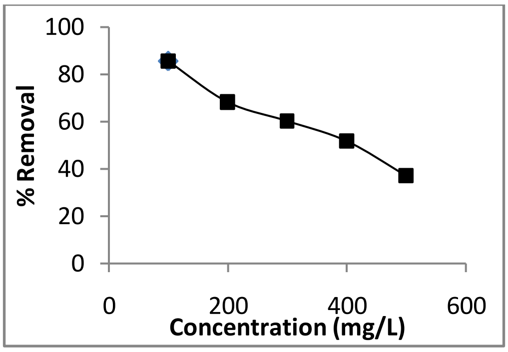

Figure 4: Effect of Initial Dye Concentration

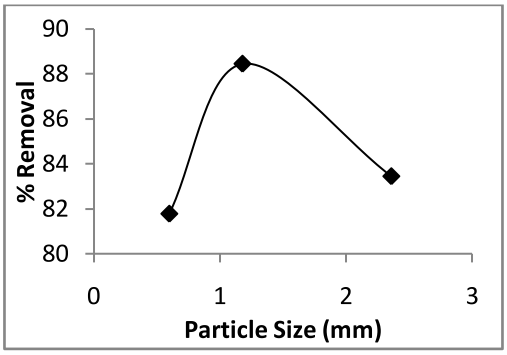

Figure 5: Effect of Adsorbent Particle Size

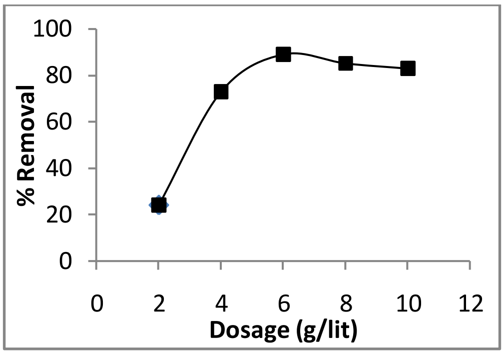

Figure 6: Effect of Adsorbent Dosage

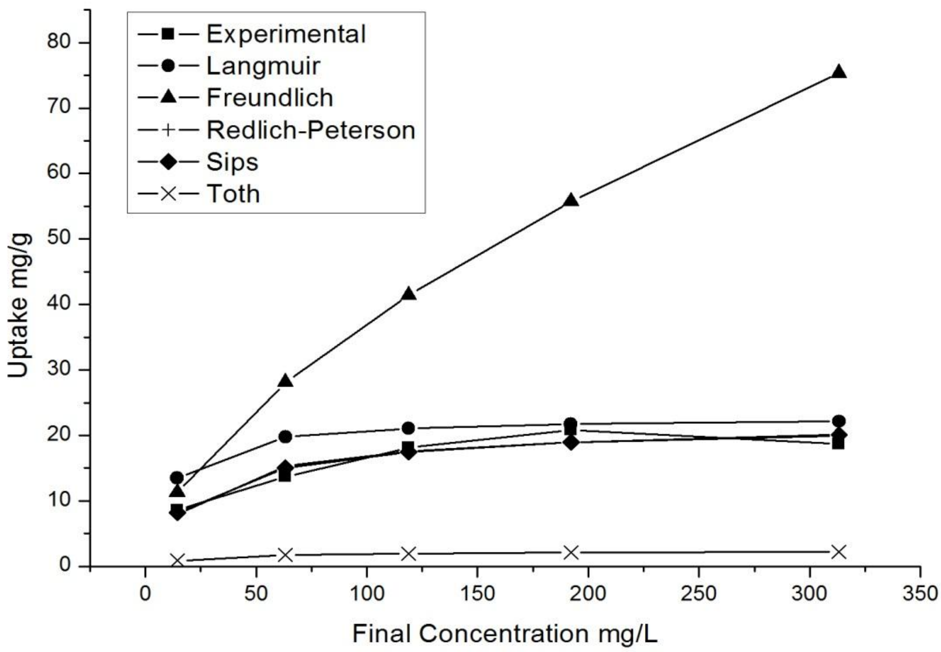

Figure 7: Isotherm plots for MG adsorption on EM_{LC}

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