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Application of *Cocos nucifera*'s husk to remove Malachite green dye and response surface modelling

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Toxic compounds are present in a vast variety of chemicals found in the environment. The study was performed to provide a remedy by using coconut husk (a waste matter) as a biosorbent to remove textile dye (i.e. malachite green dye) from synthetic solutions. The coconut husk was dried and crushed into powder form and was used for the experiment. Different parameters affecting color removal were analyzed in conventional batch mode and response surface optimization was performed. The optimum conditions of parameters (pH: 3-7, biosorbent dose: 20-50 g/L, and time: 80-300 minutes) for removal of color were found applying RSM. The model predicted the maximum removal of color to be 92.81% at pH 6.94, time 278.15 minutes, and dosage 41.10 g/L. Sustainability and circular economy can be reached with the objective of effluent treatment using biological waste matter.

Keywords: Biosorption; Coconut husk; Malachite green dye; Optimization; Sustainability; Response surface methodology (RSM).

INTRODUCTION

The United States Environmental Protection Agency (USEPA} listed the toxic organic and inorganic contaminants in 1978 [1]. Due to rapid increase in population and growth of industrialization in the country, the quality of both surface and groundwater changes day by day [2]. Maximum Industrial effluent consists of various contaminants which cause toxic consequences on human beings and environment. A large number of chemicals are found in the environment containing toxic substances. Different dissolved minerals from soil layers mix with the groundwater. The surface water is contaminated with the discharges of agricultural fields containing pesticides, fertilizers, and waste chemicals from industries and domestic waste [3-6].

Adsorption offers a distinct advantage over other methods to remove pollutants from wastewater. Adsorption can be operated in maximum chemical, physical, and biological systems. It is commonly used in industrial processes due to its sludge-free clean operation, simplicity of design, high reduction capacity, and ease of operation at a continuous scale. Biosorption is a physicochemical process where inactive biological materials accumulate pollutants, causing their removal from liquid, solid, or air medium on its surface functional groups. Worldwide evaluation of waste-biomass as adsorbents (wheat shell, rice husk, sawdust, pine bark, cereal chaff, etc.) is becoming popular as it is environmental-friendly, renewable, abundant, (diverse materials that could be used for this purpose) and cost-effective. It is a potential alternative to traditional techniques for the removal of pollutants from the contaminated effluent even from a diluted solution. As a result, research into the use of biomaterials as biosorbents of organic and inorganic contaminants has grown in popularity in recent years. The biosorbent is a potent adsorbent, less expensive than other manufactured- adsorbents. The search for new biosorbents is essential for the development of wastewater treatment rather than the use of the conventional adsorbent activated carbon [7]. Different scientists have studied MG removal using different biosorbents (Table 1) such as modified sphagnum peat moss, fish scales, cattail leaves, chemically modified biomasses of pine, oak, hornbeam and fir sawdust, eucalyptus bark, *Yarrowia lipolytica isf7, Zea mays* L. (maize) husk leaves, brown marine algae T*urbinaria conoides, Coriolus versicolor*, chlorella-based biomass, *Carica papaya* wood. The coconut's (*Cocos nucifera*) husk is widely available and not easily biodegradable due to high lignin content. Generally, this voluminous husk either ends up its life at landfill or is used to burn which simultaneously increases the air pollution and causes different lung diseases. Also many devotees in India use the coconut husk for burning purpose during puja. That also causes the emission of toxic green house gases like NOx, CO_2 at home, and CO.

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Table 1. Literature data on removal of Malachite green dye using different biosorbents

Biosorbent used	Experimental conditions	Findings	References
Modified sphagnum peat moss	a) Dye concentration: 60 mg/L b) pH: 6.5 c) Adsorbent concentration: 0.6g/L d) Contact time: 90 min e) Stirring speed: 160 rpm	Maximum adsorption capacity 121.95 mg/g at 20 °C	[8]
Fish (*Labeo rohita*) scales	a) Dye concentration: 50 mg/L b) pH: 8 c) Adsorbent concentration: 2g/L d) Contact time: 3 h e) Stirring speed: 150 rpm	Maximum adsorption capacity 38.46 mg/g at 40 °C	[9]
Cattail (*Typha angustifolia*) leaves	a) Dye concentration: 50 mg/L b) pH: 4 c) Adsorbent concentration: 0.25g/L d) Contact time: NA e) Stirring speed: 400 rpm	Maximum adsorption capacity 18.84 mg/g at 45 °C	[10]
Cetyltrimethylammonium bromide (CTAB) modified multi-component biosorbent composed of pine, oak, hornbeam and fir sawdust biomasses	a) Dye concentration: 30 mg/L b) pH: 8 c) Adsorbent concentration: 11 mg d) Contact time: 120 min e) Stirring speed: 400 rpm	Maximum adsorption capacity 52.610 mg/g	[11]
Eucalyptus bark	a) Dye concentration: 50 mg/L b) pH: 5 c) Adsorbent concentration: 0.4g d) Contact time: 270 min e) Stirring speed: 400 rpm	Maximum adsorption capacity 59.88 mg/g at 20 °C	[12]
Yarrowia lipolytica isf7	a) Dye concentration: 35 mg/L b) pH: 7 c) Adsorbent concentration: 5mg d) Contact time: 48 h e) Stirring speed: NA	Maximum adsorption capacity 155.098 mg/g	[13]
Coriolus versicolor	a) Dye concentration: 0.39 mg/L b) pH: NA c) Adsorbent concentration: 0.05g d) Contact time: 24.81 min e) Stirring speed: NA	Maximum adsorption capacity 18.84 mg/g at 45 °C	[14]
Zea mays L. (maize) husk leaves	a) Dye concentration: 200 mg/L b) pH: 6 c) Adsorbent concentration: 2.5g/L d) Contact time: 30 min e) Stirring speed: NA	Maximum adsorption capacity 81.5 mg/g at 50 °C	[15]
Brown marine algae T*urbinaria conoides*	a) Dye concentration: 100 mg/L b) pH: 8 c) Adsorbent concentration: 0.55 g d) Contact time: 150 min e) Stirring speed: 200 rpm	Maximum adsorption capacity 66.6 mg/g at 30 °C	[16]

Chlorella-based biomass	a) Dye concentration: 10 mg/L b) pH: 7 c) Adsorbent concentration: 2 g d) Contact time: 60 min e) Stirring speed: 400 rpm	Maximum adsorption capacity 9.775 mg/g	[17]
Carica papaya wood	a) Dye concentration: 10 mg/L b) pH: 10 c) Adsorbent concentration: 0.1 g d) Contact time: 24 h e) Stirring speed: 120 rpm	Maximum adsorption capacity 52.62 mg/g at 30°C	[18]

Table 2. Experimental range and levels of independent process variables

Independent variables	Range and levels (coded)				
	–α	–1	0	+1	+α
pH (A)	1.63	3	5	7	8.36
Dose (B)	9.773	20	35	50	60.22
Time, minutes (C)	5	80	190	300	374.99

Table 3. 2^3 Factorial experimental setup and percentage color removal as response

Run	pH (A)	Dose, g/L (B)	Time, minutes (C)	Experimental results (% color removal)
1	7.00	20	80	62±0.01
2	5	35	190	60±0.03
3	5	9.77	190	15±0.01
4	3	50	300	58±0.01
5	3	20	300	1.1±0.01
6	1.64	35	190	*10.5*±0.02
7	3	50	80	2.3±0.01
8	8.36	35	190	92±0.01
9	5	35	190	60±0.01
10	5	35	190	61±0.01
11	5	35	190	62±0.01
12	7	50	300	88.3±0.01
13	5	35	190	60±0.02
14	5	35	5	12±0.03
15	7	20	300	76±0.02
16	3	20	80	0.7±0.01
17	7	50	80	21±0.01
18	5	35	190	60±0.01
19	5	35	375	74±0.03
20	5	60.23	190	29±0.02

Table 4. Analysis of variance for the response surface quadratic model for color removal

Source	Sum of squares	Degree of freedom (df)	Mean square	F value	Probablity value (P value)
Model	17493.24	9	1943.69	1040.17	<0.0001
Residual	18.69	10	1.87		
Lack of fit	15.19	5	3.04	4.34	*0.0665*
Pure error	*3.50*	5	0.70		
Cor total	17511.93	19			

R^2= 0.9989; adjusted R^2=0.9980; predicted R^2=99.31

Table 5. Regression analysis by using central composite design

Model Term	Coefficient estimate	Standard error	F value	P value	Remarks
A	23.60	0.37	*4069.64*	< 0.0001	Significant
B	3.91	0.37	*111.51*	< 0.0001	Significant
C	17.70	0.37	*2288.63*	< 0.0001	Significant
AB	-10.90	0.48	*508.65*	< 0.0001	Significant
AC	3.15	0.48	*42.48*	< 0.0001	Significant
BC	13.58	0.48	*788.95*	< 0.0001	Significant
A^2	-3.01	0.36	*69.77*	< 0.0001	Significant
B^2	-3.01	0.36	*1374.33*	< 0.0001	Significant
C^2	-5.92	0.36	*270.71*	< 0.0001	Significant

Circular material management needs to be practiced following 5Rs principles (reduce, reuse, recycle, repurpose, regenerate) to recover the resources from being wasted and to recover their value as well. Segregated organic waste can be used for composting and bio gasification, which has economic value and is environmental friendly as well. Similarly, segregated non-organic dry waste can go for recycling purpose. In developing countries like India there are too many landfills for all the unsegregated mixed waste. In developed countries there are 5Rs practices which save the material from being wasted and recover its economic value as well. To achieve SDG goal 12, i.e. responsible production and consumption and circular economy of the waste generated from coconut, the present study was performed. Coconut husk was used to remove textile dye (Malachite green dye) from synthetic wastewater. The effect of pH, adsorbent dose and time on percentage removal of color was studied in conventional batch mode and in statistical optimization experiment.

MATERIALS AND METHODS

Malachite green (MG) dye

Malachite green [($C_{23}H_{25}ClN_2$) molecular weight: 365, color index: 42000] dye is extensively applied in various textile industries. It is found to be hazardous and known for its cytotoxic, genotoxic and carcinogenic potential. It was procured from Thermoelectrons LLS India PVT LTD Mumbai. The maximum absorbance of MG dye is at 621 nm. Dilute solutions of NaOH (1M) and HCl (1M) were used to adjust the pH of synthetic dye solution using a digital pH meter (Fisher Scientific) measured with standard buffer solutions.

Coconut husk

Coconut water is very popular for its mineral value in summer time. In India coconut oil also is commonly used as cooking oil and hair oil purposes. The raw coconut husk (supplementary picture) was collected from a local shop at Delhi NCR, India for the present study.

Biosorbent preparation

The coconut husk was cleaned using distilled water to separate the external dirts and dried at 60-65°C in a hot-air oven for 48 hours. Then the dried coconut husk was crushed in small particles using a motor pestle and kept under sunray for 7 days to further remove the moisture content. The coconut husk-biosorbent was kept in an air-tight bottle.

Experimental procedure for batch biosorption

Diluting the appropriate amount of stock solution in a 250 ml flask yielded 100 ml of synthetic solution (100 mg/L concentration) of Malachite green dye. Predetermined amount of biosorbent dose was added in the conical flask by agitating with a shaker (Biosphere Corporation) at 30°C temperature. The liquid sample was withdrawn at different times (60, 120, 180, 240, 300 minutes) to determine the effect of time on percentage removal of color. The pH of dye solution was varied from 3.0 to 9.0 to analyze the consequence of varying pH on percentage removal of color. The biosorbent dose was varied from 10-50 g/L to analyse the effect of biosorbent dose on percentage removal of color. After centrifugation (Bench Top Centrifuge by REMI Motors Limited) at 5000 rpm of the sample for 15 minutes, the supernatant was analysed using a colorimeter at 621 nm. The color removal of supernatant was tested by a Delux Photo Colorimeter manufactured by Labrotonics, India. All glassware was cleaned with distilled water and air-dried in a hot-air oven. The dye solution was analysed using a colorimeter before and after adsorption experiments.

The amount of dye adsorbed is calculated in percentage (%) abys equation (1):

$$\%Removal = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (1)$$

where, C_0 is the initial concentration (mgL^{-1}) of dye, C_e is the final concentration of dye after biosorption.

Optimization of experimental parameters

Statistically based central composite design (CCD) of RSM was performed to check the optimum conditions of experimental parameters (independent parameters: pH, dose, time) for maximum color removal (dependent variable: response) of MG dye solution (dye concentration: 100 mg/L). The software Design Expert Version 7.0.0 (Stat Ease, USA) was applied in this investigation. The maximum and minimum levels of experimental parameters are tabulated in supplementary Table 2. The optimal location is determined using the following formula, equation (2):

$$Y = \beta 0 + \sum_{i=1}^{K} \beta_i X_i + \sum_{i=1}^{K} \beta_{ii} X_i^2 + \sum_{i=1} \sum_{j=i+1} \beta_{ij} X_i X_j + \in \quad (2)$$

where, Y is the predicted response, X_i and X_j indicate the independent variables, β_o, β_i, β_{ii}, β_{ij}, are the statistical errors and denote regression coefficients. The trials (number 20) were carried out at factorial points (coded 1 notation), axial points (), and centre points (0) in duplicate.

RESULTS AND DISCUSSION

Effect of pH, biosorbent dose and time on % removal of color in conventional batch mode

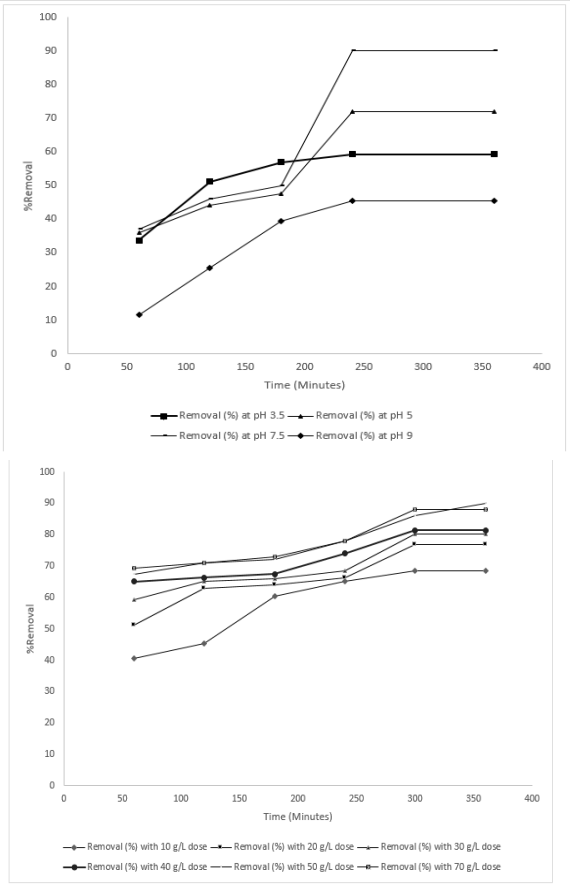

Figure 1. Effect of a) pH b) biosorbent dose on color removal at different times in conventional batch mode.

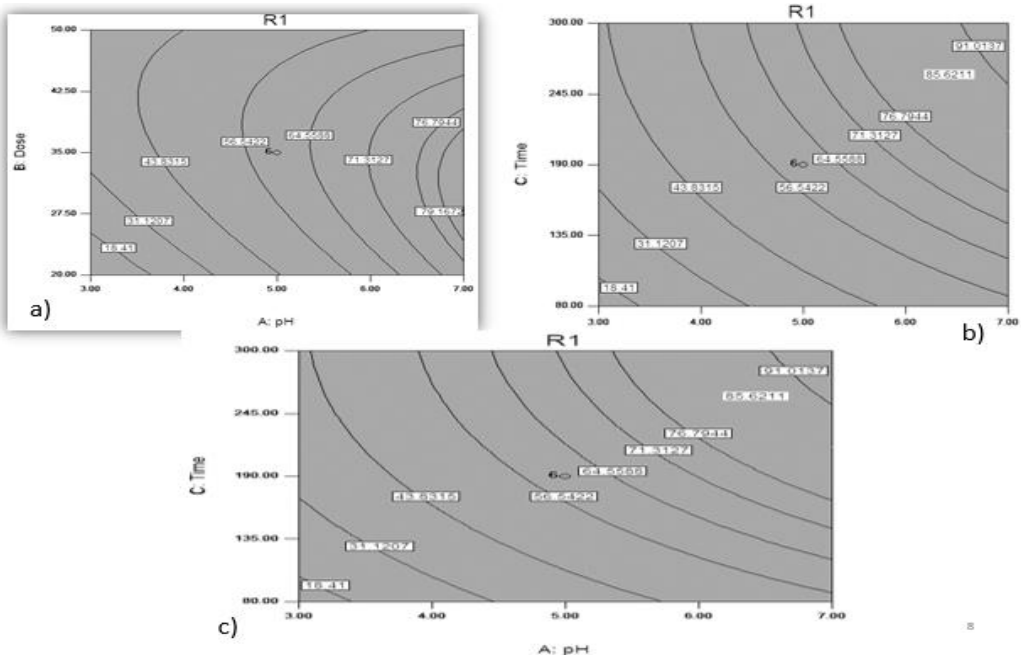

Figure 2. RSM contour plots for the consolidated effect of a) pH and biosorbent dose b) pH and time c) biosorbent dose and time on the % removal of MG dye.

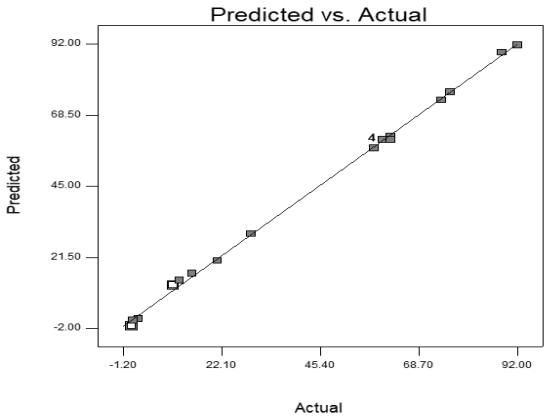

Figure 3. Comparison of the actual experimental data with predicted data by RSM model.

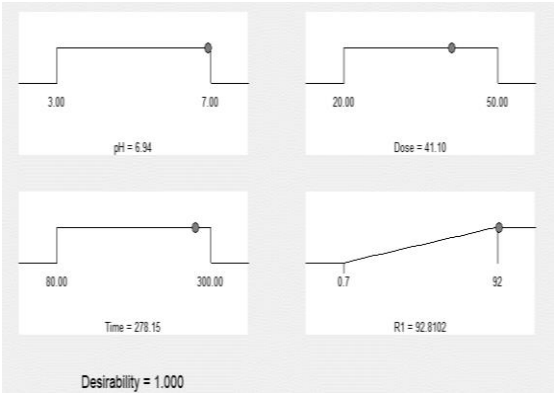

Figure 4. The RSM optimization ramp of desirability (1.000).

Figure 1 shows the biosorption of the MG dye at different pH values of the solution with time. Color removal was obtained to be in the range of 59%-90% at 360 minutes on varying the pH from 3.5 to 9 (Figure 1a). The color removal (90 %) was noticed to be maximum at pH 7.5 till 240 minutes from 100 mg/L concentration of MG dye solution. The color removal of MG dye was studied by varying the quantity of biosorbent dose (10, 20, 30, 40, 50 g/L) in the synthetic solution at different time intervals while keeping fixed other parameters (i.e., dye concentration: 100 mg/L, pH: 7, temperature: 30°C, shaking speed: 120 rpm). Percent MG removal was obtained in the range of 68% - 90% at 360 minutes, varying the dosage from 10-70 g/L (Figure 1b). The percent adsorption was increased when the biosorbent dosage is increase. The percentage color removal (90%) reaches maximum using 50 g/L biosorbent dose at pH 7.5. Initially with increasing pH and dose the removal was improved. Major color removal was noticed at pH 7.5 in conventional batch mode. Above 50 g/L dose the removal was observed to decrease. After optimum points of pH (7.5) and dose (50 g/L) the removal became stagnant or slightly reduced.

Combined effect of experimental parameters on % removal of color in response surface optimization

The integrated effect of two parameters on % removal of color is shown in the 2-D contour plots (Figures 2a,b,c). It was validated that pH, dose and time have a vigorous effect on % color removal (Table 3). Maximum color removal was predicted by the model to be 92.81% at pH 6.94 and time 278.15 minutes, dosage 41.10 g/L. The primary dye concentration at 100 mg/L and shaking speed of 120 rpm were kept settled during the experiments. In terms of actual factors, the quadratic equation 3 expresses the link between the theoretical removal and the independent process parameters:

$$\%Color\ removal = -142.63689 + 29.31439A + 4.66698\mathrm{B} - 0.012611C - 0.36333AB + 0.014318AC + 0.0082272\,BC - 0.75194A^2 - 0.059330B^2 - 0.000489636C^2 \quad (3)$$

where A is pH, B is biosorbent dose (g/L) and C is time in minutes. The removal (92%) was calculated using the optimum points and the above CCD equation. The statistical importance of the model was estimated by ANOVA (Table 4). The low probability of F-value and non-significant lack of fit, entails high significance of this statistical model. The value of determination coefficient R^2 (0.9989) indicates goodness of fit [19, 20]. The outcomes proposed that equation was preferable for the CCD model. In the recent study, A, B, C, AB, AC, BC, A^2, B^2 and C^2 are significant experimental parameters (Table 5). Figures 3 and 4 distinguish between actual experimental data and those predicted by the RSM model and the optimization ramp of desirability (1.000), respectively. The RSM optimization validated that there was prominent effect of pH, dose and time on the color removal.

Recommendation & Conclusion

The coconut husk is flabby and voluminous. The transport cost of the material is associated with it and also the chance of material loss due to overflow from the vehicle. The value chain can be disturbed in this way. Effective transportation will require more cost, and that can be an obstacle in using the husk (imagining the cost of carrying the raw materials increases) [21]. Also, another issue is regarding the preservation of the raw materials intact that are away from getting rotten. Any place, which has the problem of flood and water stagnancy (as an outcome of climate change) will stand as a problem. Effective transportation and storage are the requirements to solve these.

The waste biomass of coconut husk was examined as biosorbent to remove a textile dye;

Malachite green from synthetic solutions prepared at laboratory. The MG removal process was influenced by varying pH, time, and coconut husk-dose. The optimum color removal predicted by the model was observed to be 92.81% at pH 6.94 and time 278.15 minutes, dosage 41.10 g/L, initial dye concentration being kept fixed at 100 mg/L during the experiments. This study shows that coconut husk can be applied as an efficient biosorbent to reduce textile dyes in the effluent of a treatment plant. Further, the coconut husk is not easily biodegradable and causes a huge amount of solid waste generation.

Textile industry can collect the coconut husk from the local coconut seller through strong supply chain management. The adsorbent can be prepared easily at their R&D lab or it can be procured from relevant technical institutes *via* collaboration. The adsorbent can be used in continuous mode to treat the dye contaminated effluent in a simple agitated reactor. Also, there is scope of recovery of adsorbent and dye through desorption. In this way, waste to wealth can be aimed by focusing the circular economy & sustainability goals for effluent treatment using waste matter.

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Supplementary picture: Collected Coconut husk