International Journal of Integrated Engineering: Special Issue 2018:
Innovations in Civil Engineering, Vol. 10 No. 9 (2018) p. 77-83

DOI: https://doi.org/10.30880/ijie.2018.10.09.014

Removal of COD Using Delonix Regia Pods Activated Carbon Adsorbent for Natural Rubber Wastewater Treatment

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Received 22 March 2018; accepted 26 December 2018, available online 31 December 2018

Abstract: Leachate are very high strength wastewaters that contain a variety of pollutants that pose a serious threat to the environment if appropriate control measure is ignored. Composite adsorbent is an emerging, interesting and attractive alternative to conventional adsorbents and having the ability to act as catalysts due to their high reactivity and excellent selectivity towards specific pollutant compounds. This study investigated the potential of biocomposite adsorbent made from a combination of chitosan, feldspar and zeolite (CFZ) for the treatment of Iron (Fe) from leachate wastewater. Leachate characterization and batch adsorption experiments was conducted to determine the optimum conditions for pH, dosage and contact time parameter in the removal of Fe. The result shows that the concentration of Fe was 15.82 which exceeded the recommended limit. The optimum conditions also occurred at pH 5 with 6 gram of biocomposite dosage and at 180 minutes contact time. The corresponding removal efficiency for Fe is 90% with 0.0127 mg/g uptake capacity.

Keywords: Biocomposite, Leachate, Adsorption, Chitosan

1. Introduction

The increase in solid waste disposal involving agricultural waste contributes to the increased capacity of solid waste containment systems. Not all of the rest of nature materials can be used and processed into commercial and or industrial product, some eventually have to be discarded as waste. This waste if not managed appropriately may contribute to pollution in the environment in general and water sources in particular. New products have been studied for potential usage in wastewater remediation. Studies show that agricultural residues such as bagasse [1] can be used effectively for the removal of phosphate ions from contaminated water and used as a low-cost alternative compared to commercial activated carbon. Delonix regia tree is widely cultivated as an ornamental plant in Malaysia that produces a lot of fruits and is considered agricultural waste with potential to be employed as lignocellulose adsorbent. Adsorption method is one of the effective ways in treating wastewater and can eliminate color, odor, and other pollutants both organic and inorganic nature. Adsorption has been known as an alternative to biological and chemical methods in wastewater treatment because most of the good absorption capacity [2].

Natural rubber is one of the key sectors of agro-based industries in the Southeast Asian region. More than 60% of natural rubber production worldwide comes from Thailand, Indonesia, and Malaysia [3]. Currently, Malaysia is the fifth largest natural rubber producer after Thailand, Indonesia, Vietnam and China. Natural rubber production in Malaysia increased by 4.1% from 0.67 million tonnes in 2014 to 0.72 million tons in 2015 [4]. Natural rubber is widely used in a variety of applications and products. Processing of natural rubber (NRL) in order to meet demand in the production of products such as tires, gloves, toys and others and the high demand for natural rubber have led to environmental degradation effects [5]. The processing of natural rubber using water, chemicals and other utilities helps to produce large amounts of wastewater and sewage through a process of washing, drying, coalescence and precipitation. Malaysia produces agricultural waste by 1.2 million tonnes a year for disposal into landfills [6]. The effect of this has made the improvement of waste landfills closed before reaching maturity. The residual income has a negative impact on the environment, cost, productivity, time, social and economic industry [7,8]. This study aims to investigate

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the potential application of Delonix regia pods activated carbon for natural rubber wastewater treatment.

2. Wastewater Sampling

Wastewater samples were taken from the area of rubber industry in Kluang, Johor, Malaysia. Wastewater samples were collected from the effluent of the plant using polytetrafluoroethylene (PTFE) plastic bottles until full and tightly closed. Samples was then taken to the laboratory as soon as possible and stored in a cold room at 4° C to avoid changes due to chemical and biological reactions. All chemical analyses for the characterization of rubber wastewater was carried in accordance to the Standard Methods for the Examination of Water and Wastewater [9].

3. Media Preparation

Delonix regia pod was trimmed 5-10cm then dried in an oven at 105° C for 24 hours and allowed to cool at room temperature. This media is crushed with grinder and sifted to obtain geometric size between 1 - 5 mm. This material is immersed in phosphoric acid solution (H_3PO_4) at a concentration of 20% for 24 hours [10,11]. Next, this material was burned in a furnace at 500 ° C for 30 minutes [10]. This activated carbon was washed and cleaned with distilled water to remove H_3PO_4 and dried in oven at 105 ° C for 24 hours. The material is crushed and filtered to obtain a 150 µm size then stored and ready for use.

4. Wastewater Experimental Sampling

All experiments were conducted with 100ml of rubber wastewater in a 250 ml Erlenmeyer flask. Assay was carried out by varying dosage, pH, shaking speed and contact time using laboratory orbital shaker. It was then removed and allowed to settle for about an hour before the supernatant was withdrawn for analysis of COD. The results were considered as percentage reduction of COD according to the equation (1).

$$\%\ Removal = [[(C_i - C_f)/C_t]x\ 100 \quad (1)$$

Where C_i and C_f are defined as the initial and final COD (mg/L) concentrations respectively [12].

5. Central Composite Design (CCD) based experiment.

Design Expert Version 7.0 software was used to carry out the design of the experiments and to analyze the data statistically. The independent variables, shaking speed, pH, agitation time and dosage were optimized using CCD and response surface methodology (RSM). The variables ranges and codes applied were as outlined in table 1 to obtain the optimum condition for the variables, while COD dependent variable was investigated as response. The quadratic equation model for calculation of the optimum conditions can be represented according to Equation (2):

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i . X_i + \sum_{i=1}^{k} \beta_{ii} . X_i^2 + \sum_{i \le j}^{k} \sum_{j}^{k} \beta_{ij} . X_i . X_j + \cdots + e \quad (2)$$

where *i* defines the linear coefficient, *j* the quadratic coefficient, β the regression coefficient, *k* designate for the quantity of factors examined and optimized, while *e* constitute the random error [13].

Analysis of variance (ANOVA) was built in graphical form of the analyzed data for the determination of the interactions between the system variables and the response. The coefficient of determination R^2 evaluates the extent and suitability of the polynomial model and a measure of its significance was represented by F-test within the program [14]. Model reliability assessment was relied upon the P-value having a 95% confidence limit [15]. The optimum zone was established on the basis of the significance of variables in the interactions.

Table 1 Variables and levels studied for COD removal

Factor	Name	Units	Low Level	High Level
A	shaking speed	rpm	50	175
B	Dosage	g	0.5	6
C	pH		3	12
D	Contact time	mins	5	160

6. Results and Discussion

6.1 Wastewater characterization

Table 2 presents the characteristics of the wastewater obtained from the rubber industry and it is evident that these values are high compared to the Department of Environment Malaysia; Environmental Quality (Industrial Effluents) Regulations 2009 under standard A and standard B [4]. Hence, it is required to treat such polluted waters before discharge in to the environment.

Table 2: Rubber wastewater characteristics.

Pollutants	Unit	Value
Biological Oxygen Demand (BOD)	mg/L	3340
Chemical Oxygen Demand (COD)	mg/L	5230
Total Suspended Solids	mg/L	510
Ammoniacal Nitrogen	mg/L	65
Color	Pt.Co	345
Turbidity	NTU	134
Zinc	mg/L	0.269
Iron	mg/L	0.09
Cu	mg/L	0.04
pH		9.1

6.2 Activated carbon characterization

The results obtained from the characterization of the chemical composition are presented in Table 3.

Table 3: Chemical composition of adsorbent.

Element	%
O	23.49
Si	0.01
Al	0.05
K	0.39
C	50.31
N	21.33

It is evident that the main constituent is carbon.

6.3 Batch adsorption studies

6.3.1 Establishment of regression model equations using CCD

The outlined matrix integrating the factors designated as independent variables and the responses

Table 4: Experimentation design order from central composite design.

Standard order	Factor 1 A:Shaking Time (mins)	Factor 2 B:Dosage (mg/L)	Factor 3 C:pH	Factor 4 D:Speed (RPM)	Response COD (mg/L)
1	-1	-1	-1	-1	54.97
2	1	-1	-1	-1	55.06
3	-1	1	-1	-1	48.57
4	1	1	-1	-1	53.38
5	-1	-1	1	-1	50.46
6	1	-1	1	-1	44.75
7	-1	1	1	-1	53.55
8	1	1	1	-1	52.06
9	-1	-1	-1	1	54.98
10	1	-1	-1	1	54.45
11	-1	1	-1	1	43.67
12	1	1	-1	1	51.06
13	-1	-1	1	1	49.00
14	1	-1	1	1	46.48
15	-1	1	1	1	53.5
16	1	1	1	1	59.54
17	-1	0	0	0	73.62
18	-1	0	0	0	70.85
19	1	0	0	0	74.54
20	1	0	0	0	70.71
21	0	-1	0	0	63.42
22	0	-1	0	0	63.14
23	0	1	0	0	62.24
24	0	1	0	0	61.06
25	0	0	-1	0	71.27
26	0	0	-1	0	73.33
27	0	0	1	0	70.5
28	0	0	1	0	70.94
29	0	0	0	-1	64.06
30	0	0	0	-1	68.25
31	0	0	0	1	64.82
32	0	0	0	1	68.36
33	0	0	0	0	74.48

which comprise of the percentage removal of COD is presented in Tables 4 showing the derived empirical design array by the software..

From table 4, the percentage removals of COD ranged between 43.67 and 74.54%. For the purpose of analogy and correlation of the responses, CCD was used for the establishment of the regression equations which comprise of quadratic expressions that have been suggested by the design expert software. The model expressions were selected in accordance to successive model sum of squares and is based on polynomial's highest order. The relation between the actual and predicted experimental data was significant as demonstrated by the model's actual R^2 value of 0.9815 for COD and which were relatively close to the predicted R^2 value of 0.9230 [16]. The developed empirical equation for the percentage decontamination of COD response is presented in equations (3).

$$Y_{COD} = 73.81+ 0.44*A+ 0.096*B - 0.50*C + 0.037*D +1.59*A*B-0.96*A*C+0.79*A*D +3.17*B*C +0.034*B*D+0.97*C*D-1.32*A^2-11.29*B^2 -2.24*C^2-7.38*D^2 \quad (3)$$

The synergistic and antipathetic influence of the respective variables were elucidated by the symbol before the terms which can be positive (favourable) or negative. The occurrence of a single variable term signifies a one-factor influence; two variable terms imply a combined factor influence and then a second-order term indicates a quadratic effect.

6.3.2 Statistical analysis

The suitability of the model was additionally validated through analysis of variance (ANOVA). Table 4 illustrates the ANOVA of the quadratic model for COD removal percentages with the sum of squares, mean square, F-value and Prob. > F values. ANOVA validates the significance and the extent of the adequacy of the model. And subdividing the sum of squares for every one of the alternatives, the model as well as the error by the corresponding degrees of freedom yields the mean square magnitude.

Table 2.0 ANOVA of the response surface quadratic model for COD removal

Source	Sum of Squares	df	Mean Square	F-Value	Prob > F	
Model	2921.52	1 4	208.68	68.27	< 0.0001	significant
A-Shaking Time	3.92	1	3.92	1.28	0.272	
B-Dosage	0.18	1	0.18	0.06	0.8088	
C-pH	4.96	1	4.96	1.62	0.2189	
D-Speed	0.028	1	0.028	9.20E-03	0.9246	
AB	40.39	1	40.39	13.21	0.0019	
AC	14.9	1	14.9	4.87	0.0405	
AD	10.05	1	10.05	3.29	0.0865	
BC	160.91	1	160.91	52.64	< 0.0001	
BD	0.018	1	0.018	5.96E-03	0.9393	
CD	15.05	1	15.05	4.93	0.0396	
A^2	8.72	1	8.72	2.85	0.1084	
B^2	635.96	1	635.96	208.06	< 0.0001	
C^2	25.09	1	25.09	8.21	0.0103	
D^2	271.84	1	271.84	88.93	< 0.0001	
Residual	55.02	18	3.06			
Lack of Fit	25.85	0	2.59	0.71	0.7005	not significant
Pure Error	29.17	8	3.65			
R-Squared	0.9815					
Adj R-quared	0.9671					
Pred R-Squared	0.9230					
Adeq Precision	25.342					

The developed model terms which have value of Prob. > F less than 0.05 are significant while the converse is insignificant [16]. With regards to COD percentage removals, apparently from Table 4, the model F value obtained is 68.27 and the Prob. > F value as < 0.0001, confirming the significance of the model. Based on the statistical evaluation, it is be observed that the established models were appropriate in minimizing COD removals within the bounds of the investigated variables. Moreover, Fig. 1 shows the predicted removal values versus the experimental removal values for the COD response, depicting that the established model favourably encapsulates the interaction of the adsorption process variables and the response.

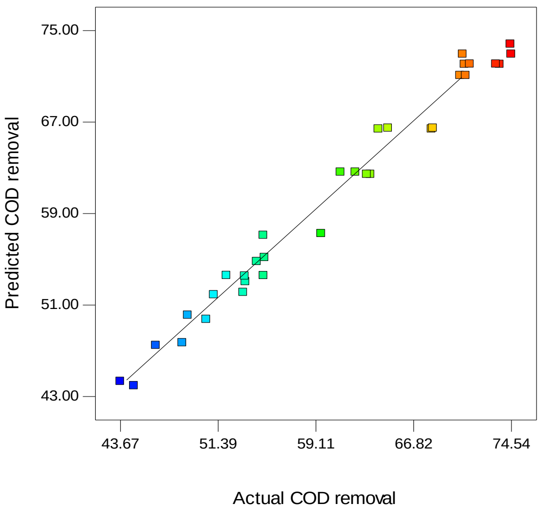

Fig 1: Predicted versus actual COD removal.

6.3.3 Effects of variables interaction

Fig. 2 (a) depicts the three dimensional response surfaces of the interaction effect of adsorbent dosage and shaking time for COD removal. It can be observed that with increase in shaking time from 5 mins to 160 mins as well as corresponding increase in adsorbent dosage from about 0.5 to 6.0 g, increased the COD removal gradually up to about 4g dosage and 100 mins shaking time before it began to decrease. This may have been due to an increased contact time during the adsorbate-adsorbent interaction up to the equilibrium state, thereafter no further adsorption could take place because of non-availability of vacant sites on the adsorbent [17-19]. Fig. 2(b) also shows the response surface interaction between pH and dosage parameter for the removal of COD response. It can be seen that with increase in the parameter values, there was a corresponding increase in COD removal up to about 70.65% after that the removal declined. This phenomena can be due to electrostatic effect between the adsorbate and adsorbent with progressive variation of pH and dosage [20-32]. The adsorption increases up to a certain parameter state where equilibrium was arrived at and thereafter electrostatic repulsion results between the adsorbate and the adsorbent with further pH variation.

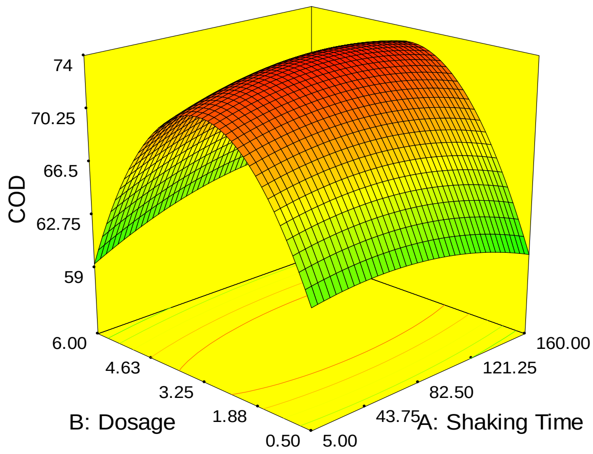

Fig 2 (a): Shaking time and adsorbent dosage effect on the removal of COD

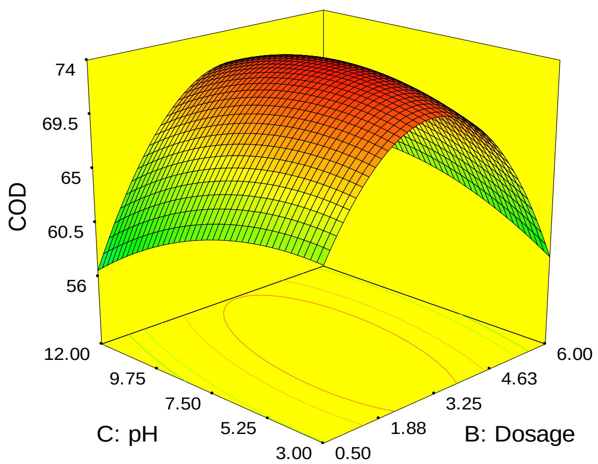

Fig 2(b): Adsorbent dosage and pH interaction effect on the removal of COD

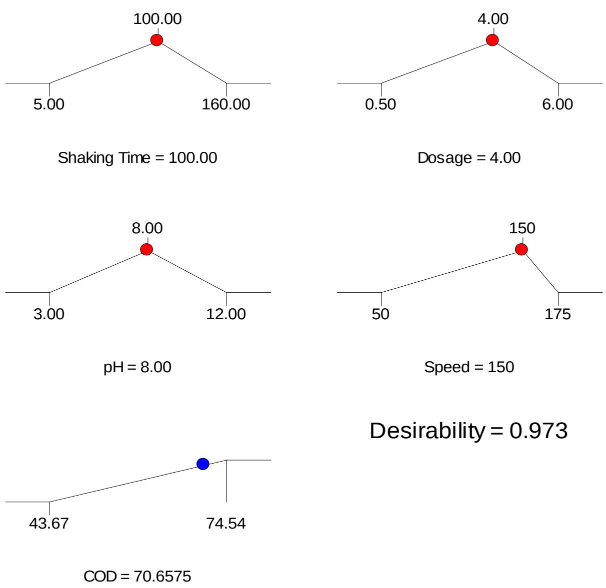

Fig 3: Optimal parameter conditions for COD removal.

7. Process optimization

The optimization of COD adsorption onto Activated carbon prepared from delonix regia pods was carried out with the application of design-expert software (Stat-Ease, Inc., Minneapolis, USA). During the optimization analysis, the COD responses criterion was set to maximum value. The optimized adsorption settings arrived were adsorbent dose of 4.0 g, 150 rpm shaking speed, contact time 100 mins with desirability value of 0.973, as shown in fig. 3. The predicted and empirical derived values were in close agreement, thus validating the model's significance. At the most favourable conditions, the removal efficiency achieved was 70.65% for COD response. This study forms part of an ongoing research on the removal of contaminants from wastewater using low cost adsorbents. It is recommended that further research be conducted to determine the effectiveness of delonix regia pods activated carbon for the removal of other contaminants such as ammoniacal nitrogen, color, and suspended solids from the natural rubber wastewater.

Acknowledgment

The authors are thankful to Universiti Tun Hussein Onn Malaysia for support and providing necessary infrastructure to carry out research work and make this research viable and effective.

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