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Removal of Malachite Green using *Polyalthia longifolia* Seeds an Effective Biosorbent

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Abstract

Removal of Malachite Green from aqueous solution is carried out using carbonized material prepared from seeds of *Polyalthia longifolia* commonly called as Ashoka. Batch adsorption study has been carried out to investigate the effect of various parameters such as, amount of biosorbent, concentration and time, temperature and pH. It is observed that the dye removal efficiency and adsorption capacity depends upon amount of biosorbent, time of agitation and concentration, temperature, pH of solution. Equilibrium data is evaluated using Freundlich and Langmuir adsorption isotherms.

Keywords: Malachite Green, Plolyalthia longifolia seeds , Carbonized Material, Biosorption.

Introduction

A large number of chemicals are found in the environment containing toxic substances. With rapid increase in population and growth of industrialization in the country, quality of both surface and ground water changes day by day. Ground water contains dissolved minerals from the soil layers from which it passes. The surface water is contaminated with run off water from agricultural fields, containing pesticides, fertilizers, and soil particles, waste chemicals from industries and domestic waste from urban and rural areas.

The optimum value for good water quality is 4-6 mg/L of DO, which is required for healthy aquatic life in water. Lower DO values indicate water pollution (Environmental Chemistry). These decrease the normal water for public water supply, aquatic and wild life, agriculture and industry. If the water is to be reused, it must be purified. In recent years a general environmental awareness has developed that is related to the actual knowledge and control of water pollution.

Different methods are available for the removal of pollutants from waste water. Effluent is usually treated by either physical or chemical processes includes, ion exchange, membrane filtration, electrochemical destruction, irradiation and ozonation. However, these processes are very expensive and could not be effectively used to treat the wide range of pollutants. The convectional biological treatment process is not very effective in treating a wastewater, due to low biodegradation of dyes.

The process of adsorption has an edge over the other methods. It is potential alternative to conventional treatment techniques for the removal of pollutants from the contaminated effluent even from the diluted solution. Adsorption is operative in most natural physical, biological, chemical system. It is widely used in industrial applications due to its sludge free clean operation, its simplicity of design, high removal capacity and ease of operation at large scale.

Activated carbon is the most widely used adsorbent as it shows excellent adsorption efficiency. The high adsorption capacity of activated carbon is associated with internal porosity and other properties such as, high surface area, pore volume, and pore size distribution. However regeneration and reuse of activated carbon makes it more costly therefore its use as adsorbent is restricted. An attempt has been made to develop cheaper and effective adsorbents from low-cost waste material. In this situation, natural raw materials are a possible biosorbents that could provide a successful solution. Evaluation of waste biomass as adsorbent is getting increased all over the world as it is renewable, widely available, cheap, environmental friendly and presence of surface functional groups. Potentially less expensive than other materials to manufacture a variety of adsorbents.

There are two basic processes to activate carbon materials; physical and chemical. Physical activation involves two steps, carbonization and activation. The precursor is developed into activated carbons using gases under heat treatment. Chemical activation can be accomplished in a single step by carrying out thermal decomposition of raw material with chemical reagents. Chemical activation processes have been carried out with acidic reagents i.e.$ZnCl_2$, H_3PO_4, HCl and H_2SO_4 and or with basic reagents KOH and K_2CO_3, NaOH and Na_2CO_3. This part highlights the necessity of cost effective biosorbents for the removal of pollutants. The activated carbon has been produced from variety of biomass by thermo chemical conversion i.e. coir pith carbon (Kavitha and Namasivayam 2007), Aloe vera carbon (Gopal and Elango 2007), Posidonia oceanica (L.) (Mohamed Chaker Ncibi *et al.,* 2006)**,** coconut husk (Tan *et al.*, 2008), jackfruit (artocarpus heterophyllus) Peel Waste (Devarly PRAHAS *et al*., 2008)**,** Ulva lactuca and Sargassum (Hajira Tahir *et al*., 2008), Jackfruit (Artocarpus heterophyllus) leaf powder (Tamez Uddin *et al., 2009*), mansonia wood sawdust(Agustine 2009), activated carbon developed from orange peel (Ahmed El Nemr*et al.,* 2009)**,** chemical treated empty fruit bunch (Saad *et al.,* 2007) and brevery waste (Jaikumar 2009).

Malachite Green (MG) is extensively used in various industries. It is found to be hazardous and known for its cytotoxic, genotoxic and carcinogenic potential. (Fessard *et al.,* 1999; Doerge *et al.,* 1998b). *Polyalthia longifolia* seeds are easily available , a garden waste and has no food value. In the present work an attempt has been made to investigate the adsorption potential of Carbonozed Material (CM) prepared from seeds of the said plant for the removal of MG.

Material and Methods

Preparation of Carbonized Material (CM)

The carbonization of dried seeds was done in absence of air in an air tight bottle, till the constant weight is obtained. The seeds were then ground and sieved to obtained uniform particle size of 0.063 mm. The carbonized material was stored in an air tight bottle and named as Carbonized Material, ‘CM’.

Fourier-Transform Infra - red (FT-IR) analysis

FT-IR analysis was performed in order to characterize the functional groups of the adsorbent (CM). A Perkin –Elmer spectrum RX/FT-IR system was used for spectral analysis.

Scanning Electron Microscope (SEM) analysis

The morphology of prepared adsorbent was studied using scanning electron micrograph for analyzing micro and macropores present on the surface of adsorbents. The scanning electron micrograph of adsorbent (CM) (0.063mm size) was obtained using Scanning Electron Microscope (Model Leica-Stereoscan-440).

Experimental procedure

Optimization of process parameters and the effect of, adsorbent dose, initial concentration and contact time, temperature and pH on adsorption are assessed by performing batch mode adsorption experiments. Appropriate amounts of sorbents are added and the solution is stirred using magnetic stirrer at 200 rpm. The solutions, after adsorption are filtered using Whatman filter paper No. 42. The absorbance is measured on colorimeter at 620 nm before and after adsorption to evaluate the initial concentration (C_0) and equilibrium concentration (C_e) of methylene blue. The pH of original MB solution is between 7.0 to 8.0 and it is not adjusted in other experiments except effect of pH.

Analytical Method

The amount of dye adsorbed is calculated in percentage (%) as,

$$\% \text{ Adsorption} = (C_0 - C_e) / C_0 \times 100 \qquad (1)$$

Adsorption capacity (q_e) is calculated from the mass balance equation as follows:

$$q_e = (C_0 - C_e) V / 1000 \times w \qquad (2)$$

Where, q_e is the quantity of dye uptake by biosorbent (mg/g) at equilibrium

C_0 is the initial concentration (mgL^{-1}) of dye.

C_e is the concentration of dye after sorption at equilibrium (mgL^{-1})

V is the volume of dye solution (ml);

W is the mass of adsorbent (g.)

Adsorption Isotherms

The linearized Freundlich isotherm is represented as,

$$\log q_e = \log K_F + (1/n) \log C_e \qquad (3)$$

The Freundlich isotherm is obtained by plotting log q_e vs. log $C_{e.}$.

The Langmuir equation is used in the linearized form (4)

$$C_e / q_e = 1/(Q_0 b) + C_e/Q_0 \qquad (4)$$

The Langmuir isotherm is obtained by plotting Ce/ qe vs. Ce

Results and Discussion

The IR spectrum of carbonized material (CM) (Figure **1**) shows a peak at 3643 cm^{-1}which indicates the presence of free –OH groups and a broad peak at 3417 cm^{-1} shows associated –OH groups. The presence of weak peak at 3057 cm^{-1} is due to aromatic C-H stretching. A peak at 2881 cm^{-1} manifests -C-H stretching of saturated alkane. The peak at 1766 cm^{-1} explains the presence of carbonyl group of cyclic ester. The peaks at 1591 and 1497 cm^{-1} confirms the presence of aromatic ring. The presence of peaks at 1380, 1128 and 1080 cm^{-1} point to the presence of – O –C = O acyl oxygen and etherial linkages of ester function in addition to the carbonyl and the carboxylate groups present on the material. Adsorption of

Malachite Green on CM may be due to presence of these groups. Scanning electron microscope analysis (Figure 2) indicates presence of porous structure of CM.

Eguilibrium data was evaluated using Freundlich (Figure 3) and Langmuir (Figure 4) isotherms. High value of correlation coefficient, $R^2 = 0.992$, indicates Langmuir isotherm is suitable for experimental data. Effect of various parameters was studied and the results were recorded. Table 1, depicts the effect of amount of adsorbent on removal of MG for various concentrations. It was observed that as the amount of CM is increased from 1 to 5 g L^{-1}, the percentage removal of MG increased from 69.38 % to 91.83 % at C_0 = 10 mgL^{-1} of MG, however above 4.0 gL^{-1} dose no significant increase in the removal was observed. Similar effect of adsorbent dose is observed for all initial concentrations (C_0) studied. The adsorption capacity (mg/g) decreases from 1 to 5 g L^{-1} dose for all studied initial concentrations as indicated in Table 2 Increase in adsorbent dose, increases surface area and availability of more adsorption sites, results in increase in the removal of dye. It was observed that as the agitation time increases (60 min.) percent removal and adsorption capacity increases for all initial concentrations (Table 3 & 4) thereafter it remains constant. This may be due to higher rate of adsorption at low concentration.

As the temperature increases removal efficiency (Table 5) and adsorption capacity (Table 6) initially increases and thereafter remains constant at given concentration. As the temperature increases driving force increases, more sites are available for the binding of molecules, results in increases in a removal efficiency and adsorption capacity. It was also observed that as the pH increases from 2 to 10, the percent adsorption (Table 7) and adsorption capacity (Table 8) increases for the studied initial concentration. This is because cationic dye interacts with OH^- ions in solution at higher pH. Acidic condition produces more H^+ ions in the system and the surface of the adsorbent have positive charge which prevent the adsorption of MG^+ ions onto adsorbent surface due to electrostatic repulsion between H^+ ions and MG^+ ions .

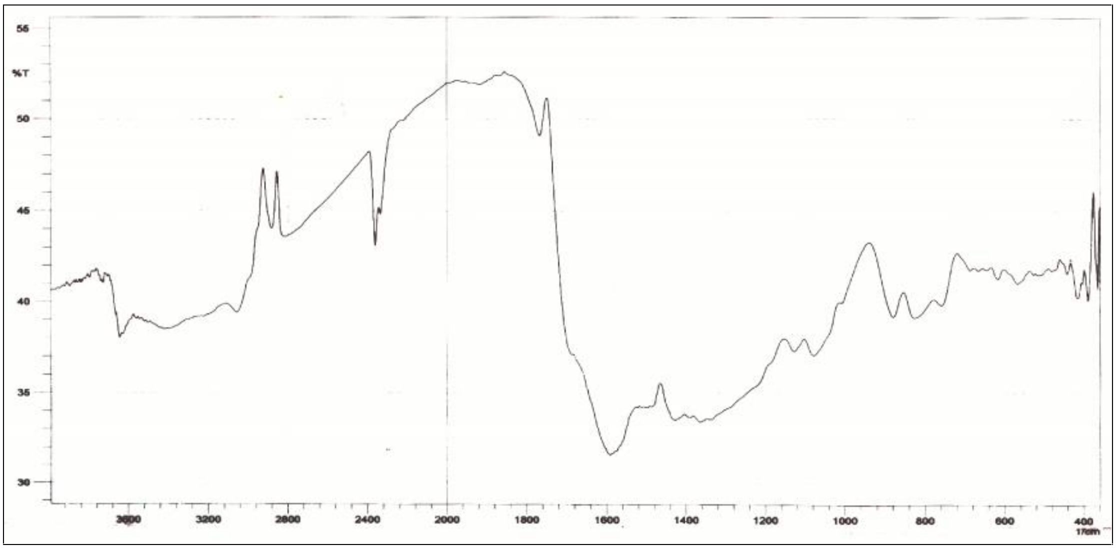

Figure 1. FT - IR spectrum of CM

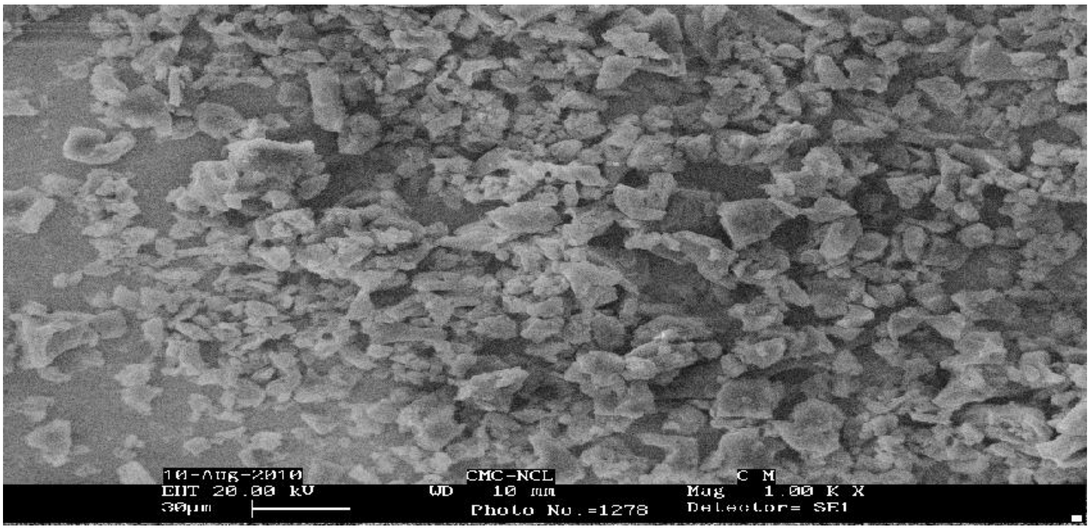

Figure 2. SEM of CM

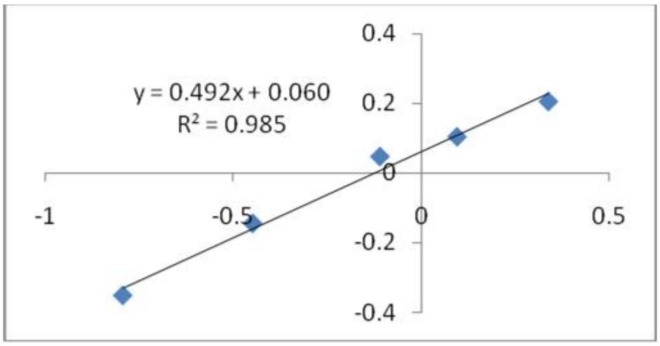

Figure 3. Freundlich Adsorption Isotherm (Plot of log x/m vs. log Ce) for Malachite Green

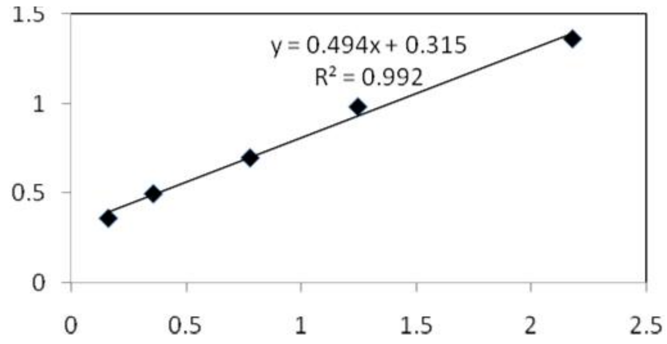

Figure 4. Langmuir Adsorption Isotherm (Plot of Ce vs. Ce/q) for Malachite Green

Table 1: Effect of adsorbent dose on the percent removal of MG using CM

(Contact time = 30 minutes, Temp. = 25 ± 2^0C)

Amount of Adsorbent (g)	10 mg / L	20 mg / L	30 mg / L
	% Adsorption	% Adsorption	% Adsorption
0.05	69.3877551	27.94117647	30.26315789
0.1	87.75510204	60.29411765	51.31578947
0.15	89.79591837	77.94117647	56.57894737
0.2	91.83673469	82.35294118	75.00
0.25	91.83673469	82.35294118	76.31578947

Table 2: Effect of adsorbent dose on the adsorption capacity of MG using CM

(Contact time = 30 minutes, Temp. = 25 ± 2^0C)

Amount of Adsorbent (g)	10 mg / L	20 mg / L	30 mg / L
	Adsorption Capacity (mg/g)	Adsorption Capacity (mg/g)	Adsorption Capacity (mg/g)
0.05	6.93877551	5.588235294	9.078947368
0.1	4.387755102	6.029411765	7.697368421
0.15	2.993197279	5.196078431	5.657894737
0.2	2.295918367	4.117647059	5.625
0.25	1.836734694	3.294117647	4.578947368

Table 3: Effect of initial concentration and contact time on percent removal of MG using CM (Temp. = 25±2^{0}C, Adsorbent dose = 4 g L^{-1})

Time (min.)	10 mg / L	20 mg / L	30 mg /L
	% Adsorption	% Adsorption	% Adsorption
1	75.51020408	67.64705882	43.42105263
5	83.67346939	73.52941176	57.89473684
10	89.79591837	79.41176471	67.10526316
20	91.83673469	85.29411765	73.68421053
30	91.83673469	86.76470588	76.31578947
60	93.87755102	88.23529412	77.63157895
120	93.87755102	88.23529412	82.89473684
180	93.87755102	88.23529412	82.89473684

Table 4: Effect of initial concentration and contact time on adsorption capacity of MG using CM (Temp. = 25±2^{0}C, Adsorbent dose = 4 g L^{-1})

Time (min.)	10 mg / L	20 mg / L	30 mg /L
	Adsorption capacity (mg/g)	Adsorption capacity (mg/g)	Adsorption capacity (mg/g)
1	1.887755102	3.382352941	3.256578947
5	2.091836735	3.676470588	4.342105263
10	2.244897959	3.970588235	5.032894737
20	2.295918367	4.264705882	5.526315789
30	2.295918367	4.338235294	5.723684211
60	2.346938776	4.411764706	5.822368421
120	2.346938776	4.411764706	6.217105263
180	2.346938776	4.411764706	6.217105263

Table 5: Effect of temperature on percent removal of MG using CM
($C_0 = 30$ mgL^{-1}; Adsorbent dose = 4 gL^{-1})

Time (min.)	25 ± 2^0C	35 ± 2^0C	45 ± 2^0C
	% adsorption	% adsorption	% adsorption
1	43.42105263	52.63157895	64.47368421
5	57.89473684	60.52631579	77.63157895
10	67.10526316	71.05263158	80.26315789
20	73.68421053	76.31578947	85.52631579
30	76.31578947	78.94736842	93.42105263
60	77.63157895	80.26315789	93.42105263
120	82.89473684	85.52631579	93.42105263
180	82.89473684	85.52631579	93.42105263

Table 6: Effect of temperature on adsorption capacity of MG using CM
($C_0 = 30$ mgL^{-1}; Adsorbent dose = 4 gL^{-1})

Time (min.)	25 ± 2^0C	35 ± 2^0C	45 ± 2^0C
	adsorption capacity (mg/g)	adsorption capacity (mg/g)	adsorption capacity (mg/g)
1	3.256578947	3.947368421	4.835526316
5	4.342105263	4.539473684	5.822368421
10	5.032894737	5.328947368	6.019736842
20	5.526315789	5.723684211	6.414473684
30	5.723684211	5.921052632	7.006578947
60	5.822368421	6.019736842	7.006578947
120	6.217105263	6.414473684	7.006578947
180	6.217105263	6.414473684	7.006578947

Table 7 : Effect of pH on percent removal of MG using CM
($C_{0.}$ = 30 mgL^{-1}; Adsorbent dose = 4 $gL^{-1,}$ Temp. = 25 ± 2^0C)

Time (min.)	pH 2	pH 4	pH 8	pH 10
	% adsorption	% adsorption	% adsorption	% adsorption
1	14.47368421	26.31578947	27.63157895	55.26315789
5	17.10526316	47.36842105	48.68421053	76.31578947
10	27.63157895	63.15789474	57.89473684	78.94736842
20	34.21052632	67.10526316	60.52631579	81.57894737
30	38.15789474	72.36842105	77.63157895	84.21052632
60	39.47368421	76.31578947	77.63157895	84.21052632

Table 8 : Effect of pH on adsorption capacity of MG using CM
($C_{0.}$ = 30 mgL^{-1}; Adsorbent dose = 4 $gL^{-1,}$ Temp. = 25 ± 2^0C)

Time (min.)	pH 2	pH 4	pH 8	pH 10
	adsorption capacity (mg/g)	adsorption capacity (mg/g)	adsorption capacity (mg/g)	adsorption capacity (mg/g)
1	1.085526316	1.973684211	2.072368421	4.144736842
5	1.282894737	3.552631579	3.651315789	5.723684211
10	2.072368421	4.736842105	4.342105263	5.921052632
20	2.565789474	5.032894737	4.539473684	6.118421053
30	2.861842105	5.427631579	5.822368421	6.315789474
60	2.960526316	5.723684211	5.822368421	6.315789474

Conclusion

Presence of various functional groups as detected from IR spectrum indicates high potential for adsorption. Scanning Electron Microscope analysis shows porous structure of CM. The adsorbent CM produced from waste biomass (*Polyalthia longifolia* seeds) is used for the removal of malachite green from aqueous solution. The main conclusions of experimental results are as follows:

R^2 values indicate Langmuir model was best for CM. The maximum amount of adsorbent dose required is 4 gL^{-1}. At lower concentration 93.87 % adsorption is observed. Observed data indicates as temperature increases percent adsorption increases. The optimum pH 10 was found suitable for adsorption of MG on CM.

CM prepared from seeds of *Polyalthia longifolia* has potential for the removal of MG from aqueous solution. Thus it can be used for the treatment of waste water.

References

Environmental Chemistry, Fourth Edition, by A. K. De, New Age International Publishers, pp 81

Kavitha D and Namasivayam C 2007 Experimental and Kinetic studies on methylene blue adsorption by coir pith carbon. Bioresource Technology. 98(1): 14-21

Gopal V and Elango K P 2007 Kinetic and thermodynamic investigations of adsorption of fluoride onto activated Aloe vera carbon. J. Indian Chem. Society. 84: 1114-1118

Leaf Sheath Fibers, [Mohamed Chaker Ncibi, Borhane Mahjoub and Mongi Seffen 2006 Studies on the Biosorption of Textile Dyes from Aqueous Solutions Using Posidonia oceanica (L.) Leaf Sheath Fibres, Adsorption Science & Technology. 24(6): 461-472

I.A.W. Tan, A. L. Ahmad, B.H.Hameed 2008 Science Direct. J. Hazardous Material. 154: 337-346

Devarly PRAHAS, Yoga KARTIKA, Nani INDRASWATI, and Suryadi ISMADJI, 2008 The use of activated carbon prepared form jackfruit (artocarpus heterophyllus) Peel Waste for Methylene Blue Removal. J. Environmental Protection Sci. 2: 1-10

Hajira Tahir, Mohmmad Sultan and Qazi Jahanzeb 2008 Removal of basic dye methylene blue by using biosorbents Ulva lactuca and Sargassum. African J. Biotechnology. 7(15): 2649-2655

Md. Tamez Uddin, Md. Rukanuzzaman, Md. Maksudur Rahman Khan and Md. Akhtarul Islam, Jackfruit (Artocarpus heterophyllus) leaf powder: An effective adsorbent for removal of methylene blue from aqueous solutions. Indian J. Chemical Technology. (2009)16: 142-149

Agustine E. Ofomaja 2009 Equlibrium sorption of methylene blue using mansonia wood sawdust as biosorbent, Desalination and water treatment. 3: 1-10

Ahmed El Nemr, Ola Abdelwahab, Amany El – Sikaily and Azza Khaled 2009 Removal of direct blue – 86 from aqueos solution by new activated carbon developed from orange peel. J. Hazardous Materials. 161(1): 102-110

Saad S A, Daud S, Kasim F H and Saleh M N 2007 Dyes removal from aqueous solution by using chemical treated empty fruit bunch at various pH, IcoSM2007. pp 297-300

Jaikumar V 2009 Effect of Biosorption Parametres Kinetics Isotherm and Thermodynamics for Acid Green Dye Biosorption from aqueous solution by brevery waste. Int. J. Chemistry. 1(1): 2-12

Fessard V, Godart T, Mourot S & Poul J M 1999 Mutagen city of malachite green and leucomalachite green in in vitro tests. J. Appl Toxicol. 19: 421-430

Doerge D R, Chang HC, Divi R L and Churchwell M I 1998b Mechanism for inhibition of thyroid peroxidase by leuco malachite green, Chem Res Toxicol, 11: 1098-1104