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Congo red dye removal from aqueous solution by encapsulated eggshell membrane using central composite design

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Abstract

Eggshell is solid wastes produced from the food industry. Commonly, eggshell and its membrane used to treat water pollution such as heavy metal removal and also dye removal. Thus, on the treatment process, it was having the material handling problem, which was needed filtration method to remove out the adsorbent from the solution, and it was not efficient when commercializing in the wastewater treatment plant. Therefore, this study was using alcohol-sodium alginate (PVA/SA) to encapsulate the eggshell membrane, and this encapsulation method also would be able to enhance the performance of raw material on the dye adsorption. In this study, the eggshell membrane (ESM) are prepared in bead form, and the optimization of the bead are performed by the removal of congo red dye at several parameters such as pH, initial dye concentration, contact time, and dosage of ESM. The central composite design was selected to optimize the adsorption process by generating 30 runs of the experiment using software Design Expert® version 11. The Fourier Transforms Infrared Spectroscopy (FTIR) analysis and Brunauer-Emmett-Teller (BET) analysis are used to characterize the ESM bead. There was found out that main functional group on ESM bead contribute on adsorption process were carbonyl group, hydroxyl group and ESM bead also having the 42.74 nm of pore size. The optimize point for each parameter was 12.63mg/L of initial dye concentration, 6.12 g of ESM dosage, pH 2.19 and 12.83 min of contact time and the optimum congo red dye removal efficiency was 98.86 %.

1. INTRODUCTION

Human uses 115.6 to 167.7 liters of water for washing, bathing, drinking, etc (Lo et al., 2018). Other than daily usage, different industries also use lots of water for industrial processing, such as in the textile industry, food industry, and energy industry. Thus, water pollution was becoming a big problem for humans. Water pollution would be caused by improper management of effluent that discharge to the water sources. The main water pollutes come from industrial effluents, such as the textile industry. From the dyeing process, around until of dye will lose and discharges with water bodies (Mansour et al., 2012). For every year, the dye industry needed to produce approximately tons of dye to supply the textile industry (Chequer et al., 2013). The stain that widely used in the batik industry has divided into two class which is anionic and cationic (Ghaly et al., 2014). The Congo red is one of the anionic dyes often used in the textile industry, which is difficult to be degraded by biological treatment. The high concentration of this dye would cause health concerns and have been banned from using in the textile industry (Afkhami & Moosavi, 2010).

There have three treatment methods, such as chemical, physical and biological. Usually, the physical approach was used to treat this wastewater by using the adsorption method. The adsorption involved adsorbate (dye) and adsorbent, such as agricultural waste, activated carbon, chitosan, etc. The adsorbent has divided into three types, which are synthetic, semisynthetic, and natural (Patel, 2019). The semisynthetic adsorbent was more advantage compare to other two kinds of the adsorbent. Nowaday was more commonly use natural adsorbent such as rice husk, seed coat, banana peel, eggshell, eggshell membrane, etc to treating wastewater. The eggshell membrane contains 95% of fibrous protein network which able contribute in adsorption process (Mittal et al., 2016). The positively charge ESM surface (amino, amide group) make it more easily form electrostatic attraction with the oppositely charged component (dye) (Liu & Huang, 2011).

In this study, using the eggshell membrane to remove the congo red dye from the aqueous solution and

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more conveniences to its encapsulated method would be used for this adsorbent. Other than handling problem during adsorption, the encapsulated method will also enhance the adsorbent's binding site. The polyvinyl alcohol-sodium alginate (PVA-SA) will use to encapsulated the eggshell membrane and optimize it performed under several parameters such as pH, dosage of ESM bead, initial dye concentration, and contact time. This optimize of ESM bead performance was conducted by using Central composite design by using Design Expert.

2. MATERIALS AND METHODS

2.1. Preparation of raw material

The eggshell was collected from the UMK cafeteria. Around 2 kg of eggshell was washed using tap water to eradicate the albumen. The eggshell membrane was separated out from the eggshell and rinse with distilled water. The eggshell membrane would be dry in the oven for 60ºC for 24 hours. After 24 hours, the dried eggshell membrane was blended into powder form and milling it by using milling machine for 10 minutes per batch.

2.2. Preparation of PVA-SA solution

30 g of polyvinyl alcohol has been dissolved into 600 mL of distilled water by heating around 60°C with continuous stirring until fully dissolved. After that, 3 g of the sodium alginate would be added to the mixture and dissolved in the same condition.

2.3. Preparation of eggshell membrane biocomposite

The ratio of the eggshell membrane powder to the polyvinyl alcohol-sodium alginate (PVA/SA) solution was 1 to 15. The 9 g of eggshell membrane powder was added to the 135 mL of PVA/SA solution (containing 5 % of polyvinyl alcohol and 0.5 % of sodium alginate) using the homogenizer for 5 minutes at 14,000 rpm. The mixture would transfer to the syringe and drop it to the CC/BA solution (6% of boric acid solution with 3% calcium chloride) to form a spherical bead. After 24 hours, the bead has been transferred out and wash with distilled water. Finally, the bead was immersed in the distilled water for further use in the experiment.

2.4. Experimental design using response surface methodology

Table 2.1 and 2.2 shows the parameter for congo red adsorption and experimental responses using central composite design model.

Table 1: Total phenolic contents of *H. polyrhizus* and *H. undatus*.

Parameter	Range	
	Low	High
Dye comcentration (mg/L)	10	70
Dosage of ESM Bead (g)	1	10
Contact time (min)	10	60
pH	2	10

Table 2: Experimental responses using central composite design model

		Factor 1	Factor 2	Factor 3	Factor 4
Std	Run	A: Dye concentration (mg/L)	B: Dosage of ESM Bead (g)	C: Contact time (min)	D: pH
21	1	40	5.5	10	6
30	2	40	5.5	35	6
29	3	40	5.5	35	6
4	4	70	10	10	2
19	5	40	1	35	6
20	6	40	10	35	6
7	7	10	10	60	2
2	8	70	1	10	2
3	9	10	10	10	2
18	10	70	5.5	35	6
23	11	40	5.5	35	2
26	12	40	5.5	35	6
1	13	10	1	10	2
12	14	70	10	10	10
28	15	40	5.5	35	6
27	16	40	5.5	35	6
11	17	10	10	10	10
17	18	10	5.5	35	6
5	19	10	1	60	2
10	20	70	1	10	10
9	21	10	1	10	10
8	22	70	10	60	2
6	23	70	1	60	2
14	24	70	1	60	10
15	25	10	10	60	10
16	26	70	10	60	10
24	27	40	5.5	35	10
25	28	40	5.5	35	6
22	29	40	5.5	60	6
13	30	10	1	60	10

2.6. Chemical analysis and characterization

The grounded ESM powder would be analysed the chemical composition by using the Fourier Transforms Infrared Spectroscopy (FTIR). 2 mg of grounded ESM powder was mixed with the potassium bromide and squeezed to form transparent pallet to spectral scanning with the wavelength 600-4000 cm^{-1}. 5 mg of dried ESM bead has been tested with the gas adsorption to measure the surface of the sample. The Brunauer-Emmett-Teller (BET) analyzer would provide the gas and physically adsorbed by weak Van de Waals forces at the surface of the sample and desorbed by decreasing the pressure with the same temperature.

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3. RESULT AND DISCUSSION

3.1. Development of regression model equation

This Design Expert® software consists of models such as linear, 2FI, quadratic, and cubic models to identify which model was significantly fit to the research response. In this research, the best fit model was the quadratic model. The R^2 for this quadratic model is 0.9585 which was very close to 1. The differences between predicted R^2 (0.7967) and adjusted R^2 (0.9197) should in the range of ± 0.2 which considered its reasonable agreement with this model.

From the coded equation, it can be found that the dye concentration (A), contact time (C) and pH (D) was showing the negative sign or negative effect to the percentage of CR removal which minimize the percentage while the dosage of ESM Bead (B) was favor the optimization of CR removal.

$$Percentage\ of\ CR\ removal = +48.96 - 1.38A + 0.0972B - 1.37C - 28.2D + 2.69AB - 0.6737AC + 0.0313AD + 0.74BC - 1.95BD + 0.5238CD + 17.45A^2 - 4.97B^2 - 6C^2 + 12.22D^2 \quad Equation\ 3.1$$

The model summary statistics and standard deviation with R^2 for the quadratic model equation is as shown in Table 3 and 4.

Table 3: Model summary statistics

Source	Sequential p-value	Adjusted R^2	Predicted R^2	
Linear	< 0.0001	0.7583	0.7128	
2FI	0.9810	0.6984	0.4080	
Quadratic	**< 0.0001**	**0.9197**	**0.7967**	**Suggested**
Cubic	0.0018	0.9885	0.3148	Aliased

Table 4: Standard deviation and R^2 for the quadratic model equation

Quadratic Model Parameter	Value
Standard Deviation	7.11
Mean	60.18
CV%	11.81
PRESS	3708.29
R-Squared	0.9585
Adj R-Squared	0.9197
Pred R-Squared	0.7967
Adequate Precision	13.5626

3.2 Statistical analysis

Determining the significant of coefficient term was based on the F-value and P-value. The larger F-value and smaller P-value (F value > P value) indicated that coefficient term was significant (Behera et al., 2018) as shown in Table 5. This quadratic model was significant with F-value 24.73 and the P-value (< 0.0001) which was less than 0.05.

Table 5: Analysis of variance (ANOVA) for the response surface quadratic model

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	17485.70	14	1248.98	24.73	< 0.0001	significant
A-Dye concentration	34.39	1	34.39	0.6810	0.4222	
B-Dosage of ESM bead	0.1701	1	0.1701	0.0034	0.9545	
C-Contact time	33.65	1	33.65	0.6663	0.4271	
D-pH	14373.04	1	14373.04	284.64	< 0.0001	significant
AB	115.35	1	115.35	2.28	0.1515	
AC	7.26	1	7.26	0.1438	0.7098	
AD	0.0156	1	0.0156	0.0003	0.9862	
BC	8.76	1	8.76	0.1735	0.6829	
BD	61.15	1	61.15	1.21	0.2885	
CD	4.39	1	4.39	0.0869	0.7722	
A^2	788.76	1	788.76	15.62	0.0013	significant
B^2	63.92	1	63.92	1.27	0.2782	
C^2	93.18	1	93.18	1.85	0.1944	
D^2	386.77	1	386.77	7.66	0.0144	significant
Residual	757.43	15	50.50			
Lack of Fit	757.43	10	75.74			
Pure Error	0.0000	5	0.0000			
Cor Total	18243.13	29				

3.3 Interaction between two independent variables

3.3.1 Initial dye concentration and pH

Figure 1 shows a contour plot of initial dye concentration versus pH. From this 3D surface plot can clearly see that the pH having the significant effect toward CR removal. From this situation, the ESM bead acquires a positive charge in the system. It was having a strong electrostatic attraction toward the negative charged (anionic) dye molecule (Ponnusamy et al, 2013). At the basic system, the ESM bead will have a higher competition to bind toward the low range of cationic adsorption site. Thus the percentage of CR removal was low at the basic condition. At the constant pH 2, the rate of CR removal decreasing due to the saturated adsorption site of the ESM bead and with the increasing the initial dye concentration need applying a high driving force to overcome the resistance between aqueous and solid phases (Elkady et al., 2011).

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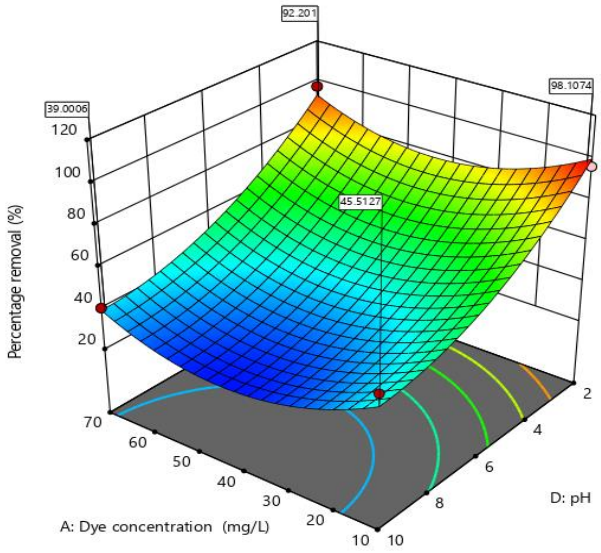

Figure 1: Contour plot initial dye concentration versus pH

3.3.2 Dosage of ESM bead and initial dye concentration

Figure 2 illustrates the effect of dosage ESM bead which shows that it able providing more surface area which mean increasing the binding site for the adsorption process which was consistence as previous study, as increasing the dosage of adsorbent will decreasing the residual dye in the solution (He et al., 2019). A further increase in the dosage not given a very significant increase in dye removal. The adsorbent's active site was fully saturated with the dye molecule (adsorbate), and the percentage dye removing was almost reaching maximum by using this adsorbent.

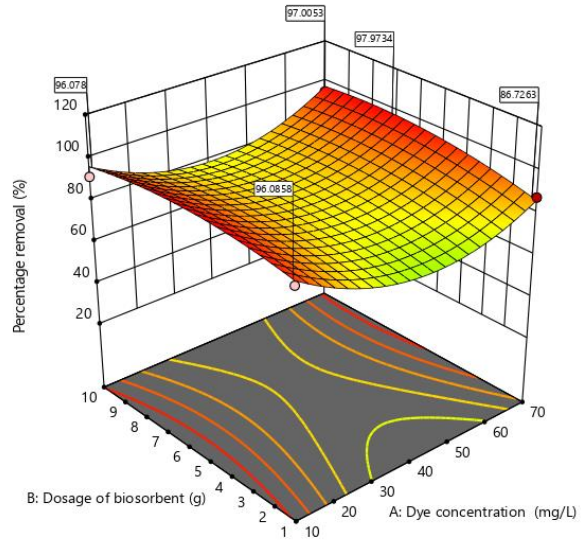

Figure 2: Contour plot initial dye concentration versus dosage of biosorbent

3.3.3 Contact time and pH

At the constant pH 2, the ESM bead performed significant adsorption with around 96.62 % dye removal at the first 10 minutes. Figure 3 shows that after increasing the contact time until 30 minutes, the dye was almost entirely removed from the aqueous solution (99.23 %). If further increasing the contact time, the dye would start desorb from the adsorbent because of high driving force causing the high concentration of CR would diffuse back to the solution (low concentration of CR).

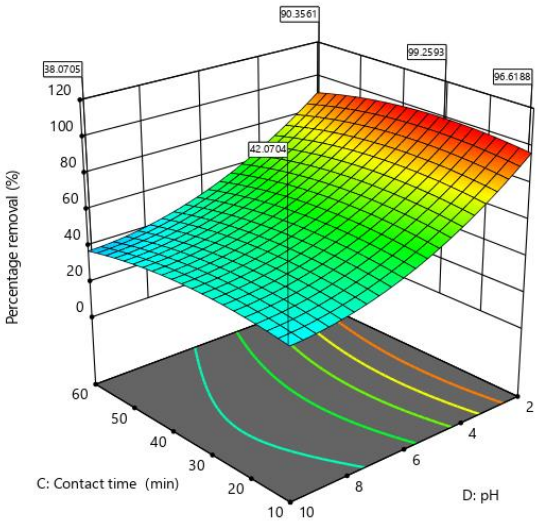

Figure 3: Contour plot of contact time versus pH

3.4 Optimization of percentage of CR removal

The optimum condition for the percentage of CR removal on the ESM bead are as shown in Table 3.4.

Table 3.4: Optimum condition for the percentage of CR removal on the ESM bead

Parameter	Low range	High range	Optimum value
Initial dye concentration (mg/L)	10	70	12.63
Dosage of ESM bead (g)	1	10	6.12
pH	2	10	2.19
Contact time (min)	10	60	12.83

3.4 Characterization of ESM bead

3.4.1 FTIR

After encapsulated ESM, there has the interaction between PVA solution and the ESM which was relevant to our result, significant change in its intensity of the functional group. The PVA was having a larger amount of hydroxyl group and causing the increasing the functional group of hydroxyls on the surface of ESM (Sulaiman, 2016). The hydroxyl group and carbonyl group on the ESM bead surface were the main functional group that contributed to the adsorption process. There was a significant change in term of FTIR graph trend slightly move upward compared to the ESM bead after adsorption as shown in Figure 4. This indicates that the functional was getting decreases due to it having some interaction between the dye molecules.

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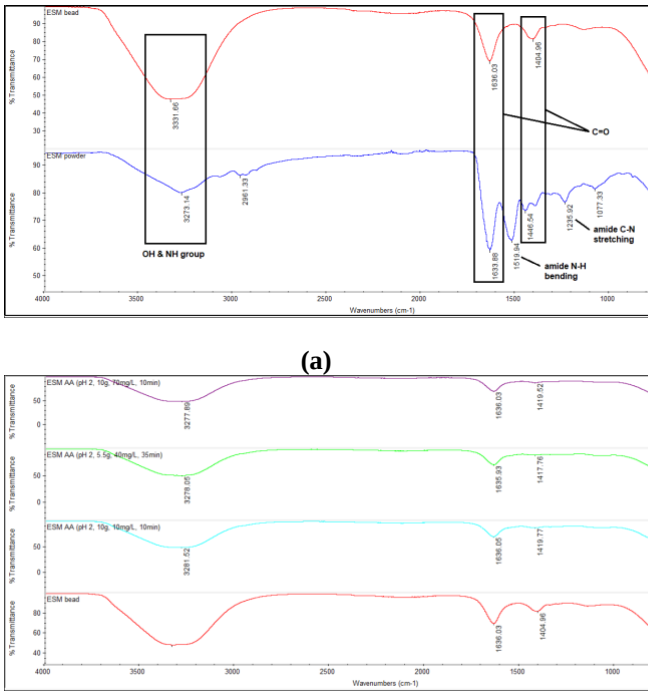

(a)

(b)

Figure 4: The FTIR spectra of (a) ESM powder and ESM bead (a) ESM bead before adsorb with three optimize result after ESM bead adsorption

3.4.2 BET

Table 6 shows the BET analysis for ESM powder and ESM bead. This study shows that the raw material having a much higher pore size, pore volume, and surface area than the ESM bead. This may because of encapsulated formulation was not providing the greater pore size of bead but only having the improvement on the specific functional group on its surface.

Table 6: BET analysis for ESM powder and ESM bead

BET analysis	ESM powder	ESM Bead
Pore size (radius) (nm)	44.14	42.47
Pore volume (cc/g)	0.06507	0.001210
Single point Surface area (m^2/g)	7.7206	0.3374
BET surface area (m^2/g)	2.948	0.057

4. CONCLUSION

The optimum parameter was at the 12.63 mg/L of initial CR concentration, 6.12g of dosage of ESM bead, pH 2.19 of dye solution, and the 12.83 of contact time and given the highest percentage CR removal (98.86%). This encapsulated method was proven that increasing the hydroxyl group on the surface of ESM bead and able provide more specific functional group to interact with dye molecules. The FTIR analysis shows that the major functional group that contributes to the adsorption process was the carbonyl group and the hydroxyl group at the peak of 1636, 1404 and 3331cm-1 respectively. Thus, this study proved that the ESM bead was able to treat the wastewater by having the high efficiency of CR dye removal from the aqueous solution.

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