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Response Surface Optimized Removal of Reactive Red HE3b from an Aqueous Solution using Pyrolytically Biochar Derive from *Euclea Divinorum* Waste Biomass

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Abstract

One of the major environmental concerns in the 21st century textile industries, is the removal of waste dyes from textile effluents due to the fact that they have been scientifically proven to be harmful, persistent and allergy inducing. Where-as most modern remediation techniques are expensive and selective making them out of reach for most third world nations, the use of agricultural wastes as alternative low-cost adsorbents has been on the rise majorly because of their availability, ease of preparation and non-selectivity where one set of adsorbent can be used for the remediation of several dyes. Biochar and activated carbon derived from these wastes are the most common forms of adsorbents from agricultural wastes because they are efficient, cheap and easy to make. In this study, wastes from the extraction process of the natural dyeing plant Euclea divinorum, were developed into pyrolytically derived biochar at 400 ℃ and subsequently used for the effective removal of the synthetic azo dye, reactive red HE3b. A 24 central composite response surface method was developed and used to examine the effects of adsorbent dosage, contact time, initial concentration and agitation speed on the adsorption of the dye in the process giving the optimum adsorption conditions. The optimum conditions from the study, were an adsorbent dosage of 0.05g, temperature 45℃, an initial concentration of 1.0 ppm and an agitation speed of 300 rpm. These, gave a percentage removal of 84.71% predicted against 84.89 % experimental, signifying the accuracy of the model and the potential adsorptive properties of the biochar. This study therefore, provided for a cheap and available alternative adsorbent for the removal of reactive red HE3b.

Key words: ***Community microfinance, empowerment, human development***

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Introduction

Over the last century, synthetically manufactured dyes not only found use in the textile industries but also in the food, pharmaceutical, cosmetic and leather industries. As the synthetic dyes gained more use courtesy of the industrialization and the rapid increase in population of different nations, so did its adverse effects on the environment begin to manifest. This is because, potentially up to between 10% - 15% percent of toxic unspent dyes are usually discharged directly to the environment especially in third world countries where effluent treatment methods are often costly or non-existent and in developed nations where remediation techniques are more advanced up to 2% of the effluents make it into the environment. Presently, the dyeing industry consumes more than 7×107 tonnes of dyes with more than 100,000 shades and variants (Carmen & Daniela, 2012; Çelekli et al., 2009; Odero, et al., 2020).

Despite the disadvantage of synthetic dyes and the advantages of natural dyes, the dye industry still relies heavily on synthetic dyes and because most of these effluents are harmful, most industries in developed nations have set advanced systems for the removal and remediation of the said textile effluents with varied success depending on the method of removal. Several chemical and physical methods have been developed for the removal of waste textile dyes such as ion exchange, centrifugation, ultrafiltration, electrocoagulation each having their own advantages and disadvantages for example, electrocoagulation is very effective but also very expensive and causes accumulation of sludge. On the other hand, ultrafiltration is very expensive but also fairly non selective and effective among others (Yagub et al., 2014, Gürses, Güneş, & Şahin, 2021)

Where-as most of these methods are fairly effective, they are often expensive and specific to types of dyes and pigments hence it cannot be used over a wide range of dyes. As a result, there is a shift of research from conventional chemical and physical methods to cheaper, effective and non-selective alternatives such as adsorption. Adsorption, refers to the process of mass transfer of compounds from an aqueous phase into and adsorbent. Adsorption, is presently favored over other types of remediation techniques because most adsorbents can be locally sourced from agricultural wastes and also because they are often effective and are non-selective(Ali, Asim, & Khan, 2012). Where-as adsorption is a very effective and cheap method for the removal of waste dyes from an aqueous media, it requires an optimization of adsorption parameters such as pH, particle size, initial concentration, temperature and time.

Optimization, refers to the process of improving the system performance to ensure that it gives maximum yields (Almeida et al., 2008).

Traditionally, scientists used to optimize this conditions by doing one parameter at a time, but with the rapid development of computational chemistry and statistical packages, more and more scientist have favored multivariate techniques such as response surface methodology, Taguchi designs and other mathematical methods (Hasan & Setiabudi, 2018; Tejada-tovar, Villabona, & Cabarcas, 2018).

Reactive red HE3B, belongs to a group of dyes that dye fabric materials by directly reacting to their fabric molecules (Kim et al., 2018). Azo dyes such as reactive red HE3B, are dyes with the group (-N=N-) as part of their building block and have been linked to environmental pollution, persistency and carcinogenicity (Mahmoud et al., 2016)

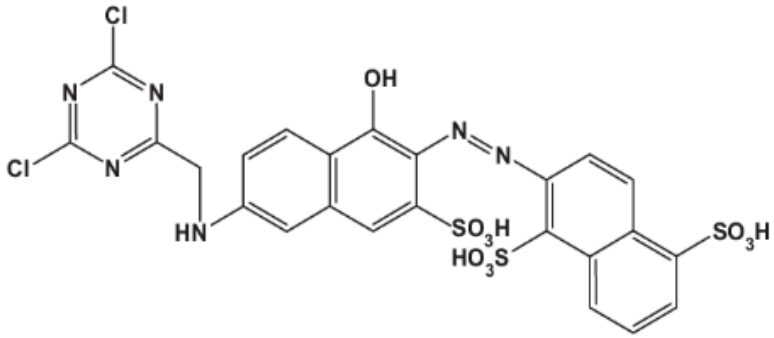

Figure 1: Chemical structure of reactive red HE3

The objective of this study, was to valorize wastes from the extraction process of the natural dyeing plant Euclea divinorum (Manyim et al., 2021), into pyrolytically derived biochar at 400 ℃ for the removal of the synthetic azo dye, reactive red HE3b.

Materials and Methods

Preparation of Biochar

The left-over biomass of Euclea divinorum were pyrolytically prepared at 400℃ with little modifications using the methods prescribed by (Song et al., 2012). The starting temperature was 200℃ in an oven, this was elevated by 50℃ every 1.5 hours till the final temperature was attained. The biochar was then cooled and sealed using air tight containers. This was done at Moi University, school of science and aerospace studies department of chemistry and biochemistry laboratories.

Chemicals

Reactive red HE3B ($C_{44}H_{24}Cl_2N_{14}O_{20}S_6Na_6$) was obtained from Rivatex Textile factory (a facility of Moi University) and used without any further processing.

NaOH and HCl used for this study were analytical grade purchased from Pyrex laboratory Nairobi.

UV Vis Measurements

UV-Vis measurements, were done using a Beckman Coulter Model DUR720 UV/VIS Spectrophotometer at a fixed wavelength λ max of 536 nm.

Experimental Design and Process Variables Optimization

Using Minitab software (USA), a 24 factorial points with a center point where n is the number of variables at 5 levels. Table 1 below, shows the factorial experimental design.

Table 1

Factorial Experimental Design

Variables	**Range and Levels**				
	-α	-1	0	+1	+α
Adsorbent dosage (g) X_1	0.10	0.11	0.12	0.13	0.14
Temperature (°C) X_2	40	45	50	55	60
Concentration (ppm) X_3	0.5	1.0	1.5	2.0	2.5
Agitation speed (rpm) X_4	100	150	200	250	300

Batch Adsorption Studies

Adsorption experiments were done as per the experimental design generated by the use of response surface methodology. Prior to analysis, a stock solution of 100 ppm was prepared by accurately dissolving 0.1 gram of the dye into 1L of distilled water. Dye adsorbed onto the adsorbent (qe) and the percentage dye removals were calculated using the equations (1) below.

The percentage dye removal, was calculated as

$$\% \text{ Removal} = ((C_i - C_t)\times 100)/C_t \quad \ldots\ldots\ldots\ldots \text{ equation 1}$$

Where V is the volume, Ci is the initial concentration and Ct is the concentration at a given time.

Results

Response Surface Methodology

The experimental design for the coded values, the true value and the experimental responses are captured in table 2 below.

Table 2

Experimental Design for the Coded Values, The True Value and the Experimental Responses

Run	Coded values				True value				Response	
	X_1	X_2	X_3	X_4	X_1	X_2	X_3	X_4	Absorbance	% Removal
1	-1	-1	-1	-1	0.03	45	1.0	200	0.043	51.1627
2	1	-1	-1	-1	0.05	45	1.0	200	0.054	20.3703
3	-1	1	-1	-1	0.03	55	1.0	200	0.049	32.6530
4	1	1	-1	-1	0.05	55	1.0	200	0.051	27.4509
5	-1	-1	1	-1	0.03	45	2.0	200	0.029	62.0689
6	1	-1	1	-1	0.05	45	2.0	200	0.044	6.81818
7	-1	1	1	-1	0.03	55	2.0	200	0.033	42.4242
8	1	1	1	1	0.05	55	2.0	200	0.043	9.30232
9	-1	-1	-1	1	0.03	45	1.0	300	0.047	38.2978
10	1	-1	-1	1	0.05	45	1.0	300	0.035	85.7142
11	-1	1	-1	1	0.03	55	1.0	300	0.051	27.4509
12	1	1	-1	1	0.05	55	1.0	300	0.05	30.4423
13	-1	-1	1	1	0.03	45	2.0	300	0.046	2.17391
14	1	-1	1	1	0.05	45	2.0	300	0.038	23.6842
15	-1	1	1	1	0.03	55	2.0	300	0.039	20.5128
16	1	1	1	1	0.05	55	2.0	300	0.026	80.7692
17	-α	0	0	0	0.02	50	1.5	250	0.038	44.7368
18	+α	0	0	0	0.06	50	1.5	250	0.035	57.1428
19	0	-α	0	0	0.04	40	1.5	250	0.034	61.7647
20	0	+α	0	0	0.04	60	1.5	250	0.044	25.0212
21	0	0	-α	0	0.04	50	0.5	250	0.059	35.5932
22	0	0	+α	0	0.04	50	2.5	250	0.053	3.77358
23	0	0	0	-α	0.04	50	1.5	150	0.034	61.7647
24	0	0	0	+α	0.04	50	1.5	350	0.049	12.2449
25	0	0	0	0	0.04	50	1.5	250	0.031	77.4193
26	0	0	0	0	0.04	50	1.5	250	0.032	71.8755
27	0	0	0	0	0.04	50	1.5	250	0.031	77.4193
28	0	0	0	0	0.04	50	1.5	250	0.030	83.3333

Statistical Analysis

The response surface polynomial equation presented in coded variables X_1, X_2, X_3 And X_4 was as shown in equation 3 below.

$$\text{Absorbance} = 0.172 + 1.54\,X_1 - 0.005\,X_2 - 0.044\,X_3 - 0.0001X_4 + 13.97X_1 * X_1 + 0.000075\,X_2 * X_2 + 0.024\,X_3 * X_3 + 0.000001\,X_4 * X_4 - 0.01\,X_1 * X_2 + 0.050\,X_1 * X_3 - 0.009X_1 * X_4 - 0.001\,X_2 * X_3 - 0.000002X_2 * X_4 + 0.00004\,X_3 * X_4 \quad \text{Equation 3}$$

$R2 = 83.26\%$

The regression coefficient (R2) of 83.26%, indicates that the model can explain 83.26% of the variations in the response as the variable change hence the model was found to be adequate for the study. The significance of the model was evaluated using the probability value where P 0.05 implies significance (Manyim et al., 2021; Tejadatovar et al.,2018)

According to the analysis of variance (ANOVA) Table, i.e., Table 3 below, the adsorbent dosage and the agitation speed were the significant variable whereas concentration and temperature were insignificant. Agitation speed, showed significant effects on the response in quadratic terms. Effects of variable interaction on the response was noted between the adsorbent dosage and agitation speed with P = 0.02.

Table 3
Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model		0.001974	0.000141	5.68	0.001*
Linear	14	0.000351	0.000088	3.53	0.030
Adsorbent dosage	4	0.000121	0.000121	4.88	0.042
Temperature	1	0.000069	0.000069	2.77	0.115
Concentration	1	0.000021	0.000021	0.84	0.372
Agitation speed	1	0.000255	0.000255	10.27	0.006
Square	1	0.001133	0.000283	11.42	0.000
Adsorbent dosage*Adsorbent dosage	4	0.000066	0.000066	2.66	0.123
Temperature*Temperature	1	0.000097	0.000097	3.90	0.066
Concentration*Concentration	1	0.001035	0.001035	41.72	0.000*
Agitation speed*Agitation speed	1	0.000172	0.000172	6.94	0.018
2-Way Interaction	1	0.000434	0.000072	2.91	0.041
Adsorbent dosage*Temperature	6	0.000004	0.000004	0.16	0.693
Adsorbent dosage*Concentration	1	0.000001	0.000001	0.04	0.843
Adsorbent dosage*Agitation speed	1	0.000324	0.000324	13.06	0.002*
Temperature*Concentration	1	0.000090	0.000090	3.64	0.075
Temperature*Agitation speed	1	0.000002	0.000002	0.09	0.767
Concentration*Agitation speed	1	0.000012	0.000012	0.49	0.492
Error	1	0.000397	0.000025		
Total	16	0.002371			
	30				

DF – degrees of freedom; SS – sum of squares; MS – mean square F – Fischer test value; p – probability value and * – significant

3D Response surface plots that independently combined the four factors and the response variables were noted in for the response plots for absorbance. The most influential parameters of the four, was the agitation speed followed by the adsorbent dosage then contact time then concentration.

Conclusion

In the present research work, waste biomass of *Euclea divinorum*, were successfully pyrolyzed in biochar and used for the adsorption of reactive red HE3B. The optimization of independent variables adsorbent dosage (X1), temperature (X2), concentration (X3) and agitation speed (X4) using response surface methodology, proved successful with % removals of 84.89%. The optimal conditions were X1=0.05, X2=45, X3=1.0 and X4=300.

Recommendation

The authors recommend that the biochar from *Euclea Divinorum* be used as alternative remediation techniques.

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