

Studies on Biosorption of Alizarin Red dye using Prawn Shell Waste Powder

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Abstract - In the present work, "Prawn shell waste powder " was used as a biosorbent to remove alizarin red dye from an aqueous solution by biosorption technique under varying conditions of contact time, pH, initial concentration of dye, biosorbent dosage, and temperature. In batch process the biosorption experiments were carried out. From the experimentation it is revealed that 30 g/L of "PRAWN SHELL WASTE POWDER" of 53µm size is enough to remove 78 % of 20 mg/L concentration of Alizarin Red dye from 50 mL of aqueous solution in 25 min. Results has shown that the biosorption of Alizarin red dye increased with increase in biosorbent dosage. A significant increase in percentage removal of Alizarin red dye is observed as pH value increases from 2 to 4 and the percentage removal is maximum at pH = 4. The percentage removal decreased beyond that pH. Freundlich, Langmuir and Temkin models are applied to describe the equilibrium isotherms. The kinetic studies show that the biosorption of Alizarin Red dye onto "PRAWN SHELL WASTE POWDER" follows second order kinetics. Various thermodynamic parameters such as change in enthalpy, entropy and gibb's free energy are also determined. It was found that the biosorption is endothermic, irreversible and spontaneous. Hence, the results shows that "PRAWN SHELL WASTE POWDER" is effective in Alizarin red dye removal and can be appreciably considered as most versatile, economical and feasible for reclamation of Alizarin red dye from aqueous solution.

Key Words: biosorption, Kinetics, isotherms, prawn shells, thermodynamics

1. INTRODUCTION

Nearly 70% of Earth's surface covered with water whereas 0.002% of the water is available for human consumption. With two thirds of the earth's surface covered by water and the human body consisting of 75 percent of it, it is evidently clear that water is one of the prime elements responsible for life on earth. It has been estimated that water per person per day is required in the home for drinking, preparing food, and personal hygiene is minimum of 7.5 liters, the most basic requirements for water; at least 50 liters per person per day is needed to ensure all personal hygiene, food hygiene, domestic cleaning, and laundry needs. Water pollution occurs when undesirable effluents disperse in a water system and so water quality change. Many types of pollutants such as disease-causing agents; Oxygen demanding wastes; organic chemicals; plant nutrients; inorganic chemicals; sediments; heat and radioactive substances. In most situations, the waste treated is a mixture of the preceding types of pollutants, thus greatly complicating treatment and control procedures. Many causes of pollution, including sewage, manure, household activities and chemical fertilizers, contain "nutrients" such as nitrates and phosphates. Nutrient-type water pollution causes due to the deposition of atmospheric nitrogen. Water pollution due to toxic heavy metals released by industrial activities is a serious environmental and public health issue because they tend to remain indefinitely circulating and eventually accumulating throughout the food chain. Water Treatment Methods: Sedimentation, Filtration, Aeration, Chlorination. Many new technologies has emerged to formulate the methods for purification as we as saving methods of water for future generations.

2. MATERIALS AND METHODS

2.1 Preparation of biosorbent:

Prawn shell waste powder was used for the biosorption of Alizarin Red dye. The prawn shells were collected from local fish market, and washed with tap water to remove dirt and impurities. Then the washed prawn shells are allowed to dry under the sunlight until the shells become crispy. The washed and dried material was crushed with the help of a centrifugal mixer to get uniform particle sizes.

2.2 Preparation of dye solutions:

From Kemphasol (India) the Alizarin Red dye was obtained and used without further purification the dye. A 1000mg/L stock solution was prepared by dissolving 1 g of Alizarin Red dye in 1000 ml of distilled water. As per the required quantities the stock solution was later diluted. The pH values of Alizarin Red dye Solutions were adjusted with 0.001 N NaOH or HCl solutions using a pH meter. In this Biosorption the experiments were carried out in batch process using 250ml conical flask and the mixture was agitated at a constant agitation speed in an orbital shaker. At room temperature all the experiments were carried.

2.3 Analysis of the sample:

The concentrations of the dye solutions were determined at the characteristic wave length using UV- Spectrophotometer.

3. RESULTS AND DISCUSSION

3.1 Characterization of Prawn shell waste powder

3.1.1 Fourier Transform Infra Red Spectroscopy (FTIR):

The FTIR is an important tool to identify characteristic functional groups of the biosorbent, which are capable of adsorbing dyes. The FTIR spectroscopy provides structural and compositional information on the functional groups presented in the sample. The functional groups present in the Prawn shell waste powder were investigated by FTIR spectra within the range of 400-4000cm-1 wave number. Figs.1 (a) and 1 (b) show the band positions in the FTIR spectra of the Prawn shell waste powder before and after Alizarin Red dye biosorption. The FTIR spectra of *Prawn shell waste powder* before and after biosorption of Alizarin Red dye shows some of the biosorption peaks are shifted or disappeared and new Red dye onto the biosorbent surface.

FTIR spectrum of untreated *Prawn shell waste powder* is presented in fig. 1 (a). The peaks at 1029.99 cm⁻¹ denotes the involvement and stretching of C-O. The band at 1074.35 cm⁻¹ is due to the presence of stretching of C-O. The bands at 1159.22 cm⁻¹ is due to the presence of S=O stretching. Due to the presence of C-O stretching the band 1309.67 is formed. The band at 2364.73 cm⁻¹ assigned to N=C=O stretching. The band at 2721.56 cm⁻¹ suggests the presence of C-H stretching of aldehydes. The bands at 2843.03, 2889.37 and 2935.66 cm⁻¹ indicates the stretching of C-H bonds.

FTIR spectrum of untreated *Prawn shell waste powder* is presented in fig. 1 (b). The sharp peak at 1014.06 cm⁻¹ denotes the involvement of C-N stretching bands. The peaks at 1028.06, 1074.35, 1116.78 cm⁻¹ indicates the presence of C-O stretching bonds. The peak at 1357.25 cm⁻¹ suggests the presence of C-H bending of alkanes. The bands at 2879.72, 2889.37 and 2938.66 cm⁻¹ indicates the stretching of C-H bonds of alkanes.



Figure -1: (a) FTIR spectrum of untreated Prawn shell waste powder



Figure -1: (b) FTIR spectrum of treated Prawn shell waste powder

3.1.2 SEM analysis for untreated Prawn shell waste powder:

The SEM images are taken by applying 10kV voltage with different magnification times for the clarification of surface. These SEM observations of fibrous superficial structure of untreated *Prawn shell waste powder* are depicted in fig. 2(a). It is evident from analysis that the surface area is uneven, heterogeneous and pores on the surface of the powder.



Fig. 2 (a) Electron microscopes of untreated Prawn shell waste powder

3.1.3 SEM analysis for AR dye treated Prawn shell waste powder:

SEM analysis after biosorption figs.2 (b) shows that the surface has irregular texture with globular, elongated grains and shiny particles over the surface of AR dye loaded which are abscent in the fresh biosorbent. These elongated grains show that the AR dye particles are adhered onto the surface of the prawn shell biomass. The clustered grains like morphology, on treated biosorbent denote increased active surface area. The research results were reported by various authors.





3.2 Equilibrium studies on biosorption of Alizarin Red dye

3.2.1 Effect of agitation time:





Duration of equilibrium biosorption is defined as the time required for heavy metal concentration to reach a constant value during biosorption. The equilibrium agitation time is determined by plotting the % biosorption of Alizarin Red dye against agitation time as shown fig. 5.3 for the interaction time intervals between 1 to 180 min. For 53 μ m size of 10 g/L biosorbent dosage, 20 % of Alizarin Red dye is biosorbed in the first 5 min. The % biosorption is increased briskly up to 25 min reaching 45 %. Beyond 25 min, the % biosorption is constant indicating the attainment of equilibrium conditions.

3.2.2 Effect of biosorbent size:

The variations in % biosorption of Alizarin Red dye from the aqueous solution with biosorbent size are obtained. The results are drawn in fig.5.4 with percentage biosorption of Alizarin Red dye as a function of biosorbent size. The percentage biosorption is increased from 30 % to 45 % as the biosorbent size decreases from 152 to 53 μ m. This phenomenon is expected, as the size of the particle decreases, surface area of the biosorbent increases; thereby the number of active sites on the biosorbent also increases.



Fig. 4 Effect of biosorbent size on % removal of AR dye

3.2.3 Effect of pH:





In the present investigation, Alizarin Red dye biosorption data are obtained in the pH range of 2 to 8 of the aqueous solution ($C_0 = 20 \text{ mg/L}$) using 10 g/L of 53 µm size biosorbent. The effect of pH of aqueous solution on % biosorption of Alizarin Red dye is shown in fig.5.5. The % biosorption of Alizarin Red dye is increased from 45 % to 62 % as pH is increased from 2 to 4. The % biosorption is decreased from 62 % to 40 % as pH increases from 4 to 8. The reason beyond this is low pH depresses biosorption due to competition with H⁺ions for appropriate sites on the biosorbent surface. However, with increasing pH, this competition weakens and Alizarin Red dye ions replace H⁺ ions bound to the biosorbent.

3.2.4 Effect of initial concentration of Alizarin Red dye:

The effect of initial concentration of Alizarin Red dye in the aqueous solution on the percentage biosorption of Alizarin Red dye is shown in fig.6. The percentage biosorption of Alizarin Red dye is decreased from 62 % to 42.7 % with an increase in C_0 from 20 mg/L to 200 mg/L.



Fig. 6 Variation of initial concentration with % biosorption of AR dye

3.2.4 Effect of biosorbent dosage:

The percentage biosorption of Alizarin Red dye is drawn against biosorbent dosage for 53 µm size biosorbent in fig.7. The biosorption of Alizarin Red dye increased from 62 % to 77 % with an increase in biosorbent dosage from 10 to 30 g/L. Such behavior is obvious because with an increase in biosorbent dosage, the number of active sites available for Alizarin Red dye biosorption would be more. The change in percentage biosorption of Alizarin Red dye is marginal from 84 % to 85 % when 'w' is increased from 30 to 80 g/L. Hence all other experiments are conducted at 30 g/L dosage.





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3.2.5 Effect of temperature:



Fig. 8 Effect of temperature on % biosorption of AR dye

Adsorption Isotherms:

Irving Langmuir developed an isotherm called Langmuir isotherm. It is one of the most widely used simple two- parameter equations. The Langmuir equation is:

$$q_e/q_m = bC_e / (1+bC_e)$$
(1)

Equation (1) can be rearranged as

$$(C_e/q_e) = 1/(bq_m) + C_e/q_m$$
(2)

From the plots between (C_e/q_e) and C_e , the slope $\{1/(bq_m)\}$ and the intercept (1/b) are calculated. Further analysis of Langmuir equation is made on the basis of separation factor, (R_L) defined as $R_L = 1/(1+bC_e)$.

Langmuir isotherm is drawn for the present data and shown in Fig. 9. The equation obtained 'n' $C_e/q_e = 0.06683 C_e + 5.9253$ with a good linearity (correlation coefficient, $R^2 \sim 0.9935$) indicating strong binding of Alizarin Red dye ions to the surface of prawn shells powder.



Fig. 9 Langmuir isotherm for % biosorption of AR dye

Freundlich isotherm:

Freundlich presented an empirical biosorption isotherm equation that can be applied in case of low and intermediate concentration ranges. It is easier to handle mathematically in more complex calculations. The Freundlich isotherm is given by

$$q_e = K_f C_e^n$$

Taking logarithms on both sides, we get

$$\log q_e = \log K_f + n \log C_e$$

Freundlich isotherm is drawn between $\log q_e = 0.7158 \ln C_e - 1.1904$; $\ln C_e$ and $\ln q_e$ in Fig. 10 for the present data.

The resulting equation has a correlation coefficient of 0.9957. The 'n' value in the above equations satisfies the condition of 0 < n < 1 indicating favorable biosorption.



Fig. 10 Freundlich isotherm for % biosorption of AR dye

Temkin isotherm:

Temkin and Pyzhev isotherm equation describes the behavior of many biosorption systems on the heterogeneous surface and it is based on the following equation

$$q_e = RT \ln(A_T C_e)/b_T$$

The linear form of Temkin isotherm can be expressed as

$$q_e = (RT/b_T) \ln(A_T) + (RT/b_T) \ln(C_e)$$



Where $A_T = \exp [b(0) \times b(1) / RT]$ $b(1) = RT / b_T$ is the slope

 $b(0) = (RT/b_T) ln (A_T)$ is the intercept

and b = RT/b(1)

The present data are analyzed according to the linear form of Temkin isotherm and the linear plot is shown in Fig. 11. The equation obtained for Alizarin Red dye biosorption is: $q_e = 2.6828 \ln C_e 4.7444$ with a correlation coefficient 0.98955. The best fit model is determined based on the linear regression correlation coefficient (R). From the Figs. 9, 10 & 11, it is found that biosorption data are well represented by Langmuir isotherm with higher correlation coefficient of 0.9935, followed by Temkin and Freundlich isotherms with correlation coefficients of 0.9639 and 0.9957 respectively.



Fig. 11 Temkin isotherm for % biosorption of AR dye

Langmuir	Freundlich	Temkin
isotherm	isotherm	isotherm
qm = 14.9633	Kf = 0.304099	AT = 0.3313
mg/g	mg/g	L/mg
B = 0.011(L/g)	n = 0.7158	bT = 938.99
R2 = 0.9935	R2 = 0.9957	R2 = 0.9639

Adsorption kinetics:

Lagergren plot and pseudo second order kinetics plot for biosorption of Alizarin Red dye are drawn in figs. 12 & 13. Table-2 & 3 summarizes the rate constant values for first and second order rate equations. It is noted that both first and second order rate equations satisfactorily.



Fig. 12 first order kinetics for % biosorption of AR dye



Fig. 13 second order kinetics for % biosorption of AR dye



Fig. 14 Vantoff's plot for % biosorption of AR dye

Van't Hoff's plot is drawn in fig. 14. From the data, Gibbs free energy change (ΔG) is calculated to be -6077.06 J/mol for biosorption of Alizarin Red dye. The negative ΔG value indicates thermodynamically feasible and spontaneous nature of biosorption. The ΔH parameter is 11.696989 kJ/mol.K. The negative ΔH indicates the exothermic nature of biosorption. ΔS parameter is found to be 20.09492 J/mol K for Alizarin Red dye biosorption. The positive ΔS .

Optimization using Response Surface Methodology (RSM)

The parameters that have greater influence over the response are to be identified so as to find the optimum condition for the biosorption of Alizarin Red dye ions. The quadratic model is used in the present study, to relate four independent variables and percentage biosorption of Alizarin Red dye. The regression equation for % biosorption of Alizarin red dye (Y) is function of pH (X1), Co (X3), w (X2) and T (X4). The variations in the corresponding coded values of four parameters and response are presented in **table-4**

Table-4

Levels of different process variables in coded and un-coded form for % biosorption of Alizarin Red dye using Prawn shell waste powder

Variables	Independent parameters	Range and level				
		-2	-1	0	1	2
X1	pH of the aqueous solution	2	3	4	5	6
X2	Initial metal ion concentration, C_0 , mg/L	10	15	20	25	30
X ₃	Biosorbent dosage, w, g/L	0.5	1	1.5	2	2.5
X ₄	Temperature, T, K	283	293	303	313	323

The following equation represents multiple regression analysis of the experimental data for the biosorption of Alizarin Red dye: Y = $-4148.77 + 54.75 X_1 + 9.77 X_2 + 64.44 X_3 + 26.12 X_4 - 6.32 X_1^2 - 0.23 X_2^2 - 20.17 X_3^2 - 0.04 X_4^2 - 0.08 X_1 X_2 - 0.49 X_1 X_3 - 0.12 X_2 X_3 - (3)$



Table – 5
Results from CCD for biosorption of Alizarin Red dye using Prawn shells powder

D N		NO(C)	VO()	N/A (TT)	% Biosorption	
Run No.	X1(pH)	X2(Co)	X3(W)	X4(T)	Experimental	Predicted
1	3	15	1	293	56.02	55.96667
2	3	15	1	313	57.2	57.15833
3	3	15	2	293	58.69	58.74167
4	3	15	2	313	60.12	60.08333
5	3	25	1	293	60.08	60.12500
6	3	25	1	313	61.5	61.46667
7	3	25	2	293	61.68	61.70000
8	3	25	2	313	63.22	63.19167
9	5	15	1	293	62.58	62.62500
10	5	15	1	313	64.02	63.96667
11	5	15	2	293	64.38	64.40000
12	5	15	2	313	65.92	65.89167
13	5	25	1	293	65.12	65.08333
14	5	25	1	313	66.6	66.57500
15	5	25	2	293	65.7	65.65833
16	5	25	2	313	67.28	67.30000
17	2	20	1.5	303	53.18	53.22500
18	6	20	1.5	303	64.02	63.99167
19	4	10	1.5	303	58.18	58.22500
20	4	30	1.5	303	63.82	63.79167
21	4	20	0.5	303	61.89	61.95833
22	4	20	2.5	303	65.5	65.45833
23	4	20	1.5	283	65.19	65.24167
24	4	20	1.5	323	68.12	68.07500
25	4	20	1.5	303	83.88	83.93000
26	4	20	1.5	303	83.88	83.93000
27	4	20	1.5	303	83.88	83.93000
28	4	20	1.5	303	83.88	83.93000
29	4	20	1.5	303	83.88	83.93000
30	4	20	1.5	303	83.88	83.93000

Table - 6

ANOVA of Alizarin Red dye biosorption for entire quadratic model

Source of variation	SS	Df	MS	F	P>F
(1)pH (L)	174.798	1	174.79	11487.8	0.000000
рН (Q)	1094.444	1	1094.4	71924.1	0.000000
(2)Concentration(L)	46.844	1	46.844	30784.8	0.000000
Concentration(Q)	896.406	1	896.40	58909.9	0.000000
(3)Dosage (L)	18.533	1	18.533	12179.3	0.000000

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Dosage (Q)	697.565	1	697.56	45842.7	0.000000
(4)Temperature(L)	12.717	1	12.717	8357.1	0.000000
Temperature(Q)	507.867	1	507.867	33375.1	0.000000
1L by 2L	2.764	1	2.764	1816.4	0.000000
1L by 3L	0.975	1	0.975	640.8	0.000000
1L by 4L	0.014	1	0.014	9.1	0.008753
2L by 3L	1.387	1	1.387	911.2	0.000000
2L by 4L	0.012	1	0.012	7.6	0.014713
3L by 4L	0.020	1	0.020	13.3	0.002355
Error	0.023	15	0.002		
Total SS	2524.404	29			

df- degree of freedom; SS- sum of squares; F- factor F; P- probability. R²=0. 99999; R² (adj):0. 99998

The correlation coefficient (R2) provides a measure of the models variability in the observed response values. The closer the R2 value to 1, the stronger the model is and it predicts the response better. In the present study the value of the regression coefficient (R2 = 0.99998) for Eq. (3) indicates that 0.002% of the total variations are not satisfactorily explained by the model (Table-6). The ANOVA

Table-6 can be used to test the statistical significance of the ratio of mean square due to regression and mean square due to residual error. From the table, it is evident that, the F-statistics value for entire model is higher. This large value implies that % removal can be adequately explained by the model equation. Generally P values lower than 0.05 indicates that the model is considered to be statistically significant at the 95% confidence level. The % biosorption prediction from the model is shown in Table-5. From Table-6, it is known that all the squared terms and the linear terms of all the variables are significant (P < 0.05).

Terms	Regression Coefficient	Standard error of the coefficient	t- value	p- value
Mean/Interc.	-4148.77	7.139367	-581.112	0.000000
(1)pH (L)	54.75	0.305460	179.225	0.000000
рН (Q)	-6.32	0.007448	-848.080	0.000000
(2)Concentration(L)	9.77	0.061092	159.964	0.000000
Concentration(Q)	-0.23	0.000298	-767.525	0.000000
(3)Dosage (L)	64.44	0.608007	105.994	0.000000
Dosage (Q)	-20.17	0.029793	-677.068	0.000000
(4)Temperature(L)	26.12	0.045574	573.048	0.000000
Temperature(Q)	-0.04	0.000074	-577.717	0.000000
1L by 2L	-0.08	0.001950	-42.619	0.000000
1L by 3L	-0.49	0.019504	-25.315	0.000000
1L by 4L	0.00	0.000975	3.012	0.008753
2L by 3L	-0.12	0.003901	-30.186	0.000000
2L by 4L	0.00	0.000195	2.756	0.014713
3L by 4L	0.01	0.001950	3.653	0.002355

Table – 7

Estimated regression coefficients for the Alizarin Red dye biosorption onto waste prawn shells powder

Table-5 represents the results obtained in CCD. The response obtained in the form of analysis of variance (ANOVA) from regression eq.3 is put together in table-6. Fischer's 'F-statistics' value is defined as MSmodel/MSerror, where MS is mean

square. Fischer's 'F-statistics' value, having low probability 'p' value, indicated high significance.



Fig. 16 Normal probability plot for % biosorption of Alizarin Red dye

It is evident from response surface contour plots that the % biosorption is minimal at low and high levels of the variables. This behavior confirms that there is a presence of optimum for the input variables in order to maximize % biosorption. The role played by all the variables is so vital in % biosorption of Alizarin Red dye and seen clearly from the plots. The predicted optimal set of conditions for maximum % biosorption of Alizarin Red dye is:

Biosorbent dosage = 30.79 g/L

Initial Alizarin Red dye ion concentration = 20.5639 mg/L

pH of aqueous solution = 4.2086

Temperature = 303.8597

% biosorption of Alizarin Red dye = 84.306

The experimental optimum values are compared with those predicted by CCD in table-8. The experimental values are in close agreement with those from and CCD.

Table – 8	B
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Comparison between optimum values obtained by SSO and RSM

Variable	SSO	RSM
Biosorbent dosage, w, g/L	30	30.79
pH of aqueous solution	4	4.206
Concentration, mg/l	20	20.5639
% biosorption	78	84.306



Table	_	5.7	

Alizarin Red dye uptake capacities for different biosorbents

Authors	Biosorbent	q _t , mg/g
S.A. Abo-El-Enein [14]	rice husk ash	158
Erdal Kenduzler [15]	Amberlyst 36	88
Vijayaraghavan [16]	Sargassum	20.2
Fuat Guzel [17]	black carrot	5.003
Mustafa Tuzen [18]	Pseudomonas aeruginosa immobilized multiwalled carbon nanotubes	5.83
Present investigation	PRAWN SHELL WASTE POWDER	14.9633



Fig. 17 (a) Surface contour plot for the effects of Concentration and pH of Alizarin Red dye on % biosorption



Fig. 17 (b) Surface contour plot for the effects of dosage and pH of Alizarin Red dye on % biosorption



Fig. 17 (c) Surface contour plot for the effects of Temperature and pH of Alizarin Red dye on % biosorption



Fig. 17 (d) Surface contour plot for the effects of dosage and concentration of Alizarin Red dye on % biosorption



Fig. 17 (e) Surface contour plot for the effects of Temperature and concentration of Alizarin Red dye on % Biosorpion



Fig. 17 (f) Surface contour plot for the effects of Temperature and dosage of Alizarin Red dye on % Biosorpion

CONCLUSION

In this investigation the main aim is to determine the suitability of Prawn Shell waste powder as a biosorbent for the removal of Alizarin Red dye from aqueous solutions. The equilibrium, kinetic and thermodynamic studies are carried out for biosorption of Alizarin Red dye experimentally and theoretically. The analysis of the experimental and theoretical data is presented below as results by the following conclusions: The equilibrium agitation time for Alizarin Red dye biosorption is 25 minutes. Percentage biosorption of Alizarin Red dye from the aqueous solution increases significantly with increase in pH from 2 (47 %) to 4 (62 %). The optimum dosage for biosorption is 30 g/L. The maximum uptake capacity of 14.9633 mg/g is obtained at 303 K. The maximum biosorption of Alizarin Red dye (84.306) onto Prawn shell waste powder is observed when the processing parameters are set as: pH = 4.2086, C₀ = 20.5639 and w = 30.79 g/L using RSM. The investigation also reveals the endothermic nature of biosorption as Δ H (11.696989 J/mole) is positive, irreversible nature of biosorption as Δ S (20.09492 J/mole-K) is positive and spontaneity of biosorption as indicated by negative Δ G (Δ G = -6077.06 J/mole). Hence the above said Prawn shell waste powder is effective and efficient biosorbent and is capable of removing Alizarin Red dye.

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