Investigation on removal of malachite green using EM based compost as adsorbent

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1. Introduction

The textile industry releases the waste water into the natural streams and the environment which may contain more contaminants such as acids, bases, dissolved solids, toxic organic and inorganic compounds and colors. These toxic contaminants cause major hazards to the environment and living entity. Dyes and pigments present in wastewater have high visibility. Thus even minor release into the environment may cause the appearance of color which attracts the critical attention of public and local authorities. Also, usage of this stained water creates many diseases to the human being and animals. There are more than 100,000 commercial dyes exist and more than 7 million tons dye is used annually (McMullan et al., 2001; Pearce et al., 2003). A synthetic dye in wastewater can be removed by traditional methods like adsorption by (living or dead) microbial biomass and bioremediation systems are commonly applied to the treatment of industrial effluents, because many microorganisms such as bacteria, yeasts, algae and fungi are able to accumulate and degrade different pollutants (McMullan et al., 2001; Fu and Viraraghavan, 2001).

Malachite green (MG) is a basic (cationic) dye, which is water-soluble mainly applied to acrylic fibers, wool and silk. On the other hand, MG discharged into receiving water bodies, even at low concentrations, will affect the aquatic life and cause detrimental effects in liver, gill, kidney, intestine and gonads. In humans, it may cause irritation to the gastrointestinal tract upon ingestion. Also when contacted with skin causes irritation, redness and pain (Daneshvar et al., 2007).

Biological treatment is often the most economical alternatives to eradicate the dye in an industrial wastewater when compared with other physical and chemical processes. Biodegradation methods such as fungal decolorization, microbial degradation, adsorption by (living or dead) microbial biomass and bioremediation systems are commonly applied to the treatment of industrial effluents, because many microorganisms such as bacteria, yeasts, algae and fungi are able to accumulate and degrade different pollutants (McMullan et al., 2001; Fu and Viraraghavan, 2001).

Biosorption is a well-established technique for the removal of textile dyes (Chowdhury et al., 2011) from aqueous solution. A variety of materials are used as adsorbents for dyes and this include activated carbon, starch xanthate, alumina, low-grade
manganese ore, crushed coconut shell, fly ash, sawdust, rice husk carbon, wood charcoal, bituminous coal and lignite (Huseyin et al., 2008). The use of these waste materials for the purpose of wastewater treatment can play a significant role to solve the disposal problems. Numerous 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 (Reddy et al., 2012) from their aqueous solution.

Compost is a porous, solid matrix that is capable of adsorbing various organic and inorganic compounds (Devinny et al., 1994) and appears to be a feasible alternative to the activated carbon (EPA, 1998). Compost has been used as a filter medium to remove the pollutants from contaminated air streams for more than 20 years because of its high porosity, high adsorptive capacity and good moisture retention characteristics (EPA, 1998). Compost contains large amount of organic carbon and may be used to remove the pollutants from water and wastewater. Although some waste-derived compost does not meet the requirements for fertilizers, they can still be used as adsorbents (Ryziol-Komosińska et al., 2011).

This study was aimed to investigate the possibility of Effective Microorganisms based compost (EMKC), which was prepared from the kitchen solid waste, as a non-conventional low cost adsorbent in the removal of MG from aqueous solution. To the best of our knowledge, this study is the first attempt on EM based Kitchen waste Compost (EMKC) onto biosorption process.

2. Materials and methods

2.1. Adsorbent

Compost was prepared from kitchen solid waste which was collected from the college hostel pantry and canteen. The compost bed was prepared by the number of layers with cow dung, kitchen waste and saw dust, which are sprayed by Effective Microorganisms.

Effective Microorganisms (EM) is a mixture of several organisms that has a reviving action on humans, animals and the natural environment (Higa, 1995) and has also been described as a multiculture of coexisting anaerobic and aerobic beneficial microorganisms (E.M. Trading, 2000). EM in a dormant state was procured from a local vendor and was activated before application. Activation involves the addition of water and jaggery to the dormant EM as recommended by Sekaran et al. (2005). Within 30 days, the volume of compost bed was dropped substantially due to thermophilic process and white mold appeared on the biomass with a sweet smelling. At this point, the matured compost was collected and dried. The prepared adsorbent (EMKC) was air dried for 24 h and oven dried at a temperature of 70 °C for 2 h and sieved to different particle sizes.

2.2. Characterization of adsorbent

The physico-chemical composition of EMKC was characterized. The pH of adsorbent was measured using a pH meter (Ecosan, EUTECH Instruments), moisture content through oven dry method, organic carbon by Walkley and Black titration method (Walkley and Black, 1934), nitrogen and phosphorous by a UV–visible spectrophotometer (Merck, Spectroquant Phara 300) and potassium by a digital flame photometer. Fourier transform infra-red spectra of the EMKC samples were obtained using a Perkin-Elmer Paragon 500 FTIR. The sample, prepared as KBr disc, was examined within the range 400–4000 cm⁻¹ to identify the specific functional groups responsible for the biosorption. To determine the morphological structure and surface characteristics of EMKC and MG-loaded EMKC, the samples were coated under vacuum with a thin layer of gold and examined by scanning electron microscopy (FESEM, Hitachi).

2.3. Adsorbate

Malachite green oxalate (C.I. = 42,000; molecular formula=C₃₂H₅₄N₄O₁₂; and molecular weight=927.01 g/mol) was purchased from Merck Chemicals. The dye was used in experiments without further purification.

The MG stock solution was made up to a concentration of 2000 mg/L by dissolving an accurately weighed quantity of dye in deionized water and was subsequently diluted to the required concentrations. The pH of working solutions was adjusted to the desired pH values by 0.1 M HCl and 0.1 M NaOH.

2.4. Equilibrium studies

Batch mode adsorption studies of MG were carried out to optimize and investigate the effect of different parameters such as pH, contact time, adsorbate concentration, adsorbent particle size and adsorbent dose. Batch equilibrium studies were carried out in 100 mL dye solutions, taken into 250 mL Erlenmeyer flasks, of different initial concentrations (50–1000 mg/L) at pH 8 by adding fixed amount of sorbent. The contents of the flask were agitated at 150 rpm in an incubator orbital shaker (Technico) at 30 °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 the UV visible spectrophotometer at 620 nm. The amount of dye adsorbed by the EMKC is calculated from the following equation:

\[ Q = V \times \left( C_0 - C_f \right) / M \]  

(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.

2.5. Isotherm and kinetic study

Five equilibrium isotherm models were used to fit the experimental data for adsorption of MG onto EMKC and can be represented as follows (Huseyin et al., 2008; Langmuir, 1916; Jiang et al., 2013a, 2013b):

Freundlich model: \[ Q = K_f \cdot C_f^{1/n} \]  

(2)

Langmuir model: \[ Q = Q_{\text{max}} \cdot b \cdot C_f / (1 + b \cdot C_f) \]  

(3)

Redlich–Peterson model: \[ Q = \frac{K_{RP} \cdot C_f}{1 + a_{RP} \cdot C_f^{1/nf}} \]  

(4)

Sips model: \[ Q = \frac{K_s \cdot C_f^{n_s}}{1 + \alpha_s \cdot C_f^{n_s}} \]  

(5)

Toth model: \[ Q = \frac{Q_{\text{max}} \cdot b \cdot C_f}{(1 + (b \cdot C_f)^{1/\mu})^{\mu}} \]  

(6)

where \( K_f \) is the Freundlich constant (mg/g) (L/mg)¹/n, \( n \) is the Freundlich exponent, \( Q_{\text{max}} \) is the maximum dye uptake (mg/g), \( b \) is
the Langmuir equilibrium constant (L/mg), \( K_L \) is the Redlich–Peterson isotherm constant (L/g), \( q_0 \) is the Redlich–Peterson isotherm constant (L/mg)\( \beta \), \( \beta_L \) is the Redlich–Peterson model exponent, \( K_2 \) is the Sips model isotherm coefficient (L/g)\( \beta_2 \), \( a_s \) is the Sips model coefficient (L/mg), \( b_L \) is the Sips model exponent, \( b_2 \) 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 is calculated using

\[
% \text{Error} = \frac{\sum_{i=1}^{N} (Q_{\text{exp},i} - Q_{\text{cal},i}/Q_{\text{exp},i})}{N} \times 100
\]

where \( Q_{\text{exp}} \) and \( Q_{\text{cal}} \) are the experimental and calculated dye uptake values and \( N \) is the number of measurements.

In order to analyze the adsorption kinetics during MG removal, the pseudo-first and second-order kinetic models were used. The linear forms of kinetic models are as follows (Ho and McKay, 1998):

Pseudo-first order model:

\[
\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t
\]

Pseudo-second order model:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t
\]

where \( q_e \) is the amount of dye sorbed at equilibrium (mg/g), \( q_t \) is the amount of dye sorbed at time \( t \) (mg/g), \( k_1 \) is the pseudo-first order rate constant (1/min) and \( k_2 \) is the pseudo-second order rate constant (g/mg min). All the model parameters were evaluated by non-linear regression using Sigma Plot (version 4.0, SPSS, USA) software.

3. Results and discussion

3.1. FT-IR study

The Fourier transform infra-red (FT-IR) spectrum of \( EM_{KC} \) is shown in Fig. 1. The spectrum showed specific peaks in fingerprint region (500–1500 cm\(^{-1}\)) for the mono-substituted and para-disubstituted benzene rings which refers to the peak at 1585 cm\(^{-1}\) for the C=C stretching of the benzene rings. Also, the peak at 1130 cm\(^{-1}\) could be attributed to aromatic C–N stretching vibrations. Peak at 2870 cm\(^{-1}\) confirmed the presence of C–H asymmetric stretching vibrations. Similar peaks were observed during adsorption of methylene blue onto activated carbon (Ho et al., 2009) and during degradation of dimethyl phthalate (Jiang et al., 2013a, 2013b). The peak at 725 cm\(^{-1}\) indicates symmetric out of plane bending of the ring hydrogen. These bands were clear evidence that MG was adsorbed by the adsorbent \( EM_{KC} \).

3.2. SEM study

Scanning electron microscopy (SEM) analyses of \( EM_{KC} \) before and after MG adsorption are illustrated in Fig. 2. The surface area with an irregular morphology as well as a high number of pores can be visualized from SEM image of \( EM_{KC} \) before adsorption. This morphology can corroborate to high cation exchange capacity values, such as those obtained, due to the high number of sites for dye adsorption (Pereira and Arruda, 2003). The greater number of pores generally increases biosorption of dye onto the biomass surface (Uzun, 2006). Fig. 2 clearly illustrates the difference in morphology of before and after adsorption of MG. This is due to occupation of MG onto the pores of \( EM_{KC} \).

3.3. Effect of solution pH

The effect of solution pH was investigated by agitating 100 mg/ L of 100 mL MG solution with the desired amount of adsorbent \( EM_{KC} \) at different pH from 2 to 9. At equilibrium, the percentage removal of dye and uptake at different pH was estimated. The binding of MG by \( EM_{KC} \) was found to be affected significantly by pH, with a maximum adsorption capacity being observed at pH 8.0 with recorded uptake of 23.8 mg/g. According to the results, the dye removal efficiency of \( EM_{KC} \) increases from 49.0% to 95.1% with the increase of pH from 2 to 8. Lower removal percentage of MG by \( EM_{KC} \) at low pH conditions may be due to presence of excess H\(^+\) ions in the solution. At these acidic pH conditions, the functional groups on the surface of \( EM_{KC} \) will be protonated by H\(^+\) ions and thus the overall charge of the biomass will be positive. On the other hand, basic dyes release colored positively charged dye ions in solution. Since the overall charge of the biomass at strong acidic conditions is positive, the electrostatic attraction of MG is less and hence relatively lower uptake was observed. This aspect can also be verified by pH of the point of zero charge (pH\(_{pzc}\)), which was determined according to powder addition method (Jirekar et al., 2014) and was found to be 6.4 for \( EM_{KC} \). At pH < pH\(_{pzc}\), the adsorbent surface becomes positively charged (Stumm and Morgan, 1996). At higher solution pH i.e., pH > pH\(_{pzc}\), the overall surface charge of the adsorbent turn negatively charged, which enhances binding of positively charged MG through electrostatic forces of attraction (See et al., 2012).

3.4. Effect of initial dye concentration

The optimum solution pH 8 was used to investigate the effect of initial dye concentration. The initial dye concentration was varied from 50 to 1000 mg/L with fixed amount of adsorbent dosage. According to the results, the MG removal efficiency of \( EM_{KC} \) decreases (96.8–66.3%) whereas the amount sorbed was increased (12.11–136.6 mg/g) with the increase in dye concentration (50–1000 mg/L). A higher initial dye concentration was identified to have a higher driving force for transporting cations from ambient liquid to the cell surface, resulting in a faster sequestration and higher adsorption capacity (Saeed, 2013). However, the binding sites on the surface of \( EM_{KC} \) may be fewer compared to the moles of dye at high initial concentration, which affected percentage removal.

![Fig. 1. FT-IR spectrum of \( EM_{KC} \) loaded with MG.](image-url)
3.5. Effect of adsorbent particle size

The effect of EMKC size on MG biosorption was studied at fixed pH of 8 and 100 mg/L initial MG concentration. Several sizes of EMKC were used, which include 0.6, 1.18 and 2.36 mm. From the results, MG biosorption capacity increased by decreasing the particle size of EMKC. This variation may be due to the larger external surface area for biosorption as EMKC particles became smaller. The larger surface area to volume ratios of EMKC particles would increase the availability of exterior surface for MG binding and enhance dye uptake capacity. Although the smallest particle size (0.6 mm) resulted in slightly better MG biosorption performance compared to 1.18 mm particles, its increase in uptake was less than 0.6% compared to 1.18 mm particles. It is also desirable to use rigid and relatively big particles in continuous sorption processes as it can tolerate extreme operating conditions (Vijayaraghavan et al., 2006). Considering these aspects, EMKC particle size (1.18 mm) was selected for further experiments.

3.6. Effect of adsorbent dosage

To investigate the optimum dosage, the dose of adsorbent was varied from 2 to 12 g/L at fixed pH (8), initial dye concentration (100 mg/L) and adsorbent particle size (1.18 mm). From the analysis of experimental data, it was observed that the MG removal efficiency increased with increase in EMKC dosage. The percentage biosorption increased from 76.22% at lower biosorbent dosage (2 g/L) to 95.67% at higher biosorbent dosage (4 g/L). Further increase in EMKC dosage had no influence on percent removal. On the other hand, the MG uptake capacity of the EMKC was found to have reduced from 23.92 mg/g at low biosorbent dosage (4 g/L) to 8.25 mg/g at high biosorbent dosage (12 g/L). An increase in sorbent concentration generally increases the bounded dye molecules because of an increase in surface area of the sorbent, which in turn increases the binding sites. In contrary, the dye uptake decreases by increasing the EMKC dosage and this may be due to complex interactions of several factors. The important factors being at high sorbent dosages the available dye molecules are insufficient to cover all the exchangeable sites on the biosorbent, usually resulting in low dye uptake (Aksu and Çağatay, 2006). Thus, for the present study, 4 g/L was selected as optimum EMKC dosage.

<table>
<thead>
<tr>
<th>Isotherm Models</th>
<th>Isotherm Constants, Regression Co-efficient and Percentage Error</th>
</tr>
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<tbody>
<tr>
<td>Freundlich</td>
<td>( K_F ) ( 1/n ) ( R^2 ) % Error</td>
</tr>
<tr>
<td>Langmuir</td>
<td>( q_m ) ( K_a ) ( R^2 ) % Error</td>
</tr>
<tr>
<td>Redlich-Peterson</td>
<td>( KRp ) ( \alpha_R ) ( \beta_R ) ( R^2 ) % Error</td>
</tr>
<tr>
<td>Sips</td>
<td>( Ks ) ( a_s ) ( b_s ) ( R^2 ) % Error</td>
</tr>
<tr>
<td>Toth</td>
<td>( Q_{max} ) ( b_T ) ( n_T ) ( R^2 ) % Error</td>
</tr>
</tbody>
</table>

Table 1. Isotherm constants for MG adsorption on EMKC.
3.7. Sorption isotherm modeling

In the design of an adsorption system, the sorption isotherm is important to evaluate functional relationship between adsorbent and adsorbate at constant temperature. The model constants along with regression coefficients for all five isotherm models examined are summarized in Table 1.

The calculated 1/n value in the Freundlich isotherm was found to be 0.33 which is less than 1, indicating favorable adsorption. 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 (Malik, 2003). In the Redlich–Peterson model, the constant $\beta_0$ observed as maximum compared to the Sips model constant $\beta_p$. Based on the high regression coefficient and low percentage error, the Sips model fitted the equilibrium data very well compared to the other models. Fig. 3 shows MG equilibrium isotherm curves as predicted by five isotherm models.

3.8. Kinetic studies

To understand the reaction pathways and the sorption mechanism, the extrapolation of batch kinetic data is necessary for the design of columns in the treatment of industrial effluents. The investigation on the mechanism of adsorption and potential rate controlling steps like chemical reaction and mass transfer are used to test the experimental data.

The experimental kinetic curves along with kinetic data as predicted by pseudo-first and second-order kinetic models during MG biosorption onto EMKC at various initial dye concentrations are presented in Fig. 4. Results revealed that rate of MG biosorption by EMKC were fast with time for equilibrium attainment increased with increasing dye concentration. It is also worth noting that the increase in initial dye concentrations enhanced dye uptake and decreased percentage dye removal. This is because at lower concentration, the ratio of the initial moles of dye molecules to the available surface area is low and subsequently the fractional sorption becomes independent of initial concentration. However, at higher concentration the available sites of sorption became fewer compared to the moles of dye present and hence the percentage dye removal is dependent upon the initial dye concentration (Padmesh et al., 2005).

The kinetic data of MG onto EMKC has been examined using the pseudo-first and second-order kinetic models. The corresponding model constants along with regression coefficient and percentage error values are presented in Table 2. The values of $R^2$ for pseudo-first order were above 0.90 with % error values less than 22.69. The model is able to predict uptake values reasonably close to that of experimental values. In contrary, pseudo-second order model predicts the sorption behavior over the whole range of studies with higher regression coefficient and it is in agreement with a chemisorption mechanism being the rate controlling step.

However, several authors observed the tendency of the model to over-predict the equilibrium uptake values (Ofomaja et al., 2010; Vijayaraghavan and Balasubramanian, 2012). The rate constant ($k_2$) decreased when the initial MG concentration increased.

### 4. Conclusion

In this study, the sorption capacity of matured and thermophilic EMKC to remove MG from aqueous solution was investigated.

- EMKC had exhibited the maximum MG uptake at optimum experimental conditions of pH 8, initial dye concentration 1000 mg/L, adsorbent particle size 1.18 mm and adsorbent dosage 4 g/L.
- EMKC showed a maximum percentage dye removal of 95.7% and experimental uptake of 159.22 mg/g upon optimized experimental conditions.
- Two parameter models (the Freundlich and Langmuir) and three parameter models (Redlich–Peterson, Sips and Toth) were used to describe MG isotherm data. Based on the regression coefficient and percentage error, the Sips model fitted better for the experimental data compared to the other models.
- The kinetic models of pseudo-first and second-order models were used to evaluate experimental MG kinetics data at different MG concentrations. From the predicted uptakes and $R^2$ values, the pseudo-second-order model fitted well for the obtained experimental data.
- Considering that kitchen wastes can be easily procured at low cost and the developed biosorbent is expected to be economically viable for removal of basic dyes from aqueous solution.

From this investigation, it was concluded that, EM based Kitchen waste compost (EMKC) can be successfully utilized as low cost, alternative, eco-friendly and effective biosorbent for the treatment of dye-bearing industrial wastewater.

### Appendix A. Suplementary information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ecoenv.2015.04.033.

### References

